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université de BORDEAUX

THÈSE PRÉSENTÉE

POUR OBTENIR LE GRADE DE

DOCTEUR DE

L'UNIVERSITÉ DE BORDEAUX

ÉCOLE DOCTORALE DES SCIENCES & ENVIRONNEMENTS

SPÉCIALITÉ : Hydrogéologie, Environnement

Par

Nabaz MOHAMMED

INVESTIGATING THE BEHAVIOR OF ALLUVIAL SYSTEMS, THANKS TO THE CLASSICAL, ISOTOPIC AND EMERGING TRACERS.

CASE STUDY OF THE ALLUVIAL AQUIFER OF THE ALLIER RIVER (AUVERGNE, FRANCE)

Sous la direction de: Philippe LE COUSTUMER
(Co-directeur: Héléne CELLE-JEANTON)

Soutenue le 19/05/2014

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ABSTRACT

Hydrodynamic, hydrochemical (major ions, traces, pharmaceuticals and pesticides), and isotopic investigations (oxygen-18 and deuterium) were carried out on 19 points, including boreholes, piezometer, surface water, and springs from February 2011 to November 2012, to assess groundwater quality in the unconfined shallow alluvial aquifer of the Allier River (one of the main tributary of the Loire River). The study area, located near the city of Clermont-Ferrand (France), plays an important socio-economic role as the alluvial aquifer is the major source of drinking water for about 100 000 inhabitants. The objective of the project aims at understanding the functioning and the vulnerability of alluvial aquifers that occupy a pre-eminent position in the hydrogeologic landscape both for their economic role - production of drinking water and agricultural development - and for their ecological role. Moreover, this study also targets at determining the factors and processes controlling shallow groundwater quality and origin. The water circulates from the south, with a natural alimentation from the hills in the non-pumped part of the alluvial aquifer. In the pumping zone, this general behaviour is altered by the pumping that makes the water from the Allier River enter the system in a large proportion. Four end-members have been identified for the recharge of the alluvial groundwater: rainfall, Allier River, surrounding hills' aquifer and the southern non-pumped part of the alluvial system. Results indicate that, despite the global Ca-HCO_3 water type of the groundwater, spatial variations of physico-chemical parameters do exist in the study area. Ionic concentrations increase from the Allier River towards east due either to the increase in the residence time or a mixing with groundwater coming from the aquifer's borders. Stable isotopes of the water molecule show the same results: boreholes close to the river bank are recharged by the Allier River (depleted values), while boreholes far from the river exhibit isotopic contents close to the values of hills' spring or to the southern part of the alluvial aquifer, both recharged by local precipitation. One borehole (B65) does not follow this scheme of functioning and presents values attesting of a probable sealing of the Allier River banks. Based on these results, the contribution of each end-member has been calculated and the functioning of the alluvial system determined. According to this general scheme of functioning, origins of pollution (agricultural, urban) have been determined and clues to the protection of such hydrosystems defined.

Keywords: Alluvial aquifer, Allier River, stable isotopes, pesticides, pharmaceuticals

RÉSUMÉ

L'objectif de la thèse vise à déterminer les facteurs et processus qui contrôlent l'origine et la qualité des eaux souterraines alluviales et ainsi à mieux comprendre le fonctionnement et la vulnérabilité des aquifères alluviaux qui occupent une place prééminente dans le paysage hydrogéologique mondial tant pour leur rôle économique - production d'eau potable, développement agricole - que pour leur rôle écologique. Des mesures hydrodynamiques, hydrochimiques (ions majeurs, traces, molécules phytosanitaires et pharmaceutiques) combinées à des déterminations isotopiques (oxygène-18, deuterium, carbone-13) ont ainsi été effectuées sur 19 points incluant puits, piézomètres et eaux de surface, de février 2011 à novembre 2012, afin d'évaluer l'origine et la qualité de l'eau souterraine dans l'aquifère alluvial de la rivière Allier, un des principaux tributaires de la Loire. La zone d'étude, située près de la ville de Clermont-Ferrand (France), joue par ailleurs un rôle socio-économique majeur, la nappe alluviale de l'Allier constituant la principale ressource en eau potable pour une population d'environ 100 000 habitants.

D'un point de vue hydrodynamique, l'eau souterraine circule généralement du sud au nord, avec une alimentation naturelle à partir des coteaux adjacents, dans la partie non-pompée de l'aquifère. Dans la zone de pompage, cette circulation naturelle est modifiée par le pompage qui fait pénétrer l'eau de la rivière Allier dans l'aquifère. La recharge de l'aquifère dépend alors de quatre pôles de mélange : pluie, rivière Allier, coteaux adjacents et partie sud, non-pompée, de l'aquifère. Les résultats chimiques et isotopiques obtenus permettent de cartographier la contribution de chaque pôle de mélange. La contribution de l'Allier est significative dans la majorité des puits et atteint 100 % pour certains puits situés à proximité immédiate des berges. L'influence de l'Allier diminue vers l'est, la composition chimique des eaux démontrant une participation croissante des eaux provenant des coteaux ou de la partie du sud de l'aquifère.

La contamination/pollution de l'aquifère a été explorée du point de vue des éléments traces indésirables ou toxiques, des molécules pharmaceutiques et phytosanitaires. L'analyse des éléments traces indique une origine mixte naturelle et anthropique (principalement agricole). Les puits exploités pour l'alimentation en eau potable présentent tous des concentrations au-dessous des normes imposées par la Directive européenne 98/83/CE. Les concentrations en éléments traces des puits localisés près des coteaux sont généralement plus élevées. 35 molécules phytosanitaires ont été positivement détectées tant dans les eaux de surface que

dans les eaux souterraines ; l'atrazine et le diflufenican, parmi les herbicides les plus utilisés, sont les molécules les plus fréquemment mesurées avec dépassement des normes pour l'atrazine. La présence de molécules phytosanitaires dans l'ensemble des points étudiés démontrent que cette pollution doit s'envisager à l'échelle locale mais aussi à l'échelle du bassin versant, l'Allier présentant les concentrations les plus fortes et le plus grand nombre de molécules détectées. Quant aux molécules pharmaceutiques, l'eau souterraine est généralement moins contaminée que l'eau de surface. On peut toutefois noter des variabilités spatiales. Les concentrations mesurées près des coteaux sont généralement plus hautes que celles de l'Allier et on peut noter la présence de molécules non détectées dans l'Allier, attestant d'une contribution des coteaux. De manière générale, les puits majoritairement alimentés par l'Allier démontrent des concentrations et un nombre de molécules pharmaceutiques et phytosanitaires plus faible que la rivière, confirmant les capacités d'épuration de la nappe alluviale.

Ces résultats mettent en évidence la vulnérabilité de l'aquifère face aux pollutions. Les parties méridionale et orientale du site sont affectées par des arrivées d'eaux de qualité médiocre démontrant l'importance de la définition d'un périmètre de protection adaptée. Près de l'Allier, une attention particulière doit être portée non seulement aux pollutions ponctuelles qui peuvent se produire sur le cours de la rivière, mais également aux pollutions chroniques liées notamment aux rejets des stations d'épuration pourvoyeurs de polluants tels les molécules pharmaceutiques. Toutes les informations acquises devront être incluses dans les stratégies de gestion d'eau souterraine afin protéger la durabilité de cette ressource de valeur. Les résultats s'appuient sur les investigations menées sur la nappe alluviale de l'Allier, néanmoins la méthodologie utilisée et sa transposition à des systèmes analogues est l'une des perspectives majeures de cette étude.

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INTRODUCTION

Alluvial aquifers associated with major river valleys are important sources of abundant good quality drinking water (Moyce et al., 2006; Menció et al., 2013). Alluvial sediments, mainly composed of gravel, sand, silt or clay deposited in river channels or on floodplains, present advantageous characteristics for exploitation for they are mostly unconfined, shallow and highly permeable. However, due to their shallow and unconfined nature, alluvial aquifers are vulnerable to contamination and pollution from surface activities (Lyverse and Unthank, 1988; Böhlke, 2002; Bhattacharya et al., 2006).

Environmental concerns related to groundwater generally focus on the impact of pollution and quality degradation in relation to human uses, particularly domestic supply. Due to high population growth and industrialization, greater amounts of domestic, agricultural and industrial effluents are discharged; that leads to the pollution of surface water and groundwater in shallow aquifers (Chae et al., 2004; Négrel et al., 2004; Andrade and Stigter, 2011). Many different sources and processes can be responsible for the contaminants polluting the surface and groundwater. The commonly found contaminants in groundwater due to agriculture are nitrate, chloride, sodium, calcium, magnesium, ammonia, phosphate, pesticides, and trace elements (Spalding and Exner, 1993; Lalitha et al., 2012). Detailed hydrochemical research is needed to evaluate the different processes and mechanisms involved in polluting water (Helena et al., 2000). More recently, due to advanced analytical methods, trace metals as toxic inorganic pollutants and pharmaceuticals as emerging organic pollutants become a part of the long term water monitoring in EU (e.g. Buzier et al., 2008; Pesavento et al., 2009), USA (e.g. Balistrieri and Blank, 2008; Barnes et al., 2008), Canada (e.g. Alfaro-De la Torre et al., 2000), Australia (e.g. Denney et al., 1999), Japan (e.g. Nakada et al., 2008), China (e.g. Fan et al., 2009). Although, these compounds have only recently been recognized as environmental contaminants, they have gained the attention of the general public and the scientific community.

The growing concern for groundwater quality has placed significant demands on groundwater management programmes. An efficient water management aims to protect, assess, and monitor these valuable resources. The effective management of water resources requires

information on both quantity and quality of groundwater (Mogheir and Singh, 2002). Effective usage and management of groundwater depend on understanding sources of recharge and flow conditions, complemented by geochemical studies, in the target aquifers. An integrated assessment of the connection between geochemical processes and groundwater flow in an aquifer provides a greater understanding of spatial variations in groundwater quality and its availability (Han et al., 2009).

To better understanding the functioning and contamination susceptibility of groundwater from alluvial hydrosystems, hydrodynamical, hydrochemical (major ions, traces, pharmaceuticals and pesticides), isotopic (oxygen and hydrogen stable isotopes) and biological investigations have been conducted to assess groundwater quality in the unconfined shallow alluvial aquifer of the Allier River (main tributary of the Loire River) and to determine the functioning of this system. Why do we focus on this aquifer? Because it plays an important socio-economic role due to its suitability for drinking, agricultural and industrial purposes for the city of Clermont-Ferrand which has more than 100,000 inhabitants. However, this shallow alluvial aquifer is surrounded by extensive agricultural activities. Generally, alluvial aquifers in agricultural area have been severely affected by indirect or direct input of agrochemicals. Moreover, this system is also influenced by the waste water from treatment plants in the upper catchment. Data from this study will contribute to improve the understanding of the factors that control groundwater quality in such hydrosystem and thus contribute to the sustainable management of groundwater resources from alluvial aquifer.

The questions addressed in this work are:

1) How groundwater circulates in the alluvial aquifer of the Allier River?
2) What are the main chemical characteristics of groundwater?
3) What are the processes involve in groundwater chemistry?

The scientific approach used to address these questions combines: (1) analysis of groundwater chemistry to identify spatial and temporal patterns in major ions; (2) analysis of stable isotope of oxygen and hydrogen to estimate the origin of groundwater; (3) analysis of trace elements, pharmaceuticals and pesticides to determine the quality of groundwater and also to evaluate the anthropogenic influences. All the results are presented in four chapters. The first chapter presents the study site and the methodology adopted. The second chapter

deals with all the spatial and temporal results obtained through the chemical and isotopic survey carried out during two years, in terms of functioning of the system. The third chapter focuses on the contamination of alluvial groundwater and presents data gathered from traces, pharmaceuticals and pesticides measurements which are of great concern in such a site. At last chapter four highlights the main results on the functioning and vulnerability of the alluvial aquifer of Allier River and gives some perspective of this work in terms of recommendation to alluvial hydrosystems users and of theoretical research that has to be pursued.

CHAPTER I

STUDY SITE AND METHODOLOGY

In this set of study, concerning shallow alluvial aquifer, it is fundamental to define the study area settings (location, environment, geology, hydrogeology … etc.) for the reason that they have direct influence on the quality, chemistry and origin of groundwater. The methodology is also crucial since it shows what kind of materials and equipments have been used in the study which in turn determines the quality of the data.

1. Study site

1.1. Allier basin

This study was performed in the Quaternary shallow alluvial aquifer of the Allier River, located in the Allier basin covering a total surface area of 14,310 km^2. The Allier watershed cuts eight departments (Allier (03), Ardèche (07), Cantal (15), Cher (18), Haute-Loire (43), Lozère (48), Nièvre (58) and Puy-de-Dôme (63)) from five regions (Centre, Bourgogne, Rhône-Alpes, Languedoc-Roussillon and Auvergne), although the majority located in the Auvergne (Fig.I-1). The southeastern part of the basin of the Allier downstream, in uphill of Clermont-Ferrand, is limited by the volcanic Chaîne des Puys, the Monts Dore and the Massif du Cézallier which have a dense network of mountain water courses such as Couze d'Ardes, Couze Pavin, Couze Chambon or Veyre. From the source to the confluence, the Allier River offers many contrasting landscapes due to the geological diversity of the Massif Central.

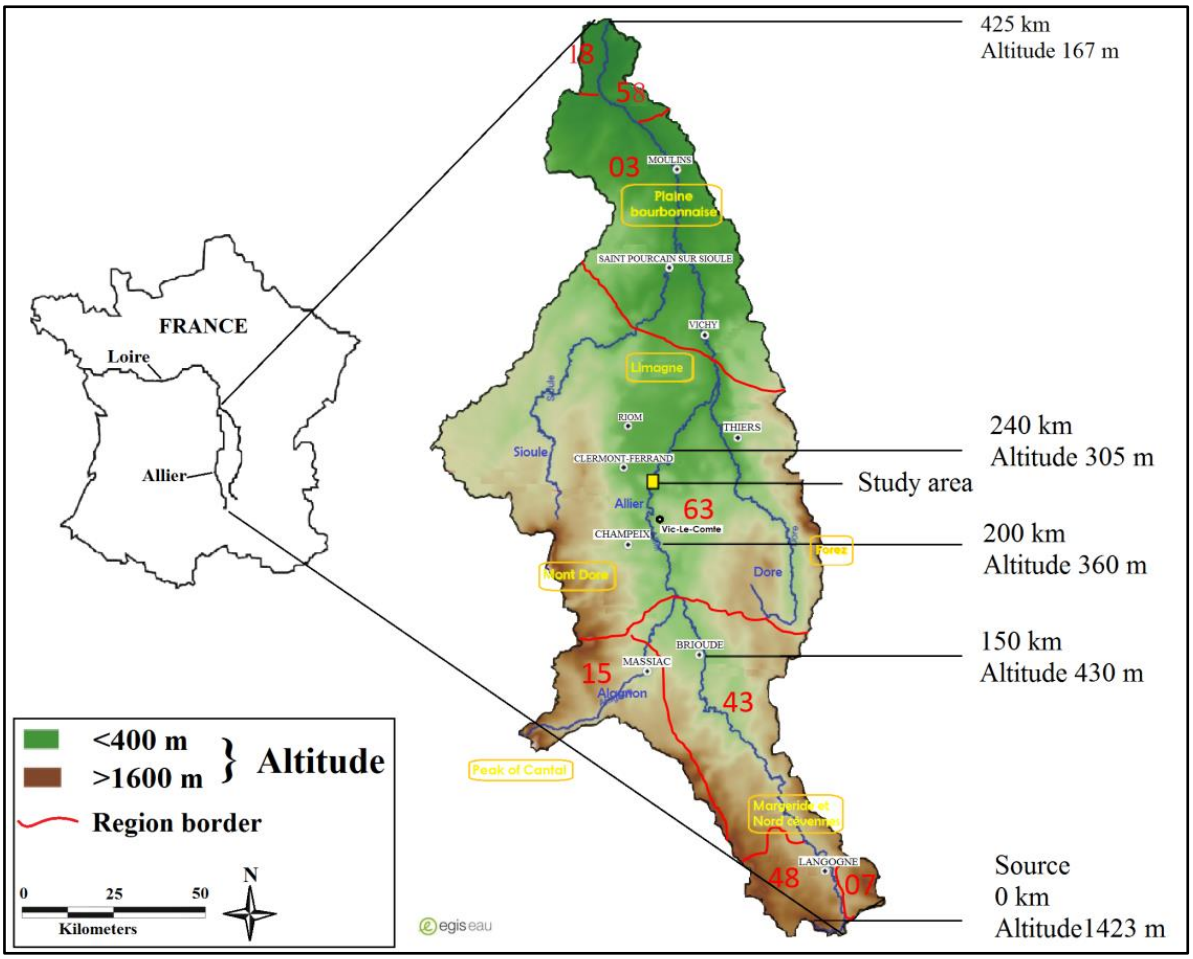

Fig.I-1: General description of Allier River basin location (adapted from: Plan-Loire, 2011)

1.1.1. Climate

The climate of the Allier basin is subjected to high spatial variability due to Allier River altitude variations from 167 to 1423 m.a.s.l., with a mean altitude of 900 m.a.s.l., and to the atmospheric mixed influences (Bertrand et al., 2008; Négrel and Roy, 1998) of oceanic (sector 1, Fig.I-2), continental (sector 2, Fig.I-2) and Mediterranean incomes in the southern part (sector 3, Fig.I-2) as well as local influences (sector 4, Fig.I-2). Rainfall is often different from one location to another (Fig.I-3), such as in the mountainous area (upstream of study area); the maximum values are reached in winter and late spring due to oceanic storms influence (about 2000 mm/year over the tops of the Monts du Cantal), and the minimum ones in the summer (about 570 mm over the Limagne basin of Clermont-Ferrand).

Allier basin receives on average 800 mm of rain annually, with an average annual temperature comprised between 5 and 6°C in the higher altitudes of the basin and 11.7°C in the lower altitudes (Bertrand et al., 2010, 2013).

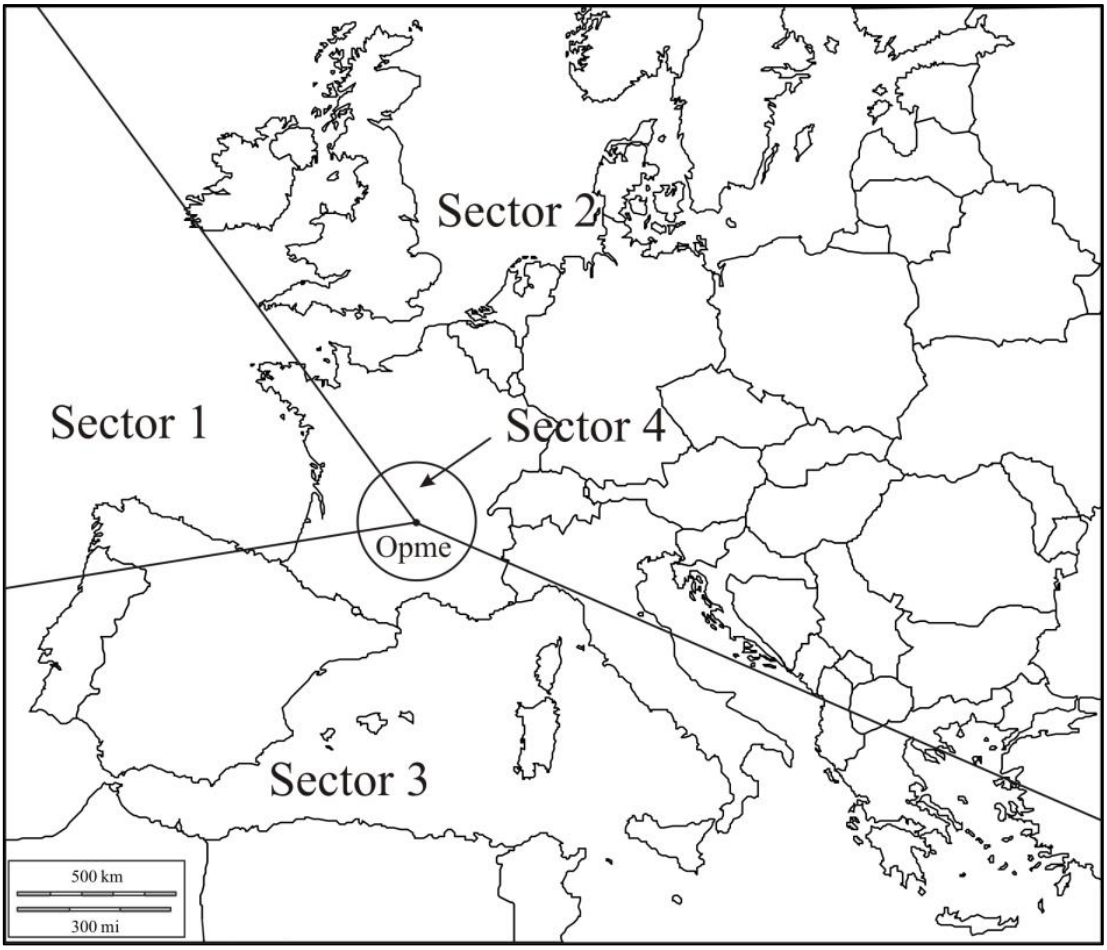

Fig.I-2: Main sectors for air masses trajectories arriving at study area: (1) oceanic, (2) continental climate, (3) Mediterranean incomes, and (4) local (adapted from: Bertrand et al., 2008).

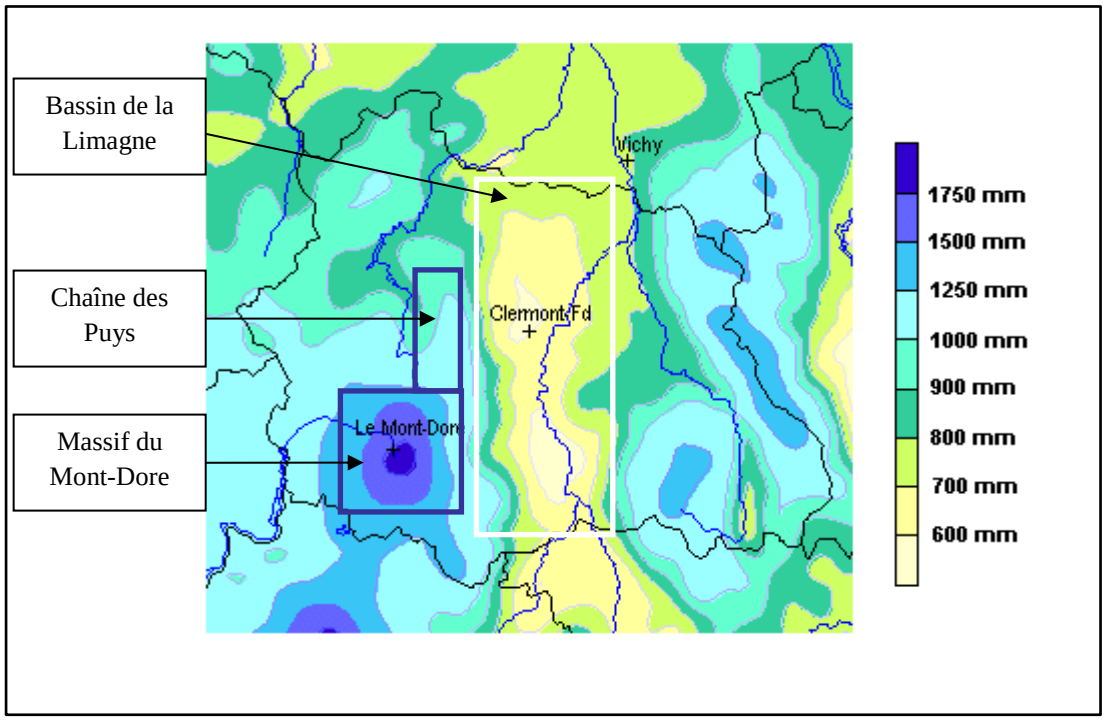

Fig.I-3: Map of annual rainfall (mm) in the Puy-de-Dôme (based on data from Météo-France).

1.1.2. Geology of Allier basin

Geologically, the Allier River basin occupies the Limagne rift valley, an elongated tectonic depression in the Hercynian crystalline Massif Central, France (Dèzes et al., 2004). The drainage basin (Fig.I-4) is underlined by Hercynian crystalline basement rocks (58%), with Cenozoic volcanic rocks (22%) mainly along the margins of the rift valley and partly calcareous Oligocene fluvio-lacustrine sediments (20%) as a rift valley fill (Korobova et al., 1997). Strong uplift of the Massif Central from the beginning of the Quaternary onwards (Dèzes et al., 2004; Ziegler and Dèzes, 2005) has forced the Allier to incise deeply into the underlying bedrock, thus forming many terraces (Fig.I-5).

Furthermore, there was on-going volcanism in the uplifted rim west of the rift valley. The Allier terrace deposits are gravelly and sandy sediments poor in clay and encompassing silicate components of granitic-gneissic and basaltic origins from Massif Central, reflecting the different lithologies within the Allier basin.The volcanic components usually predominate while the Oligocene rocks are usually rare (Veldkamp and Feijtel, 1992). Common heavy minerals of the Allier terraces are augite, green and brown hornblende, olivine, mica and opaque (Van Dorsser, 1969; Rudel, 1963; Pelletier, 1971; Pastre, 1986; Tourenq, 1986). The opaque component, which can comprise more than 50% of the fine sand fraction, is predominantly composed of basaltic rock fragments. The sediment composition has known many changes in time due to incision of the Allier, glaciations of the higher parts in the basin and volcanic eruptions (Kroonenberg et al., 1988). The ancient alluvial deposits of Allier are distinguished from recent alluvial deposits. The former (Early Pleistocene) are thin, about several meters, and are consisting of quartz, sand and little clay whereas the latter alluvium is composed of sand, gravel and rocks covered with layer of silt. These alluvial deposits are mainly located over the marly calcareous deposits of the Limagne or directly on the crystalline basement (Dadet et al., 1979). The alluvial layer is 6–15 m thick (10 m on average) and their scope ranges from a few meters to several kilometres on each side of the river. The total alluvial aquifers represent about 6% of the Allier basin, and then the total estimated volume of water contained in this alluvial layer is about 2 billion cubic meters (Livet et al., 2006).

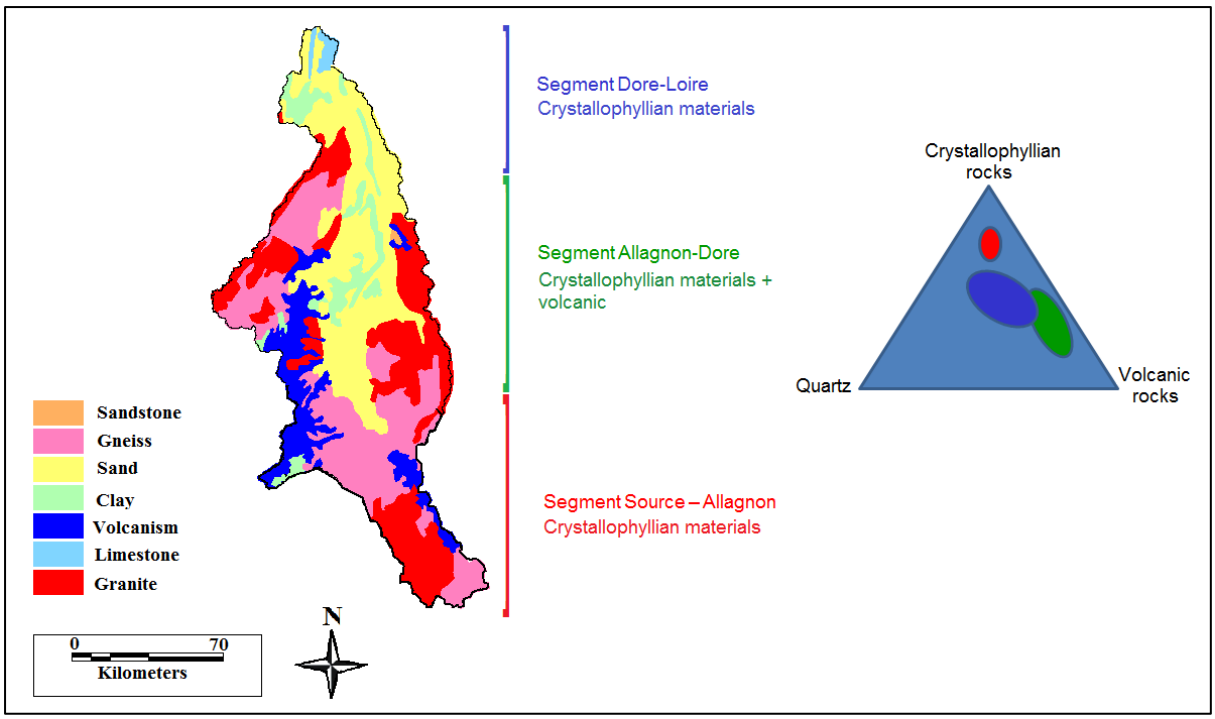

Fig.I-4: Geological map of Allier basin (adapted from report of: Rougé and Hamm, 2013), Triangle diagram showing the contribution of Chrystallophyllian rocks, volcanic rocks and quartz to the Allier sediments within the Allier basin (CETE & BRGM, 1975)

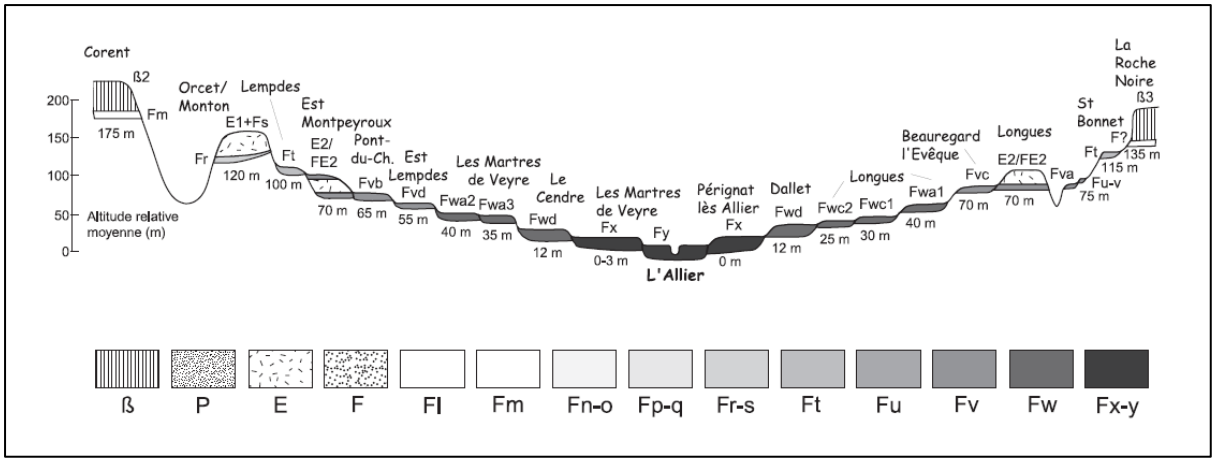

Fig.I-5: Synthetic section of alluvial and volcanic formations of Limagne des Buttes: – ß. Basaltes – P. Pyroclastites – E. Épiclastites – F. Alluvions pliocènes à galets de quartz – Fl to Fx-y. Alluvions pliocènes à holocènes regroupées par ensembles (adapted from Pastre et al., 2005).

1.1.3. Land occupations

The Allier River mainly passes through Auvergne, located in the heart of the Massif Central, a mountainous region where agriculture, especially livestock, occupies a predominant position. The upper Allier basin (Fig.I-6) is poorly occupied in terms of inhabitations and activities and used primarily for animal husbandry and agricultural activities (maize and cereal) which occupy about 71% of land cover of the basin, forest and grassland come next with 24% with only 5% urbanization (Plan-Loire, 2011). The city of Clermont-Ferrand is considered as the biggest city in Allier basin with about 140 000 inhabitants as estimated in 2011. However, the population of the total urban area near Clermont-Ferrand is estimated to be around 250 000 inhabitants (INSEE, 2011).

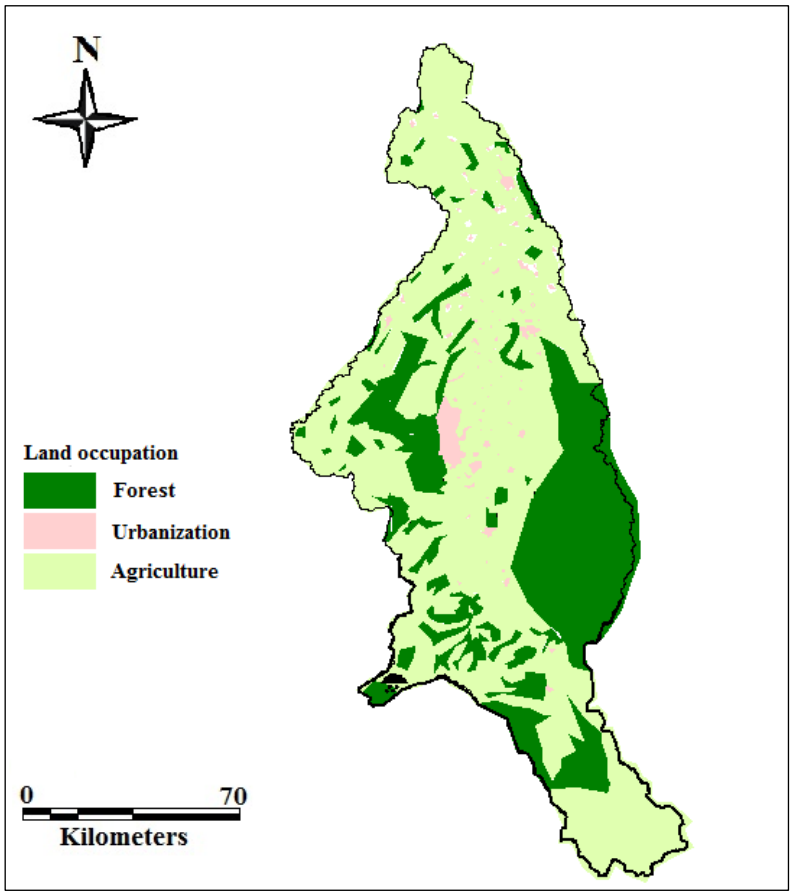

Fig.I-6: Land occupation of the Allier River's basin (adapted from report of: Rougé and Hamm, 2013).

1.2. Allier River

Allier River is the left and the largest tributary of Loire River. The Allier River originates in the Massif Central (La Maure de Gardille, 1423 m.a.s.l.), flows roughly South toward North with a total length of 425 km long and joints the Loire at the Bec d'Allier, near Nevers. It

remains one of the last wild rivers in Europe, means that the river has quite free meanders or spreads widely on the surface according the speed. The Allier is mainly recharged by rainfall which seasonally from high height in winter and low volumes in summer. The flow rate of Allier River depends strongly on the season and varies from place to place according to precipitation distribution. There are three different periods in the Allier River's hydrological cycle registered on Vic-le-Comte hydrological station, located 12 km far from the sampling site: (1) low flow rate (7.1 $m^3 s^{-1}$) during summer, (2) high flow rate in winter with possible short periods of flooding during which flow can reach 600 $m^3 s^{-1}$, and (3) lower high flow in spring (176 $m^3 s^{-1}$) corresponding to snow melt in the Massif Central. The average flow rate is of 40.4 $m^3 s^{-1}$ for the nov-2010/nov-2012 period (Fig.I-7). In the last 18 years, three big flood events were recorded. As an example, the flow rate of Allier reached to 1530 $m^3 s^{-1}$ in December 2003 at Vic-le-Comte. Large amounts of sands and gravels are transported during floods and the morphology of the river may change significantly during time (Frémion, 1995; Négrel et al., 2003).

The Allier River is a meandering river and the river-bed had often moved from a few tenths of meters in recent period (Négrel et al., 2003). Remains of old channels are still visible in places on the surface of well field, forming small linear depressions (Fig.I-8).

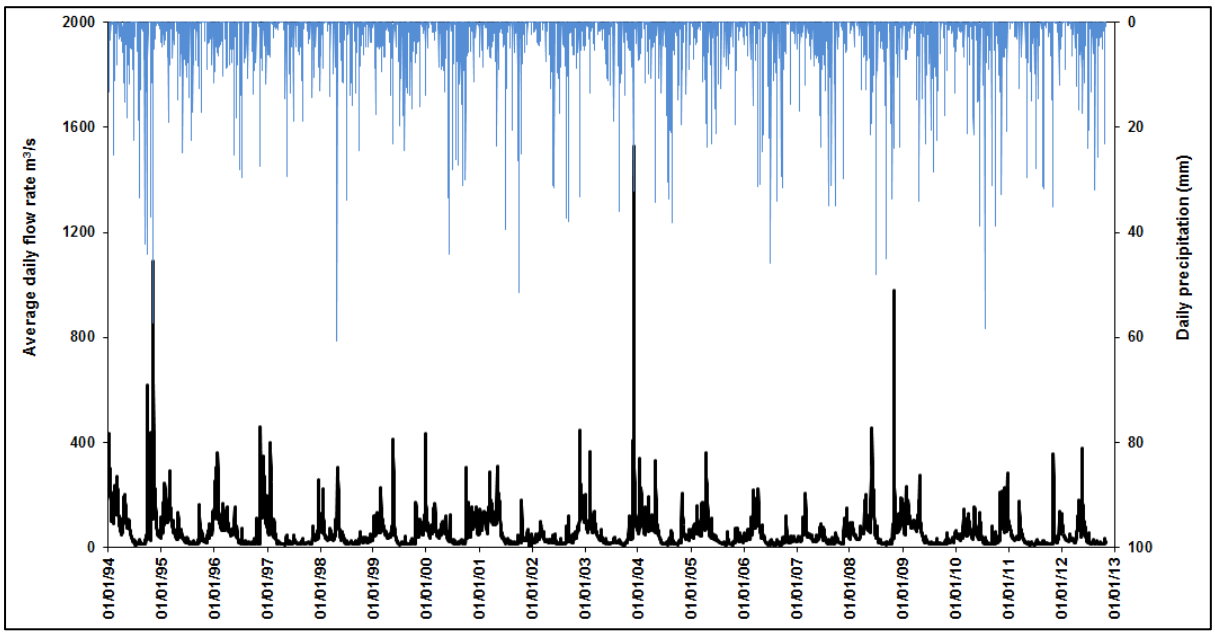

Fig.I-7: Allier River daily flow rate in Vic-le-Comte hydrological station and daily precipitation from Aulnat meteorological station (data extracted from: www.hydro.eaufrance (French Ministry of Ecology and Sustainable Development)).

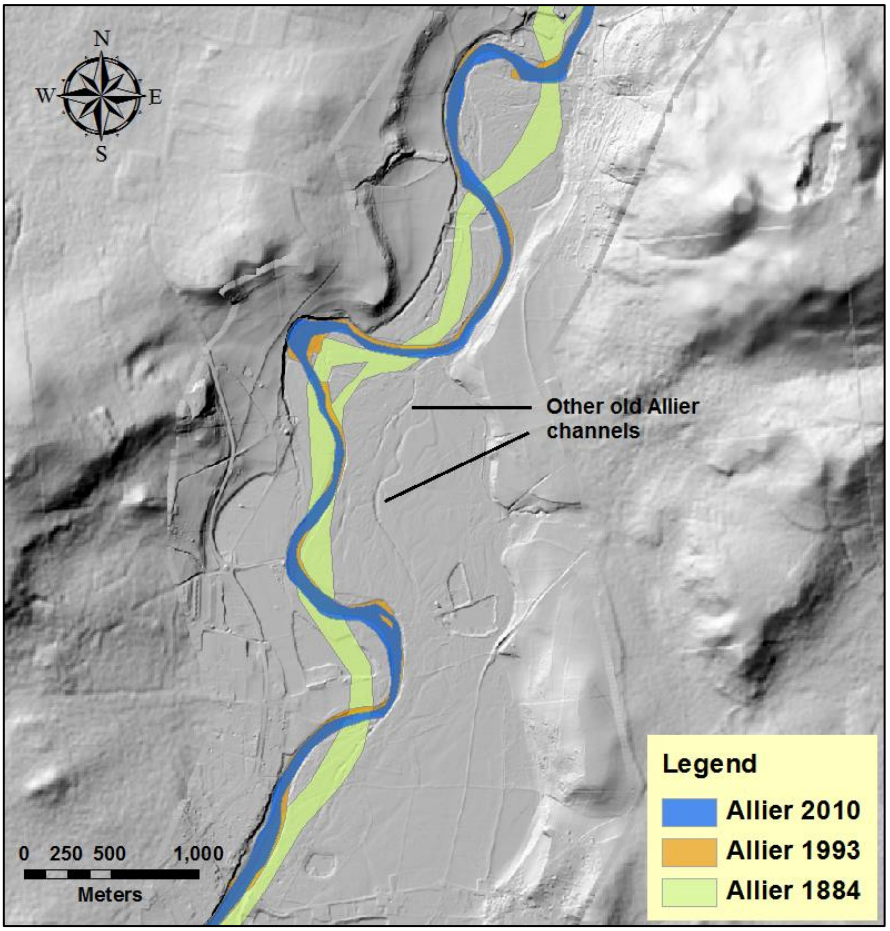

Fig.I-8: Allier River old channesl in the study area

The extraction of aggregates as well as the confinement of banks had negatives effects on the river. Indeed, to balance its course, the river needs materials to be transported. But when it cannot affect any more its banks and when activities subtract its reserves, it compensates for this lack by affecting its bed. This answer of the river causes the sinking of its bed and a decrease of the volume of the alluvial tablecloth. Within the last 50 years, the sinking of the bed observed reaches 3 meters in some places. The extraction of aggregates has been stopped since 1994 (article 11.2.I de l'arrêté du 22 septembre 1994).

1.3. Sampling site

1.3.1. Sampling points location and description

75 points were selected: 71 boreholes, Allier River, 1 piezometer, and 2 springs. Relying on the strong connection between river and associated alluvial aquifer (e.g.: Schurch and Vuataz, 2000; Han et al., 2009; Eastoe et al., 2010; Andrade and Stiger, 2011), Allier River was

sampled. Other three particular points were also chosen as follows: one piezometer (P13) not pumped for drinking water purpose and that represents the southern aquifer which is considered to be one of the recharge source of the site, and two springs, Jallat and Cognet, located in the neighbouring hills, to show the possible relation between alluvial and neighbouring hills'aquifers. The sampling site (45º45'16.20''N, 3º13'9.43''E, altitude= 320 m) is located about 20 km from the east of the city Clermont-Ferrand, France. Our investigation concerns the part of the alluvial system exploited by the City of Clermont-Ferrand for drinking water supplies. Tap-water coming from the alluvial aquifer is distributed in both sides of the Allier River in the territories of Dallet, Mezel and Cournon communes. The water taken from this part of the alluvial aquifer represents about two third of Clermont-Ferrand's requirement, the remaining third is provided by abstraction of water from volcanic aquifer sources in the Chaîne des Puys. 71 boreholes have been established in the both side of the Allier (Fig.I-9), the beginning of the exploitation returns to the 1930s. The potentiality of the field is about 950 l/s or 3420 m^3/h (Frémion, 1995). The directorate of water and sanitation (water control service) of Clermont-Ferrand has divided these boreholes into 6 groups, according to their location, as follows:

- Station B1 consists in 29 boreholes (from n°1 to 29) which have been pumped since 1933 by three pumps with a yield of about 200 l/s each.
- Station B2 is composed of 8 boreholes (from n°30 to 37) which set up in 1954; the water is exploited by two pumps with a yield of 200 l/s.
- Station B3 has been set up from 1960 to 1961 and comprises 10 boreholes (from n°41 to 50), it is exploited via four pumps.
- Station B4 has been set up between 1968 and 1970. It consists in 18 boreholes (from n°51 to 65 and n°38 to 40) and has a potential yield between 15 and 30 l/s.
- Station B5 includes 5 boreholes (from n°66 to 70) and has been exploited since 1976.
- Station B6 is composed of only one borehole (n°71) drilled in 1976 and pumped with a potential yield of 30 l/s.

These boreholes are not utilised at the same time and an automatic rotation has been established.

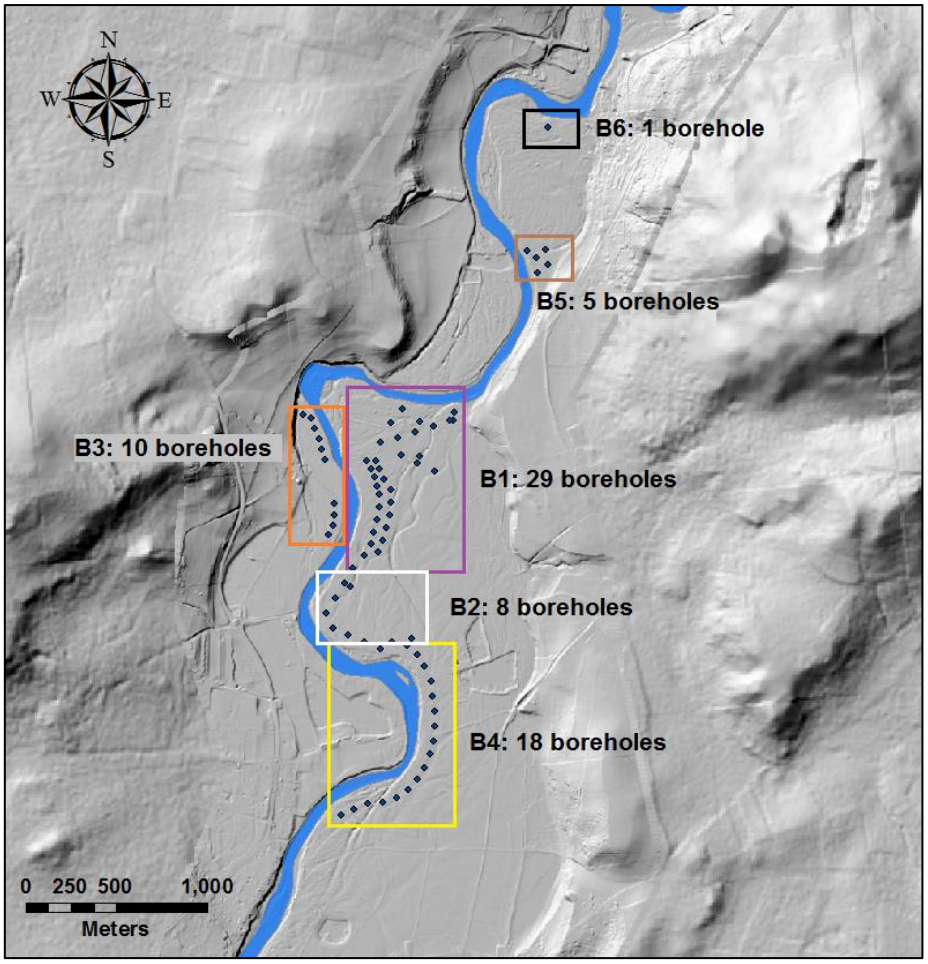

Fig.I-9: Study site location showing sampling boreholes divided to 6 groups.

The pumping process occurs usually during night (Fig.I-10a). Our sampling procedure carried out during day time so that the water levels become stabilised (Fig.I-10b).

The site exploited by Clermont-Ferrand extends to 2 km² and as a drinking water supply site, is protected from pollution through a protection perimeter (urban, agricultural and industrial activities are prohibited within the site, except small cattle breeding according to Directive Cadre, 2006).

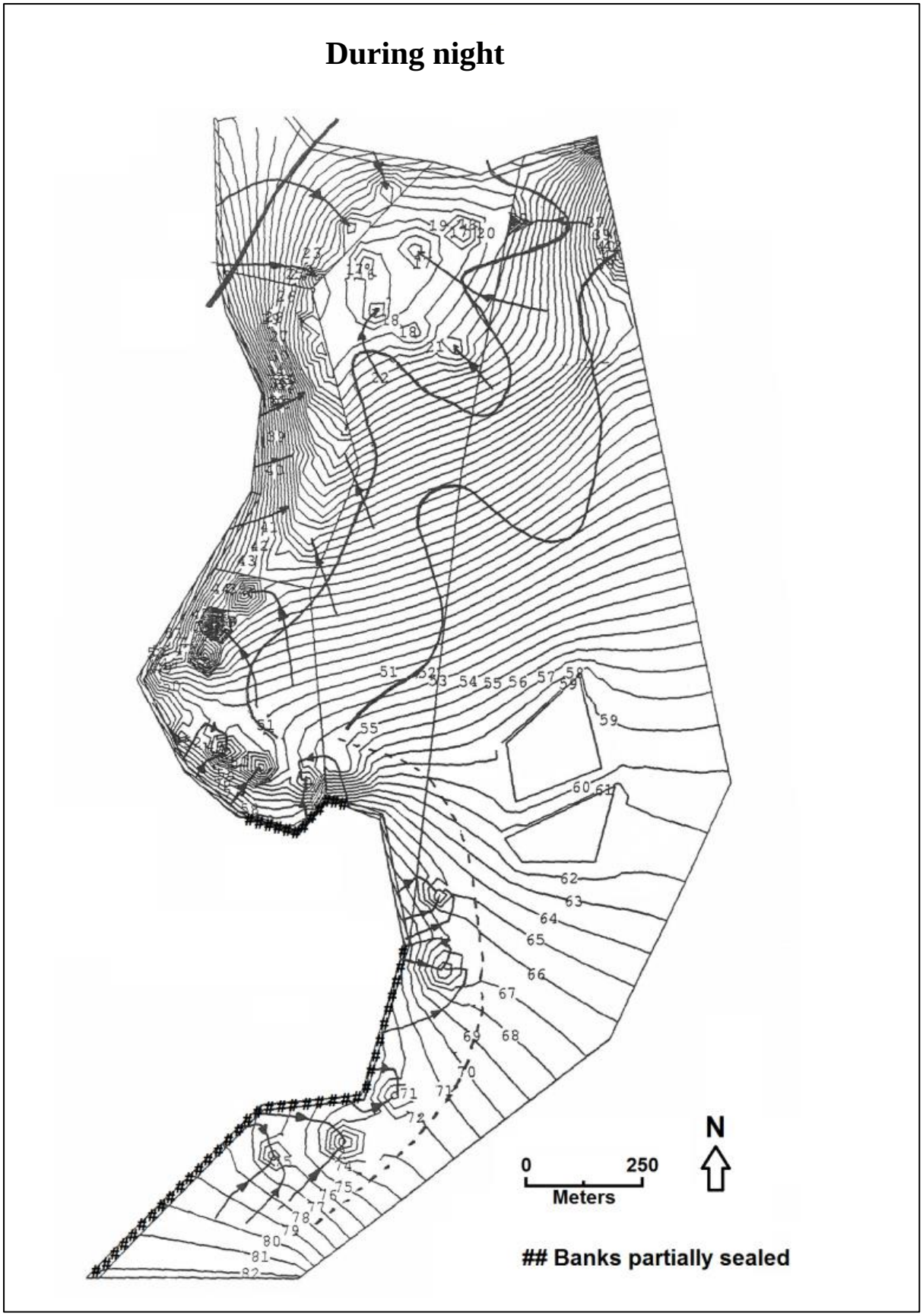

Fig.I-10a: Groundwater flow directions during night (pumping) time. (adapted from: Frémion, 1995)

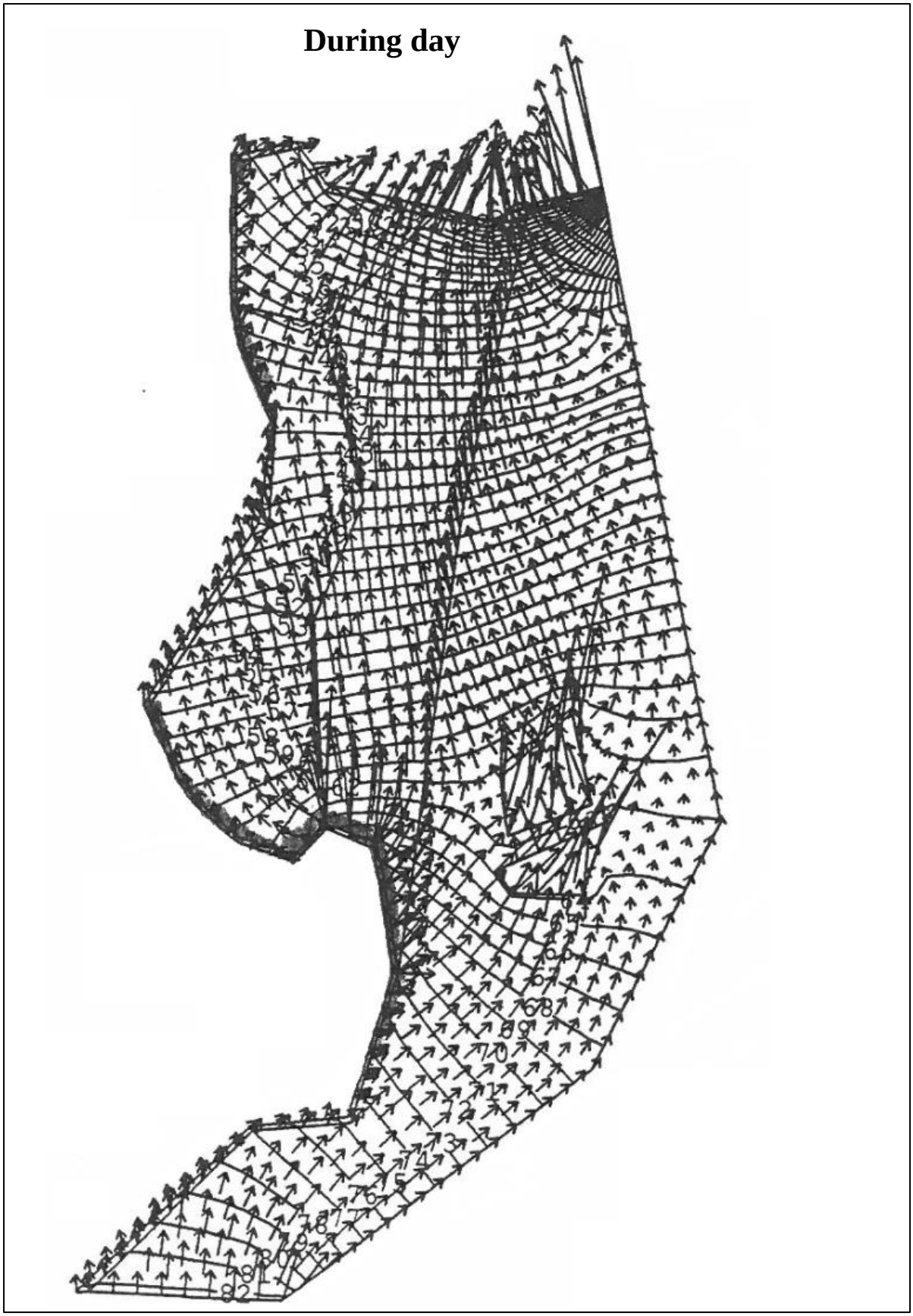

Fig.I-11b: Groundwater flow directions during day (stability) time. (adapted from: Frémion, 1995)

1.3.2. Climate settings

The climate of the study area is characterised by values extracted from Aulnat Meteo-France station located 6 km north-west from the site (Fig.I-11). The temperature and rainfall show a quite clement climate with fairly hot summer that temperatures climb to 30°C in July/August and cold winter, with temperatures generally of just below 0°C in December and January (Fig.I-12) that can reach -10°C (Meteo-France data). The study area has irregular rainfall throughout the year with an average rainfall of 570.9 mm which is one of the lowest rates in France. Snow and sleet storms can happen in winter. Most of the rainfall falls in summer, between May and September. The year 2010 and 2012 showed high precipitations and the amounts were above annual threshold while in the year 2011, the amount of rainfall is below annual threshold of the area (Fig.I-13).

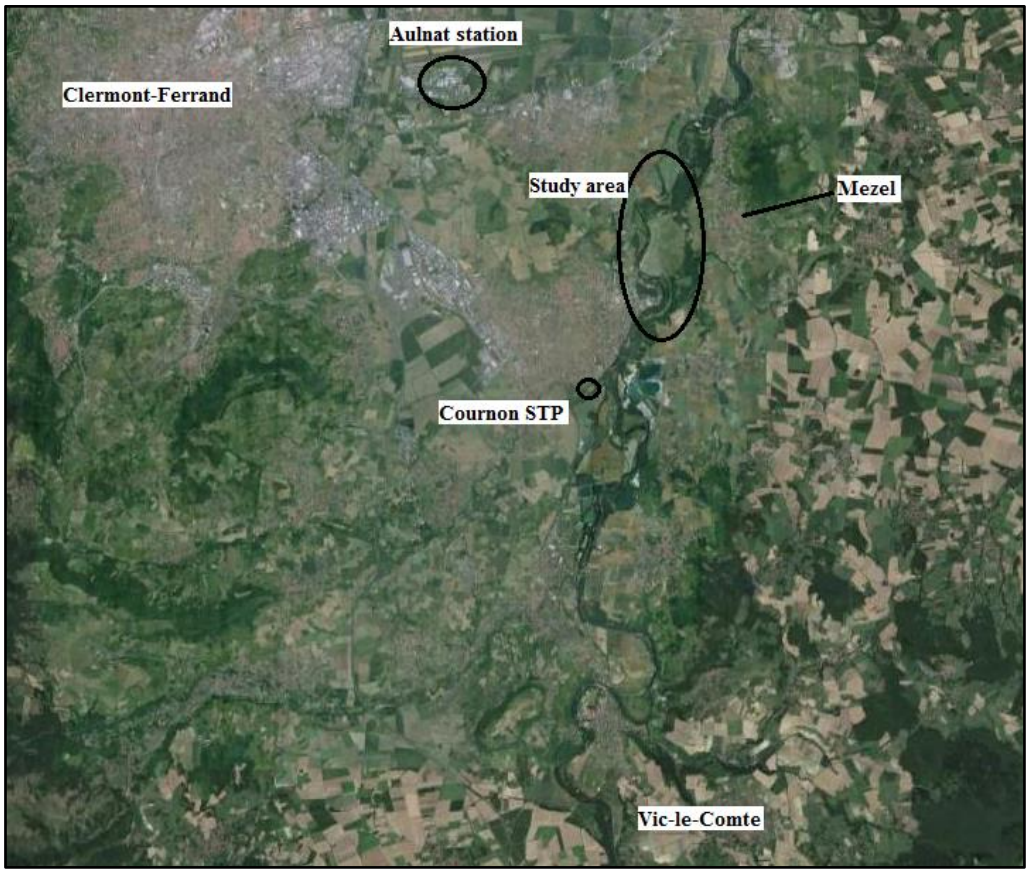

Fig.I-12: Regional map showing: study site, Mezel and Vic-le-Comte towns, Cournon STP, Aulnat meteorological station, and the city of Clermont-Ferrand.

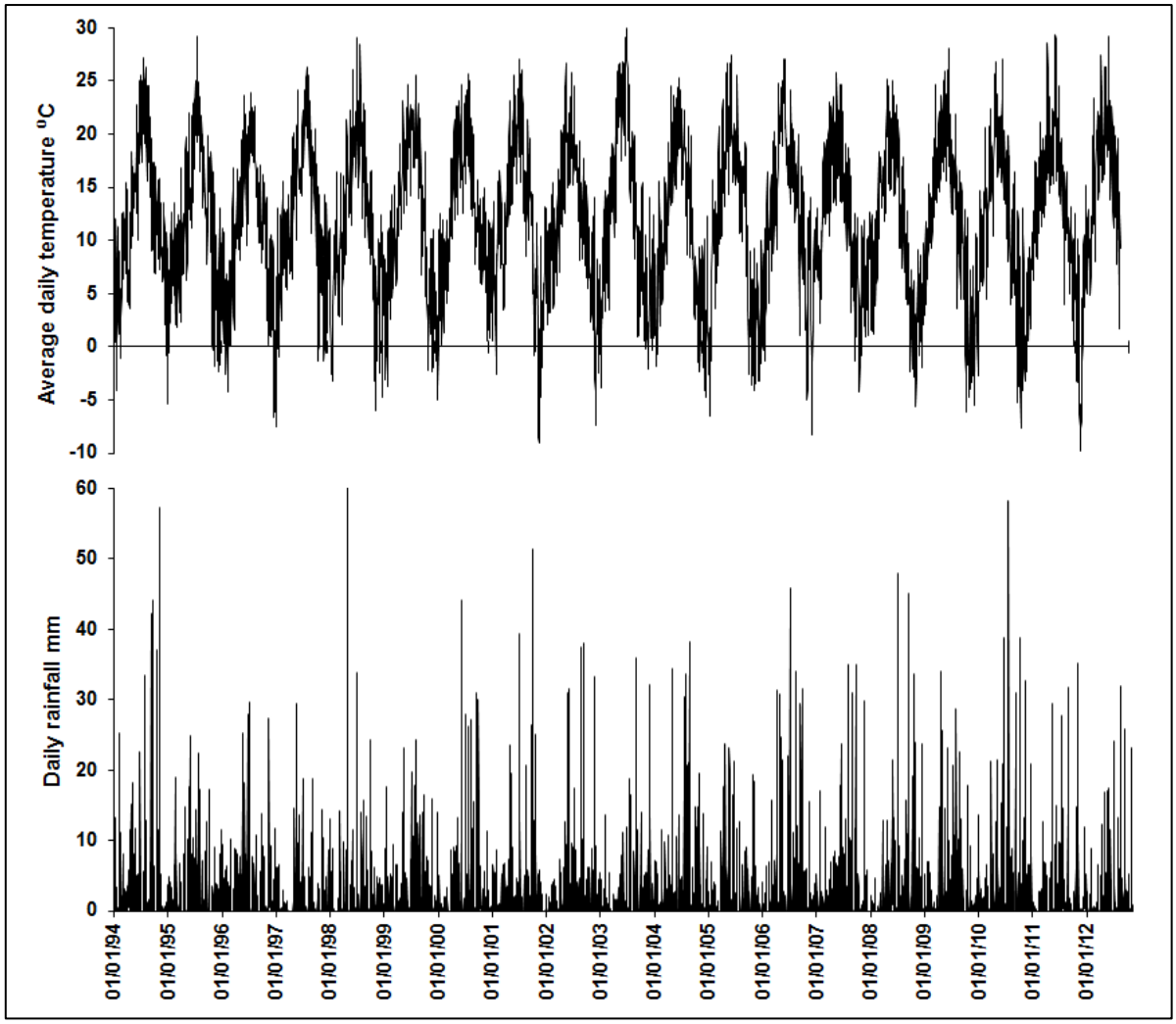

Fig.I-13: Climatic characteristics (rainfall and temperature) at Aulnat meteorological station close to study site (adapted from Meteo France).

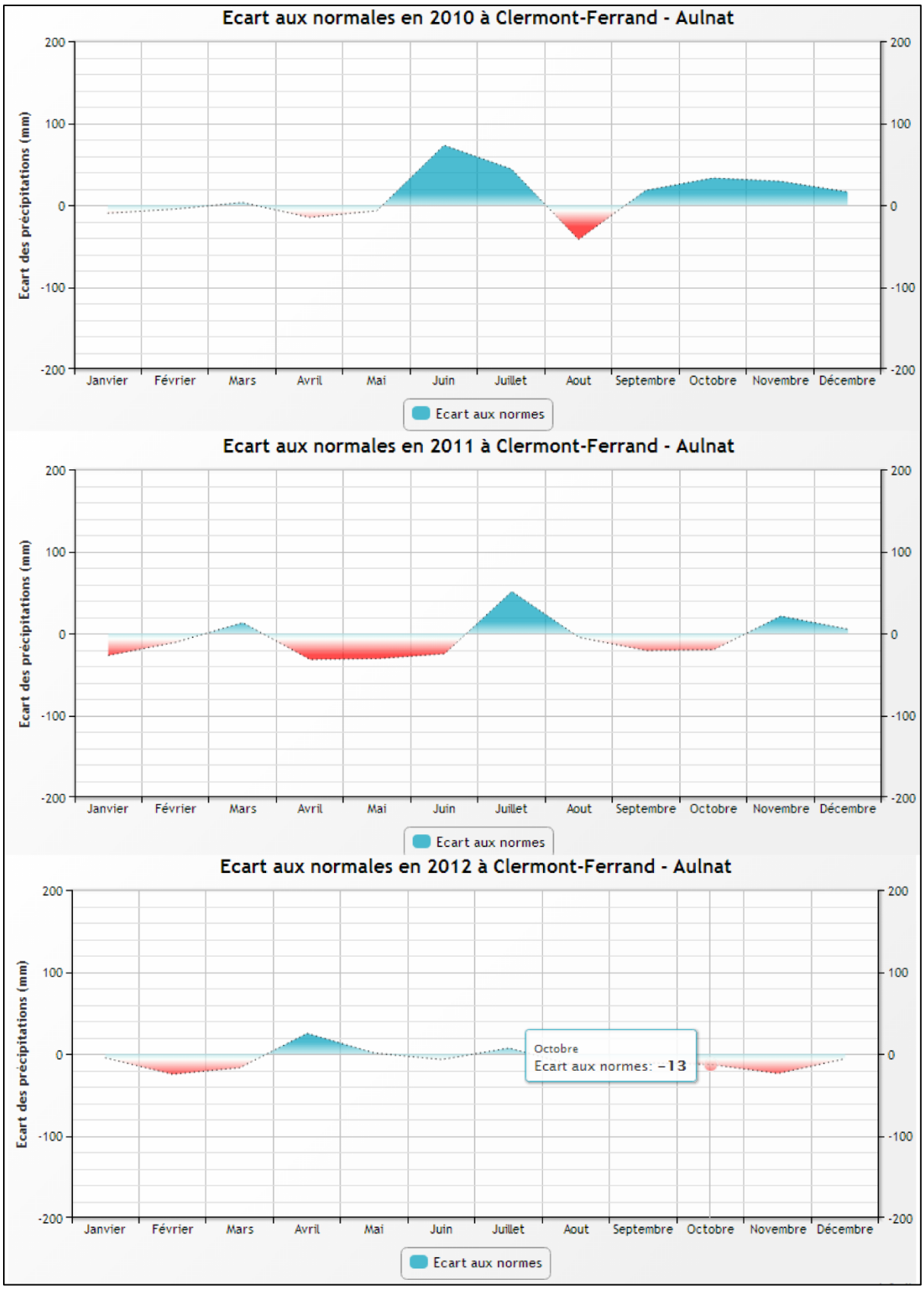

Fig.I-14: Precipitation deviation from standard for the year 2010, 2011, and 2012 from Aulnat meterological station close to the study area (adapted from Meteo France).

1.3.3. Geological setting

The Allier River alluvial aquifer consists of fine sand, coarse gravels and pebbles originated from volcanic rocks, gneiss and granite from upstream (Fig.I-14). The alluviums are mainly made of quartz (70.1%), basalt (14.2%), feldspar (13.2%) and mica (2.5%) as shown in Fig.I-15. Their thickness varies between 6 and 15 m with 10 m on average (Fig.I-16) and their scope ranges from a few meters to one kilometre on the right side of the river in our site.

Fig.I-15: Alluvial sediments of the study area.

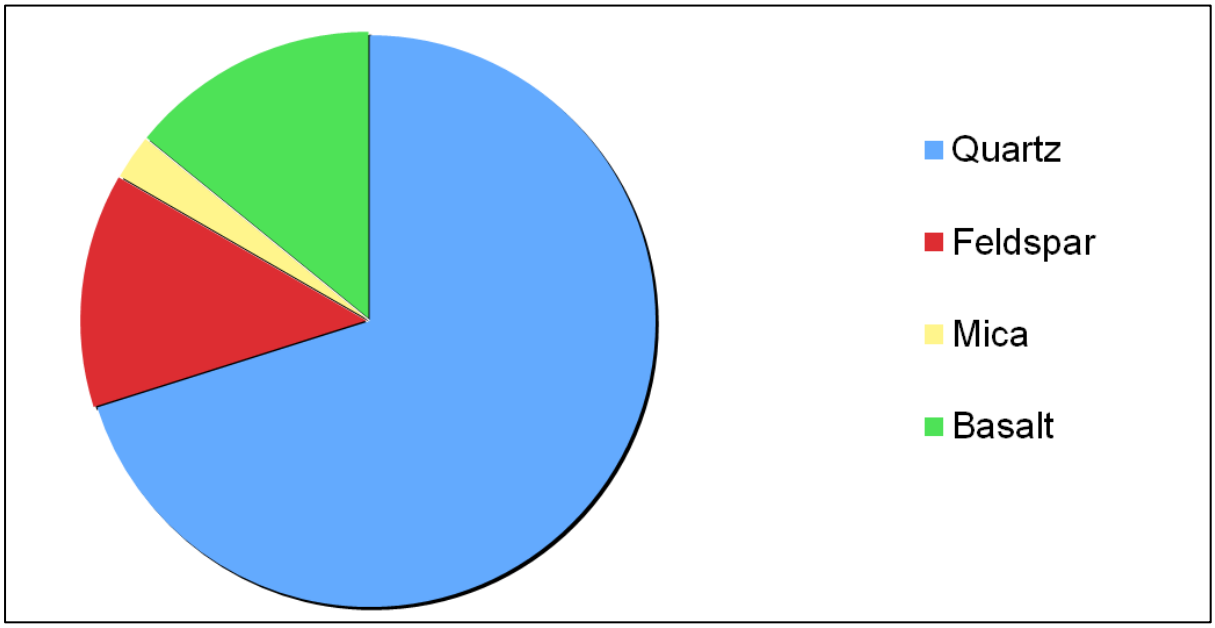

Fig.I-16: Content of minerals in alluvial sediments of study area

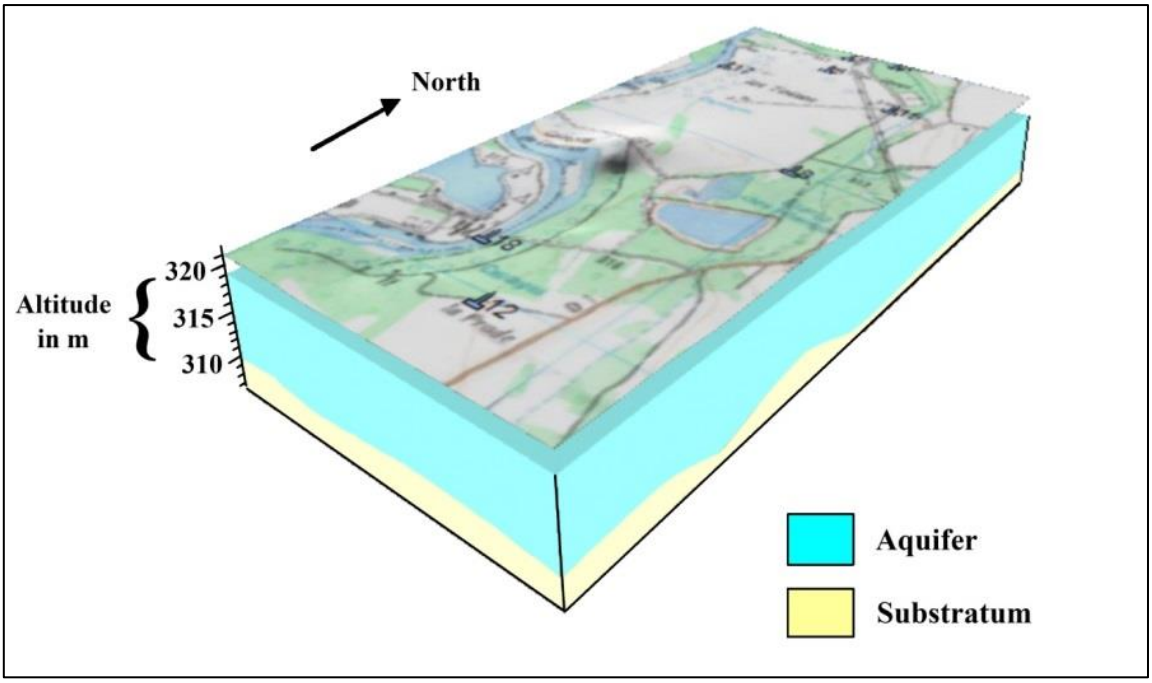

Fig.I-17: Alluvial aquifer thickness profile.

The substratum bedrock consists of dense and interconnected limestone and marls from the Limagne basin. Their permeability is, generally, from low to very low (impermeable) and the bedrock surface is not uniform (Veldkamp and Feijtel, 1992; Korobova et al. 1997).

The higher terraces are composed of colluvium made of sedimentary and volcanic formations underlying Oligocene sedimentary layers (marl, clay …). The hills surrounding the study site are mainly composed of Miocene volcano-sedimentary formations (peperite) and Miocene basalt. In the eastern side of Allier River, Puy de Mur mainly consists of peperite (Miocene volcano-sedimentary formation) (Fig.I-17).

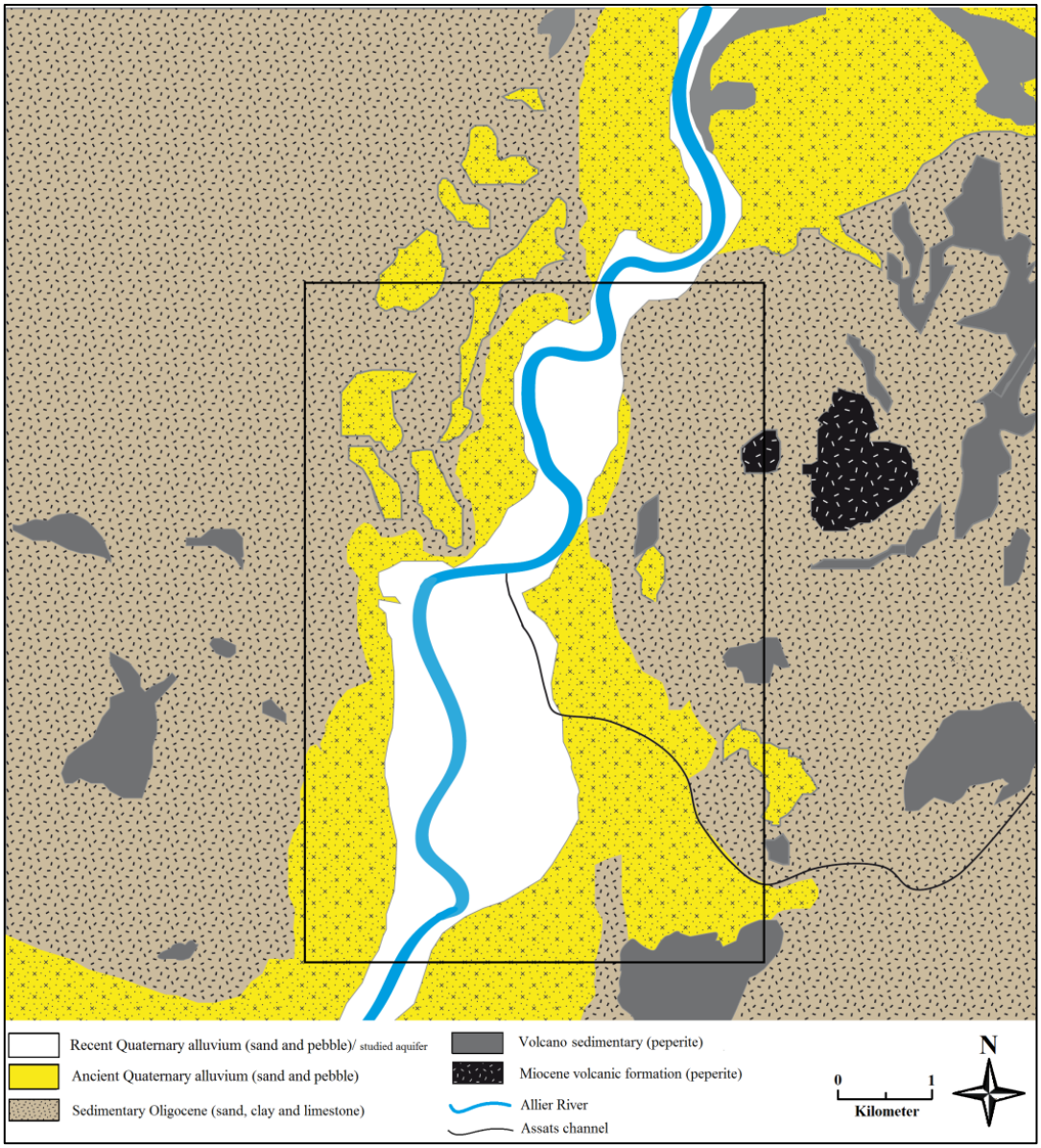

Fig.I-18: Geological map of the study site

1.3.4. Hydrogeological settings

Groundwater water is very shallow and is just between 2 to 4 m underneath the soil surface. The alluvial aquifer of Allier is unconfined and is in direct contact with surface water so that it can be affected by surface recharge and discharge.

Hydraulic conductivity of alluvial deposition vary from 10^{-3} to 10^{-4} m/s (Fig.I-18), the effective porosity is of 8% to 10% (Frémion, 1995; 1997). This high permeability makes the alluvial groundwater significantly vulnerable to pollution. On a hydrodynamical point of view, according to the pumping organisation, there are considerable groundwater–surface water interactions along the Allier River and groundwater which circulates from south to north as Allier River flows (Fig.I-19; Frémion, 1995). Regarding the water circulation,

recharge and pumping, four end-members can be identified: Allier River considered as the main source, surrounding hills which are represented by local springs of Cognet and Jallat, southern part of the alluvial aquifer which is represented by piezometer P13, and rainfall, with a possible combination of the four origins.

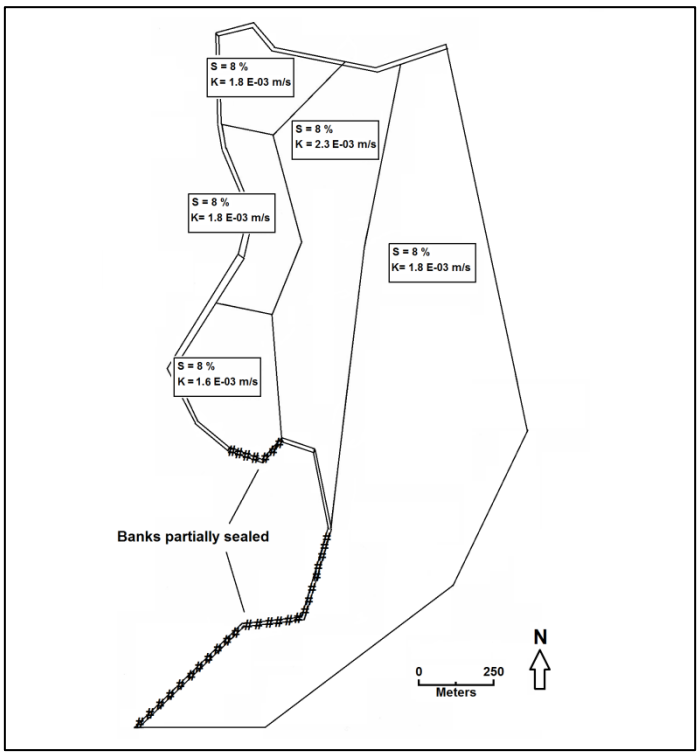

Fig.I-19: Hydraulic conductivity (K) and porosity(S) of alluvial deposition (adapted from: Frémion, 1995)

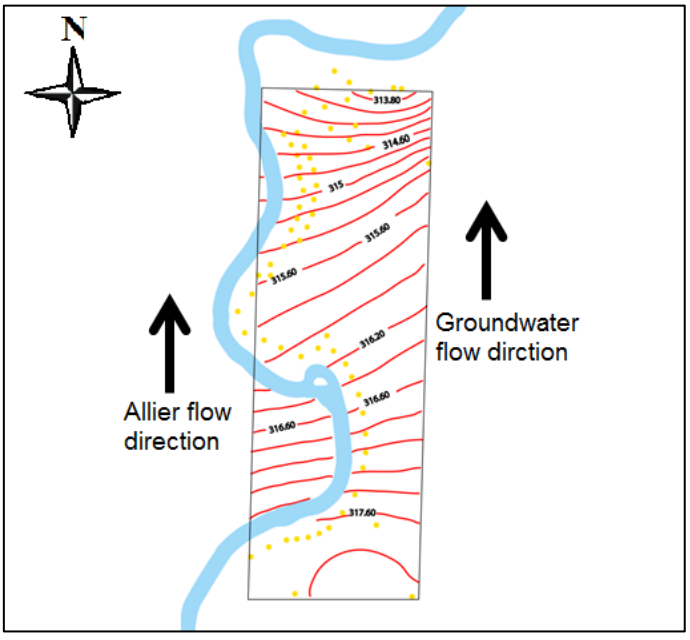

Fig.I-20: Piezometric level and flow direction of groundwater (adapted from: Frémion, 1995)

1.3.5. Environmental settings

Several potential sources of pollution can be distinguished close to the study area. Firstly, the Assats channel, one of the tributary of the Allier River that joins it on the right border, receives effluents from the local towns and gathers waters that circulate in cultivated lands. A watertight channel was built in 2004 in order to protect the sampling site. Besides, we cannot evacuate the possibility of fissures within the channel which would allow exchanges with the groundwater. Secondly, the surrounding hills are occupied by small towns and are mainly used for agricultural practices. Then the connection between the alluvial system and the Allier River has to be considered, as Allier River constitutes the drainage axis of the whole basin and collects all the waters that circulate on agricultural, urban lands. Moreover, Allier River gathered the discharge waters of 378 Sewage Treatment Plants (STPs) above the sampling site (the nearest STP is Cournon's one with 4.2 km upstream the sampling site). As some of the pollutants are not treated by STPs, notably pharmaceuticals and pesticides (Dulio et al., 2009; Soulier et al., 2011), these has to be taken into account.

We can add to these, the road salt in winter, pollution from agricultural practices in the southern part, and cattle grazing within the study site during spring and summer (Fig.I-20).

Fig.I-21: The environment of sampling site showing some sources of contamination.

2. Sampling procedure and analytical methods

2.1. Sampling design

Repetition of field measurements and laboratory analysis is an essential part of hydrochemical studies (Mazor, 2004). Sources of recharge, water table, discharge responses to precipitation or flood events, mixing processes, man-induced changes vary over time and are distinguishable by their isotopic and chemical composition, so that a seasonal input can be established (Appelo and Postma, 1993; Mazor, 2004). For this reason, a sampling design has been established including:

- 2 intensive campaigns dedicated to the spatial characterisation of waters during two contrasted periods of the water cycle;
- 46 campaigns, carried out each two weeks, in order to highlight the temporal variations of physic-chemical and isotopic parameters
- 14 campaigns, achieved each month, designed for emerging parameters measurements (pesticides, pharmaceuticals, microbiology)

2.1.1. Spatial investigations: two intensive campaigns

Two field campaigns were conducted, one in December 2010 (low flow) and the other in June 2012 (high flow), to examine the 75 selected points (cf 1.3.1) for physico-chemical parameters, major ions, traces and stable isotopes (^{18}O, ^{2}H) measurements (Fig.I-21).

The purpose of these two campaigns is to have a general view on the spatial distribution of chemical and isotopic signatures and to characterise each type of water that circulate in the study area.

2.1.2. Temporal investigations: each two weeks

To determine the functioning of alluvial system, a temporal investigation was conducted on 19 points (15 boreholes, 1 piezometer, 2 springs and 1 surface-water) selected according to their location within the field and their chemical and isotopic characteristics (Fig.I-22). The number of points selected depended on the sampling duration (each the sampling campaign should last one day maximum) and the cost of analysis, 19 points was the optimum number to match these constraints. These points were sampled bi-weekly from February 2011 to November 2012 for physico-chemical, major ions, traces and stable isotopes analysis. Among the selected boreholes, B39 is the only one that has not been pumping for about 20 years due to high manganese content.

Additionally, an automatic pluviometer (Eigenbrodt Automatic Precipitation Sampler NSA 181 with an aperture of 614cm², which opens/closes automatically during and after any rainfall events (Fig.I-23)) was installed in the study area (45º45'12.92''N, 3º12'58.42''E, altitude= 322m) in order to collect the precipitations during the study period. Rain samples were analysed weekly for major ions and stable isotopes of the water molecule.

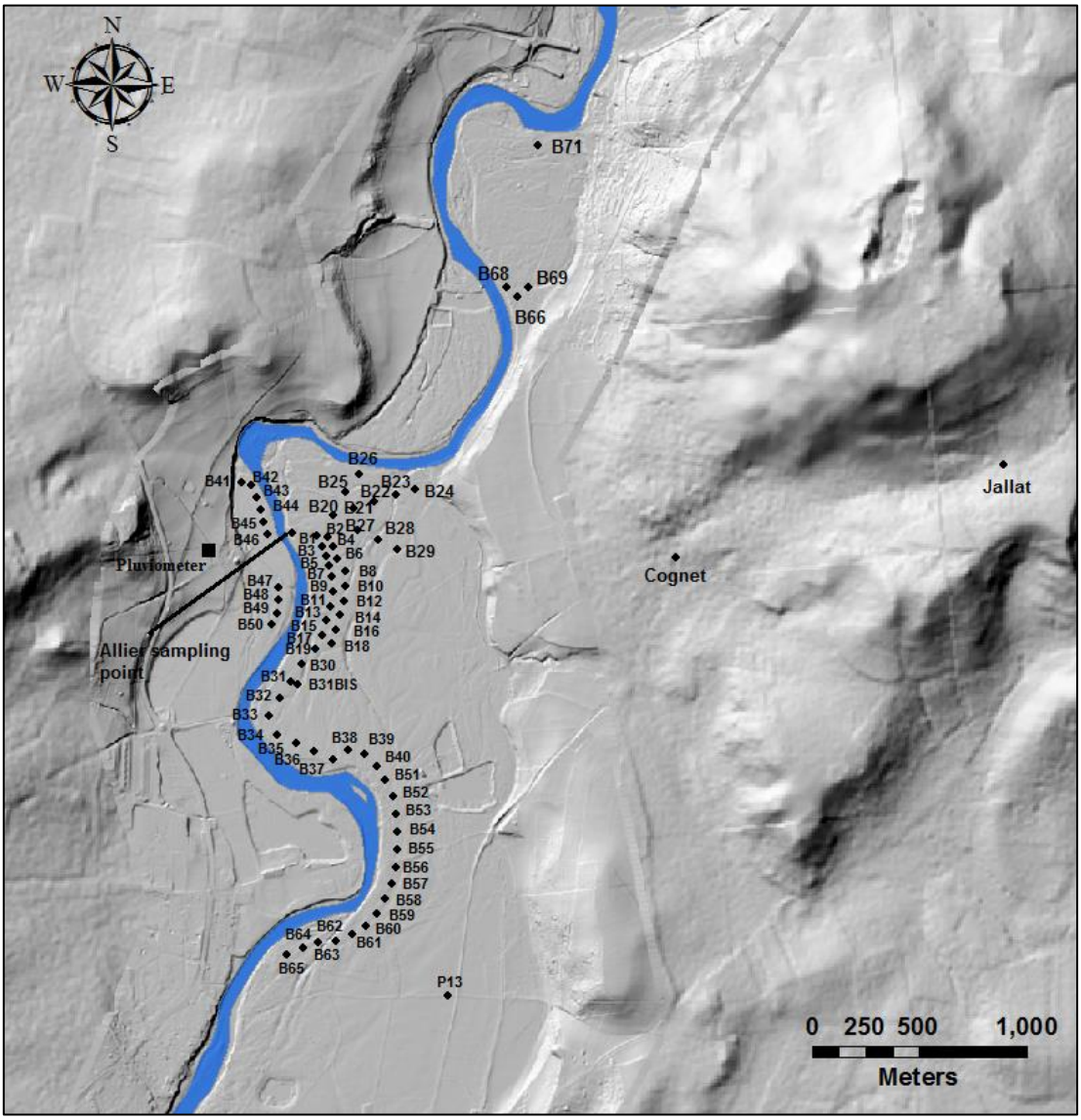

Fig.I-22: Sampling points for spatial investigation

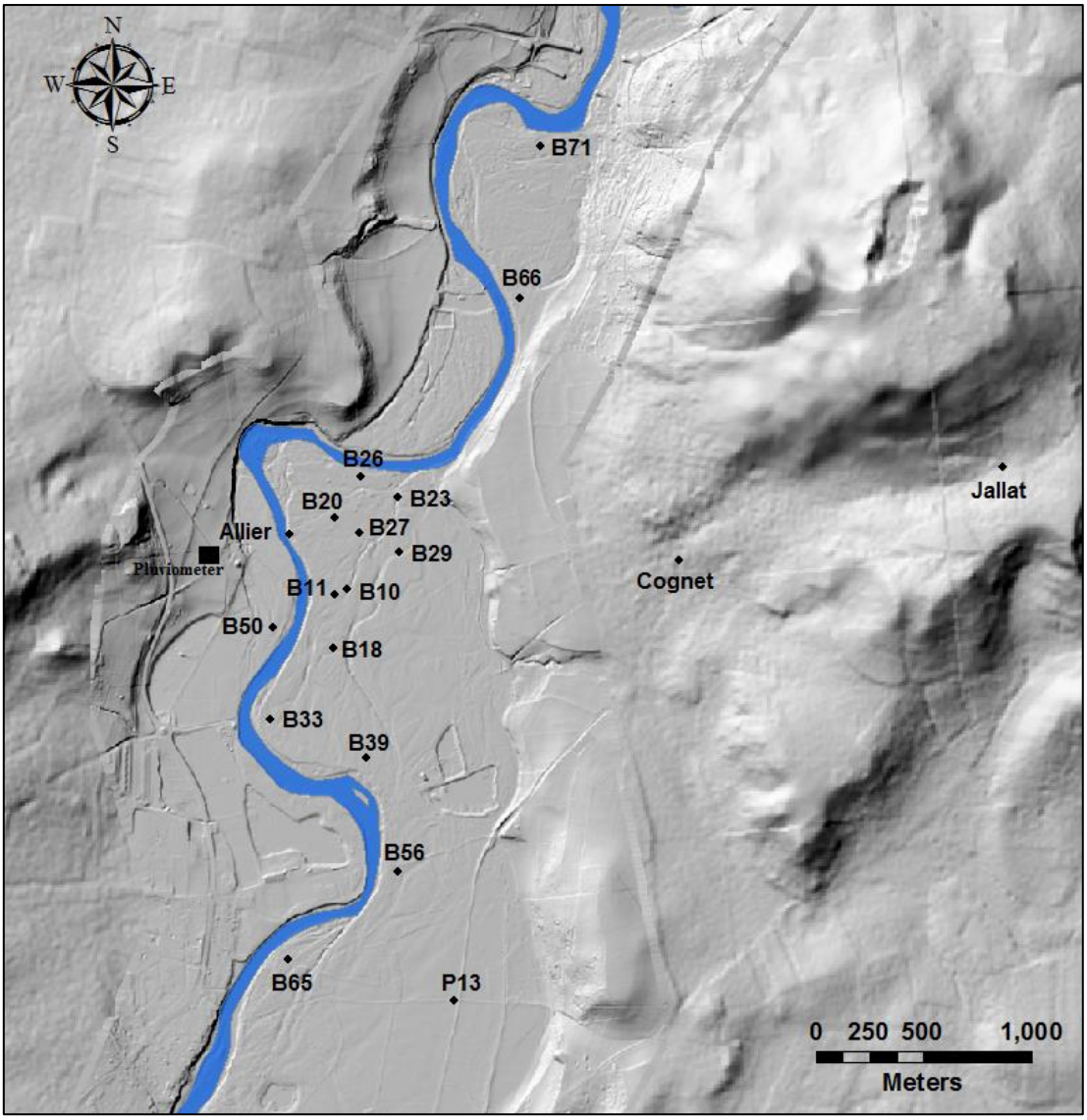

Fig.I-23: Sampling points for bi-weekly temporal investigations

Fig.I-24: Eigenbrodt Automatic Precipitation Sampler NSA 181 with an aperture of 614cm², which opens/closes automatically during and after any rainfall events

2.1.3. Temporal investigations: each month

Due to high analytical costs, only 4 sampling points (2 boreholes, 1 piezometer and 1 surface-water) were chosen, according to their chemical characteristics and location (Fig.I-24), and sampled every 4 weeks, to investigate pharmaceuticals, pesticides and microbiology from October 2011 to October 2012.

2.1.4. In situ measurement parameters

Field measurements include parameters that change in stored samples and cannot be measured in the laboratory in a meaningful way. Most conspicuous in this respect was temperature, but pH and electrical conductivity (EC) may also change between sampling and analyses in the laboratory. These parameters were measured by utilizing a portable WTW Multi 3420 set C with resolution and accuracy of ±0.1°C for temperature, ±0.01 for pH, and ±1µS/cm for EC.

The discharges of the springs (Cognet and Jallat) were measured with a 1-L container and a chronometer.

The piezometric levels of water from each borehole and piezometer were recorded by water-level dipper (Fig.I-25).

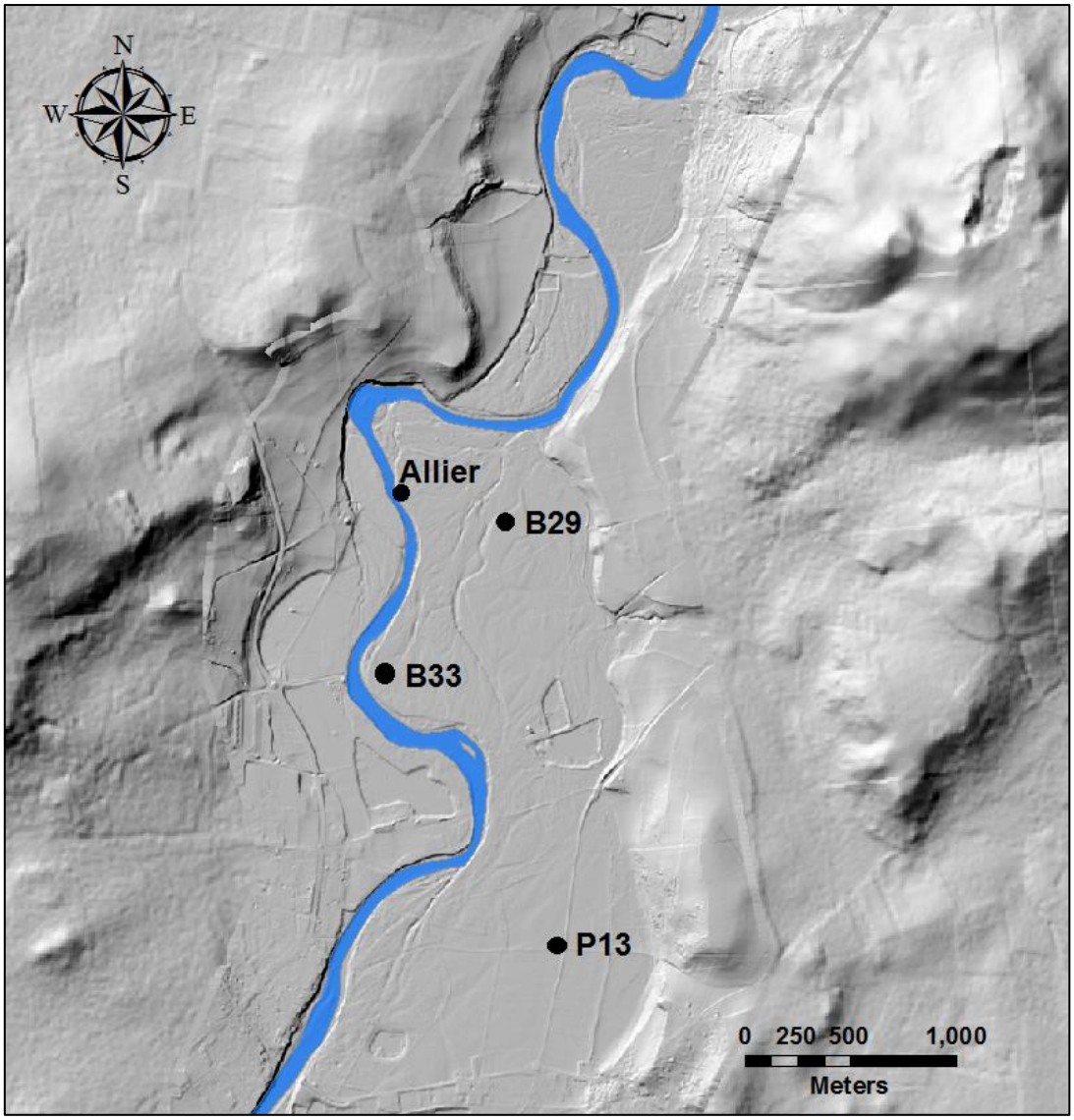

Fig.I-25: Sampling points for temporal investigation of pharmaceuticals, pesticides and biology (each 4 weeks).

Fig.I-26: Cognet spring and depth measuring of P13.

2.1.5. Analytical methods of major ions, traces, pathogenic bacteria and dissolved gases

By using narrow diameter submersible pump for boreholes and piezometers or a direct sampling for springs and surface water, water samples were collected in clean polyethylene bottles for measuring major ions (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}, HCO_3^{-}, Cl^{-}, NO_3^{-} and SO_4^{2}), traces (Li, Be, B, Al, V, Cr, Mn, F, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Mo, Cd, Sn, Sb, Ba, Nd, Gd, Hg, Pb, and U), dissolved gases (O_2 and CO_2), and silica (H_4SiO_4). Samples were collected in clean sampling PET bottles that have been thoroughly rinsed 2-3 times using the water to be sampled. Samples for traces analysis were acidified with few drops of ultrapure HNO_3 prior to analysis. All collected samples were transported to the laboratory under low temperature conditions in ice-boxes, and immediately analysed.

Major ions and traces analyses were carried out in the municipal laboratory of Clermont-Ferrand, France. The concentration of major cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}), silica and traces were determined using Mass Spectrometer ICP-MS-7700, and major anions (Cl^{-}, NO_3^{-} and SO_4^{2-}) were analysed using ion chromatography ICS-1000. Bicarbonate (HCO_3^{-}) was determined in the laboratory by volumetric titration with H_2SO_4 (0.05 mol/l, 0.1N) and has quantification limit of 0.1 mg/l. The quantification limits was ±0.01 mg/l for major cations, ±0.025 mg/l for major anions, ±0.001µg/l for traces, and ±0.01 mg/l for silica.

Turbidity was measured by WTW $TurB_{430}IR$ with quantification limit of 0.2 NTU. Dissolved oxygen was measured through WTW stirr Ox G with apparatus Oxi 197-S and has quantification limit of 0.1 mg/l. Carbon dioxide (CO_2) was determined via titration with H_2SO_4 (0.05 mol/l, 0.1N) and has quantification limit of 0.1 mg/l.

Regarding pathogenic bacteria, 100 ml of each sample has been taken and filtered through 0.45µm filter. The filter was then put in a culture to allow bacteria to grow to make possible the identification. Tergitol 7 and TTC (supplement) gel was used for coliforms and E. coli bacteria; the gel was placed for incubation during 24 h at 36±2°C. While for enterococci, Slanetz and Bartley gel was used; the gel was placed in the incubation during 48 h at 36±2°C. Then counting of pathogenic bacteria was performed.

2.1.6. Analytical methods of stable isotopes

The isotope samples were collected in 20 ml glass bottles with poly-sealed lids. Isotopic analysis of oxygen-18, deuterium-D were performed in the Hydrogeology Department of the University of Corsica (CNRS UMR 6134 SPE), and both stable isotopes of the water molecule were characterized using a liquid-water stable isotope analyser DLT-100 (Los Gatos Research) according to the analytical scheme recommended by the IAEA (Aggarwal et al., 2009; Penna et al., 2010). Hydrogen and oxygen isotope ratios are expressed by δ^2H and $\delta^{18}O$, respectively, where $\delta = [(R_{sample}/R_{standard}) -1]\ 1000(‰)$, R is the ratio of $^2H/H$ or $^{18}O/^{16}O$ in sampled water (R_{sample}) or in Standard Mean Ocean Water ($R_{standard}$). The analytical errors are ±0.1‰ for $\delta^{18}O$ and ±1‰ for δ^2H (Clark and Fritz, 1997).

2.1.7. Analytical methods for biological investigation

Fourteen campaigns have been achieved every 4 weeks from four points (Allier River, piezometer P13, boreholes B29, and boreholes B33) for microbiological investigation between October 2011 and October 2012. The analyses were carried out at the LMGE (Laboratoire de Microbiologie, Génome et Environnement), University of Clermont-Ferrand. Water from each point was collected in 1 litre sterilized glass bottle and stored under 4^0C prior to analyses.

2.1.7.1. Prokaryotic abundances

Enumeration of prokaryotes in 0.02 µm filtered glutaraldehyde (0.05% final concentration) preserved samples were performed using a FACS Calibur flow cytometer (BD Sciences, San Jose, CA, USA) equipped with an air-cooled laser, providing 15 mW at 488 nm with the standard filter set-up (Fig.I-26). Samples were diluted with filtered TE buffer (10 mM Tris – HCl and 1 mM EDTA at pH 8) and stained with SYBR green I (10,000-fold dilution of commercial stock, Molecular Probes, Oregon, USA). Mixture was incubated for 15 min in the dark prior to analysis. Populations of prokaryotes were distinguished on plots of side scatter versus green fluorescence (530 nm wave length, fluorescence channel 1 of the instrument). FCM list modes were analyzed using CellQuest Pro software (BD Biosciences, version 4.0). A blank was routinely examined to control for contamination of equipments and reagents.

2.1.7.2. DNA extraction and purification

Water samples were filtered on a 0.22 µm polycarbonate filter (Millipore, GTTP). Bacterial genomic DNA was extracted by standard alkaline lysis method from 500 mL (for P29, P33 and D13) or 250 ml (for Allier) of water samples. The filter was resuspended in 545 µl of TE buffer (pH 8). Cells were lysed with lysozyme (Sigma, 2 mg m/l, 30 min at 37 ^{0}C) and then mixed with sodium dodecyl sulphate (SDS, final concentration 0.5%), proteinase K (Sigma, final concentration 100 µg /ml) and RNase (Sigma, final concentration 100 µg/ml), and incubated for 1h at 37°C. Cell debris, proteins and humic substances were removed by adding a solution of cetyltrimethylammonium bromide (CTAB) and NaCl (1%, w/v, and 0.7 M, respectively) for 10 min at 65°C. CTAB–protein/polysaccharide complexes were extracted with 1 volume of CHCl3/isoamylalcohol (24:1) after centrifugation (10,000 × g, 4°C, 5 min). Nucleic acids were precipitated with 0.6 volume ice-cold isopropanol, washed with 70% ethanol, then dried and dissolved overnight in 50 µl of TE buffer (pH 8) at 4°C.

2.1.7.3. PCR amplification

Total genomic DNA extracts (Fig.I-26) were used as template to PCR amplify V6 to V8 variable regions of 16S rDNA gene with the bacterium-specific forward primer (MWG-Biotech) GC-968f (5'-CGC CCG GGG CGC GCC CCG GGC GGG GCG GGG GCA CGG GGG GAA CGC GAA GAA CCT-3') and the reverse primer 1401r (5'-CGG TGT GTA CAA GAC CC-3'). The PCR mix (50 µl) contained 1 × PCR buffer, 2.5 mM $MgCl_2$, 200 µM of each dNTP, 0.5 µM of each primer, 12.5 µg of bovine serum albumin (BSA, Sigma), 1.25 units of BIOTAQ DNA polymerase (Eurobio) and 5 µl of genomic DNA. DNA amplification was carried out using in a GeneAmp PCR system 2400 thermocycler (Perkin-Elmer) using the following program: 95°C for 5 min, 30 cycles at 95°C for 1 min, 58°C for 1 min and 72°C for 1min, and a final extension step at 72°C for 7 min. PCR products were analysed by electrophoresis on 0.8% agarose gel (w/v) in 1 X Tris-borate-EDTA (TBE) containing 0.5 µg/mL ethidium bromide. DNA was quantified using the DNA quantitation kit fluorescence assay (Sigma) according to the manufacturer's instructions (Fig.I-27).

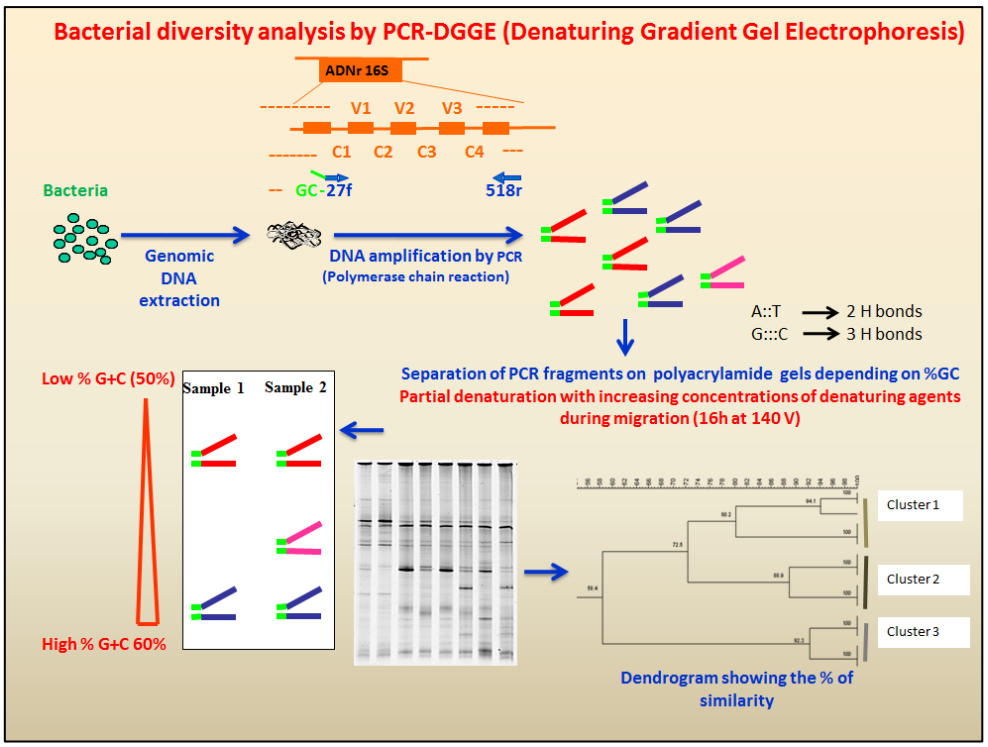

Fig.I-27: Bacterial diversity analysis by PCR-DGGE (Denaturing Gradient Gel Electrophoresis)

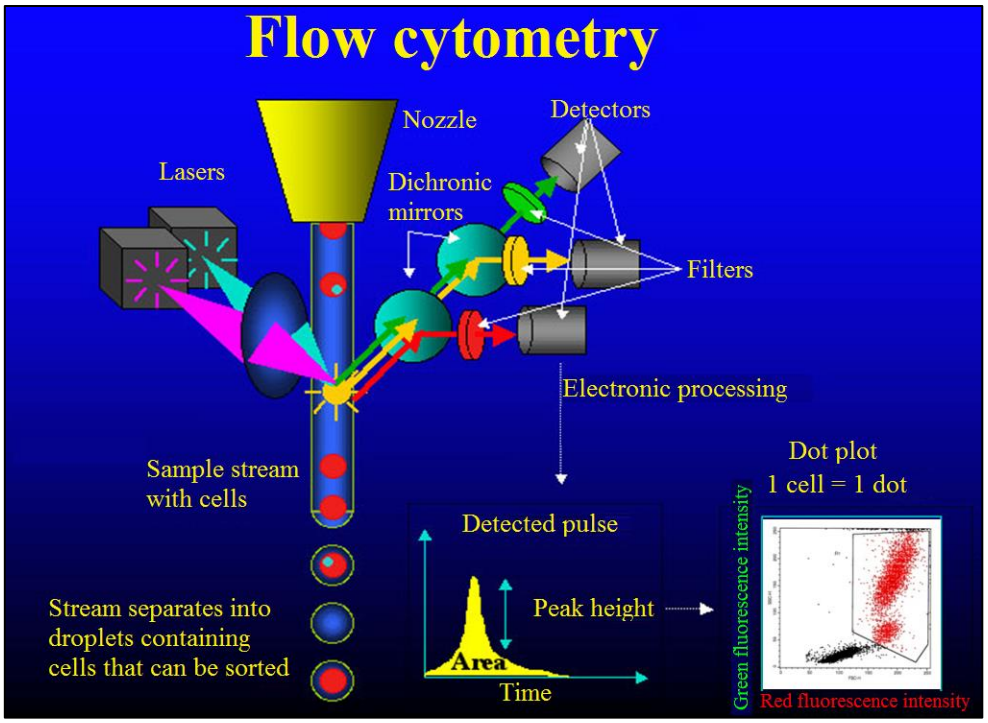

Fig.I-28: Flow cytometry for quantification of bacteria.

2.1.7.4. Denaturing gradient gel electrophoresis (DGGE) analysis

DGGE analyses were performed using a CBS Scientific DGGE system (BioRad, France) on 600ng of PCR products applied directly on 7.5% (w/v) polyacrylamide gels (Bio-Rad) containing 1 X Tris-acetate-EDTA (TAE) with a denaturing gel ranging from 50% to 60% (7 M urea and 40% formamide (vol/vol) as 100% denaturants). A 7.5% polyacrylamide stacking gel containing no denaturant was poured to create solid slots for efficient loading of the PCR products. Runs were performed in 1 X TAE for 16h at 140V at a constant temperature of 60°C. After completion of electrophoresis, gels were stained for 1h in the dark in a Gel Star nucleic acid gel stain bath (BMA) and digitized using a BioSpectrumAC Imaging System (UVP) under UV transillumination.

Numerical analysis of digitized gels was performed using the GelCompar II software (Applied Maths, Kortrijk, Belgium). Dendrograms were constructed using the DICE coefficient and the unweighted pair group method using arithmetic averages (UPGMA).

2.1.8. Analytical methods of pharmaceuticals and pesticides

A monitoring program was achieved by selecting four sampling points (Allier River, P13, B29 and B33) for pharmaceuticals and pesticides analyses, every 4 weeks. A total of 14 campaigns have been performed from October 2011 and October 2012. Grab water samples have been collected in pre-rinsed bottles of green glass, kept cool in an ice-box and immediately transported to the EUROFINS laboratory where analyses have been achieved.

Each sample has been analysed for 47 pharmaceuticals and 383 pesticides according to the following analytical procedure. Each sample was pre-concentrated through a solid phase extraction, after pH adjustment according to the physico-chemical properties of molecules, then pharmaceuticals and pesticides are adsorbed on a copolymer (styrene divinylbenzene) and eluted with methanol or a mixture of methanol/acetonitrile. After concentration, pharmaceuticals were analysed by LC-MS/MS (liquid-phase chromatography provided with a system of detection by mass spectrometry). For every dosage by mass spectrometry (tandem or MS/MS), the quantification is insured by means of two couples of characteristic ions of the molecule, the second couple serving to confirm the identification of the molecule.

The analysed 47 pharmaceuticals and 383 pesticides with detection limits and analytical methods are tabulated in Appendix D.

2.1.9. Summary

Table I-1 is highlighting the sampling procedure, parameters analysed, number of sampling points and total number of water samples.

Table I-1: The summery of sampling procedure and analytical parameters

	Two campaigns	**Monthly sampling**	**Biweekly sampling**	**weekly sampling**
Boreholes	71	2 (B29 & B33)	15	
Piezometers	1	1 (P13)	1	
Springs	2		2	
Surface waters	1	1 (Allier)	1	
Rainfall				1
Total samples	150	56	855	53
Measured parameters	Major ions, traces, physico-chemical, isotopes, dissolved gasses, pathogenic bacteria	47 pharmaceuticals and 383 pesticides, bacteria, virus	Major ions, traces, physico-chemical, isotopes, dissolved gasses, pathogenic bacteria	Major ions, physico-chemical, isotopes

CHAPTER II
FUNCTIONING OF ALLUVIAL SYSTEM OF ALLIER RIVER

Most of the results presented in this chapter have been published in the Journal of Hydrology (2013): *Isotopic and geochemical identification of main groundwater supply sources to an alluvial aquifer, the Allier River valley (France).* [doi:10.1016/j.jhydrol.2013.10.051] *(Appendix E).*

Introduction:

The alluvial aquifers are in hydraulic connection with associated streams, and the systems are typified by the relatively rapid interaction of surface water and groundwater (e.g. Négrel et al., 2003; Vanderzalm et al., 2011). Although the aquifer-stream systems are of limited areal extent in comparison to most aquifer systems, they are among the most intensively used and most historically important to people and their development, both culturally and economically (Winter et al., 1998; Ferrara and Pappalardo, 2004). In most of the alluvial aquifer systems, changes affecting one component are reflected within short periods in changes in the other components. These changes can occur quickly because of the rapid and large changes in stage and other changes that affect the surface water component of these systems and that can be transmitted to the associated sand and gravel deposits comprising the aquifer (Mauclaire and Gibert, 1998). The aquifer-stream systems (alluvial) have become an area of interest to many hydrogeochemical studies world-wide mainly due to their economical role in supplying large amount of high quality water (e.g.: Négrel et al., 2004; Li et al., 2008; Al-ahmadi and El-Fiky, 2009; Kannan and Joseph, 2010).

Water chemistry varies over time in response to seasonal changes in recharge and dilution effects of individual storms (Hess & White, 1988). Along subsurface flowpaths, waters can be modified by mineral dissolution and/or precipitation, and mixing (Dreybrodt, 1981; Herman and Lorah, 1986). For groundwater research, hydrogeochemical and isotopic (oxygen-18 and deuterium) methods have been popular tools all over the world (Guendouz et

al., 2003). Allison (1988), Kortatsi (2007) and Quiroz Londoño et al. (2008) studied the physical, chemical, and isotopic techniques available to evaluate groundwater recharge in different environments. Recently, Glynn and Plummer (2005) provide a comprehensive review of the significant contributions of geochemistry to the understanding of groundwater systems over the past 50 years. Furthermore, hydrogeochemical and isotopic methods have been successful as economical ways to study local and regional groundwater in alluvial fans, for example to determine groundwater types in the arid and semiarid environments (Schurch and Vuataz, 2000); to identify recharge sources of groundwater (Abd El Samie and Sadek, 2001; Stimson et al., 2001; Plummer et al., 2004; Li et al., 2008); to evaluate the quantity of groundwater recharge (Abu-Jaber and Wafa, 1996; Wood and Sanford, 1995; Négrel et al., 2003); to establish the interaction between surface and groundwater (Négrel et al., 2003), and to define the replenishment of groundwater (Zhang et al., 2005). These methods have provided insights into characteristics of recharge which are difficult to achieve with physical-based methods.

In this chapter, we attempt to acquire insights into groundwater characteristics in a complex alluvial system located in the Allier River basin. Based on the knowledge already acquired on the site and hydrogeochemical investigations on both groundwater and surface water, the principle objectives of this chapter are to determine the contribution of each recharge sources and to evaluate the spatial and temporal distribution of groundwater chemistry and isotopes.

1. Identification of the main flow patterns

1.1. Circulation of groundwater within the alluvial system

Depth to water is one of the very important factors because it determines the thickness of material through which infiltrating water must travel before reaching the saturated one of the aquifer. Then this factor consequently impacts the degree of interaction between the percolating contaminant and sub-surface materials (air, minerals, water) and, therefore, on the degree, extent, physical and chemical attenuation, and degradation processes. In general, the aquifer potential protection increases with depth to water. Areas with high water tables (shallow) are more vulnerable because pollutants have short distances to travel before contacting the groundwater (Böhlke, 2002; Andrade and Stigter, 2011).

In order to determine the general groundwater flow direction during day time (without pumping), two campaigns have been carried out throughout the study area from 71 boreholes and 1 piezometer; the results are displayed in Fig.II-1. An equipotential contour map of the water table indicates that groundwater generally flows from south to north in parallel with Allier flow direction; this result is in agreement with those of Frémion (1995) for the same area (Fig.I-19).

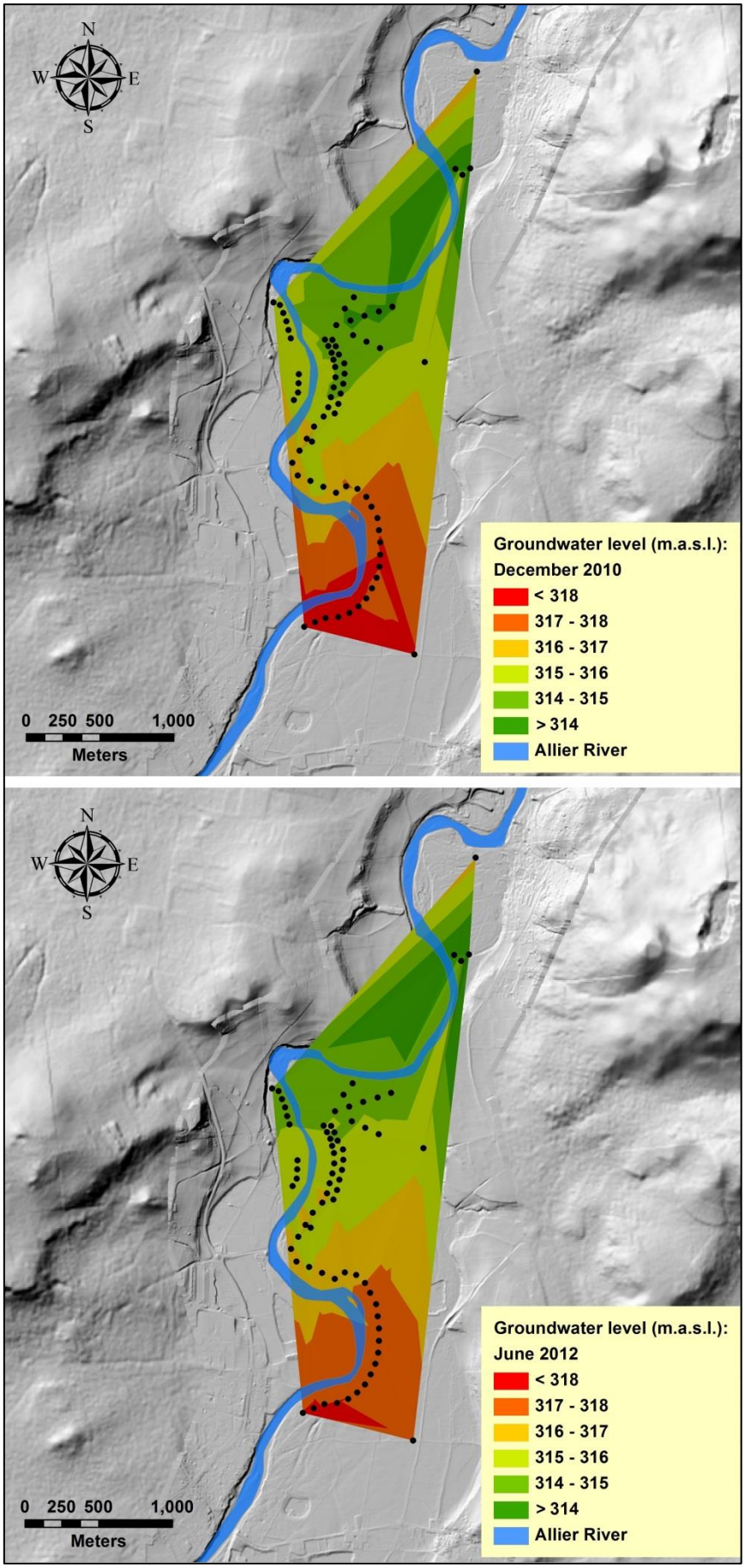

Fig.II-1: Piezometric map, during day time without pumping, showing S-N circulation of groundwater.

Seasonal variations in piezometric levels reflect fluctuations in groundwater recharge. Based on this fact, a continuous bi-weekly water level measurement has been settled for a network of 15 boreholes and 1 piezometer from February 2011 to November 2012, and compared to Allier flow rates and rainfall intensity (Fig.II-2).

The average discharge of Allier River is 38.24 $m^3 s^{-1}$ during the study period. The discharge varies seasonally as the river gets its bulk supply of water during rainy season. Therefore, the water discharge of Allier River is almost fully under the control of seasonal rainfall in whole Allier basin. The peak flow reaches to 357 $m^3 s^{-1}$ in November 2011, the 6^{th} (rainfall: 35.1 mm/day) and to 377 $m^3 s^{-1}$ in May 2012, the 23^{rd} after a heavy rainfall event (16.6 mm/day). Water-level in almost all boreholes coincides with seasonal fluctuations in flow rate of Allier River, indicating a strong connection.

Fluctuations in water level from Allier River have direct influence to the groundwater level in boreholes. Most of the boreholes, particularly those close to the Allier River, respond more quickly to these fluctuations and indicate a strong connection. While some boreholes (B39, B56, and B65) show weak respond to Allier's flow variations mostly because these boreholes are located near the sealed banks of the Allier River (Fig.I-18). Water levels in boreholes are also affected by pumping process which is usually operated during night but sometimes during day as well. Water requirement become higher during summer time for drinking water supply and also for watering gardens. Some sharp decline could then be observed in water levels during day. Piezometer P13 displays no clear seasonal variations in water-level; these fluctuations do not correspond to the ones of Allier River, indicating that P13 is not affected by Allier River recharge.

Flow rates of Cognet and Jallat springs are also measured during the same period and are compared to rainfall intensity (Fig.II-3). The discharge of Cognet spring shows continuous decrease from March 2011 and reaches a minimum value in December 2011, then starts to increase until July 2012 and finally continues decreasing. This could mainly be due to the precipitations height, above the average during 2010 that generates high flow rate in the beginning of 2011. While in 2011, the average precipitation was below threshold and cause decline in spring's flow rate (Fig.I-13). During 2012, increase of springs flow rates is in relation with fluctuations of rainfall height since the average precipitation of this year was above the threshold.

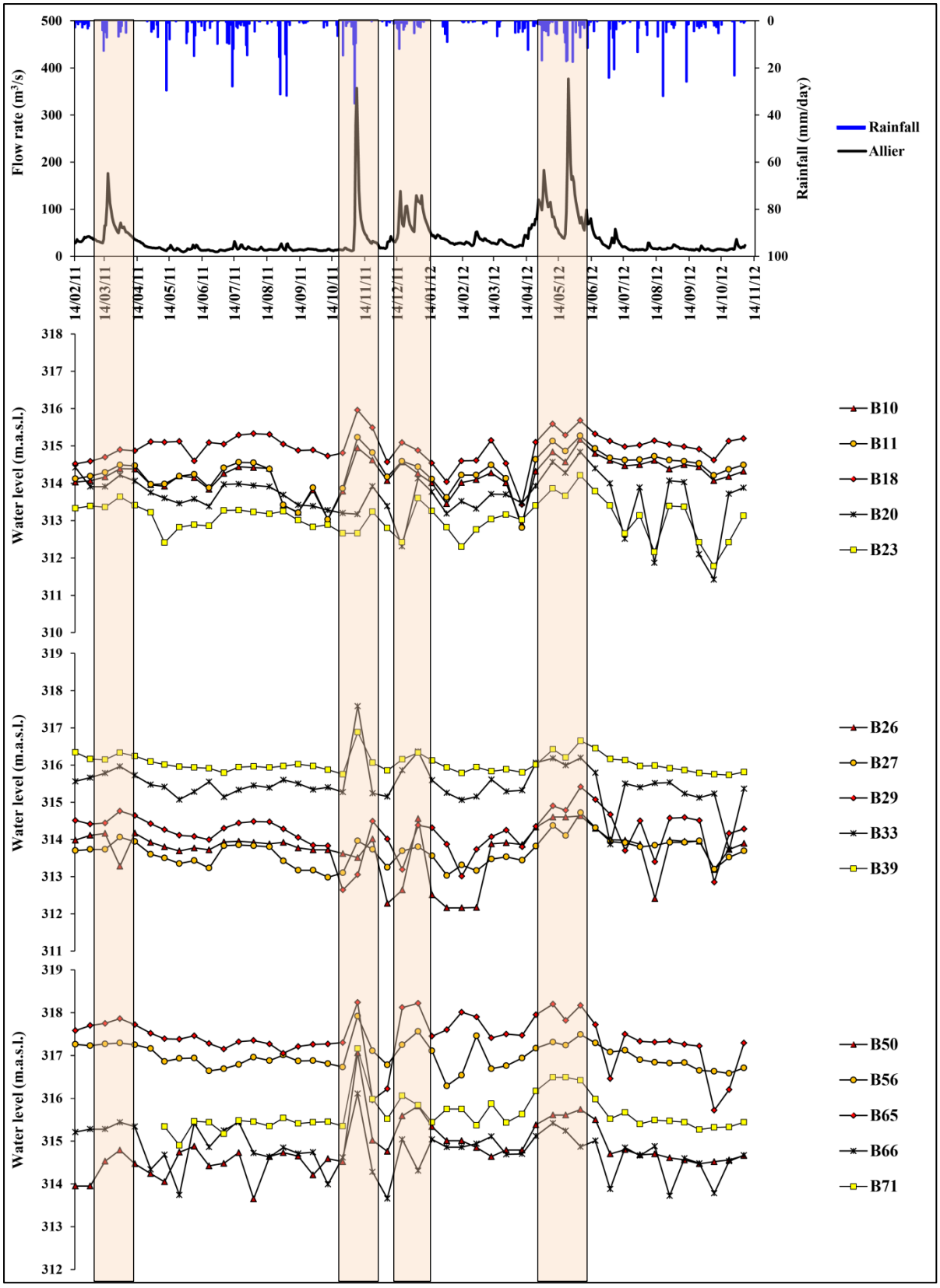

Fig.II-2: Time evolution of rainfall amount, Allier River flow rate, piezometric levels during the study period: high flow rate of Allier River corresponds in general to high piezometric levels.

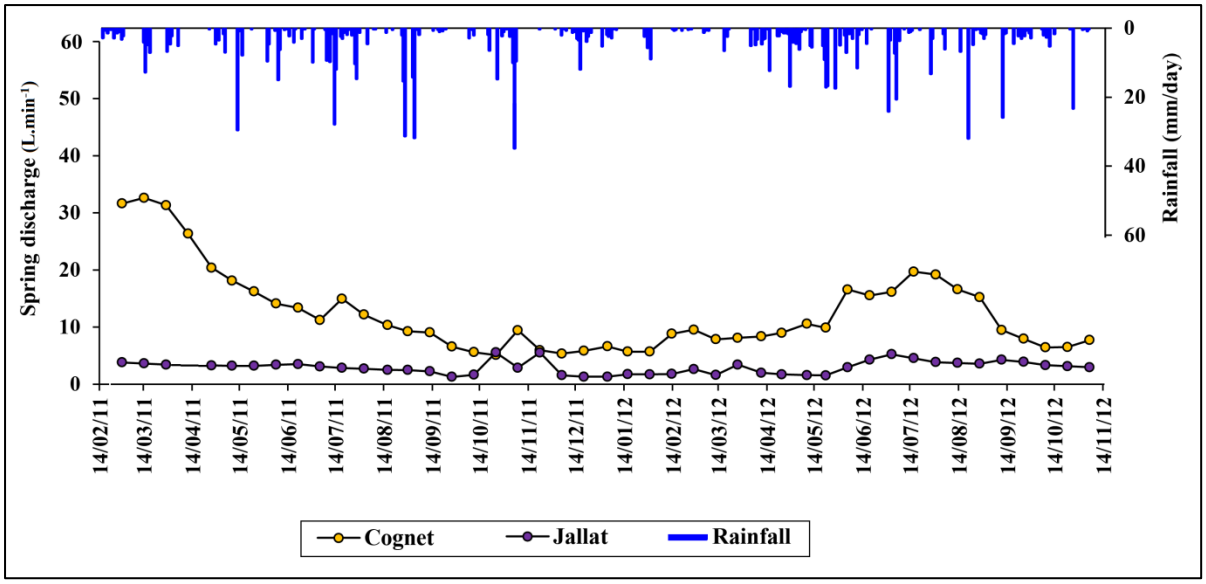

Fig.II-3: Time evolution of rainfall amounts and springs discharges (L.min^{-1}) during study period.

1.2. Identification of the end-members

Frémion (1995, 1997) determined the water circulation (Fig.I-10) during pumping process (mostly during night). Fig.II-4 thus shows that the alluvial aquifer of Allier can be recharged by four main sources: Allier River, neighbouring hills, southern part of the aquifer and rainfall. Allier River is well connected to the alluvial deposits and is considered to be the main recharge source since the alluvial aquifer is pumped, which in turn increases the discharge of water from Allier River to aquifer. The second recharge source is the hills located on the both sides of the Allier River valley with a likely influence of both groundwater and surface water. This origin is represented by Cognet and Jallat springs. A part of groundwater can come from the southern part of the alluvial aquifer. The last end member is the local precipitation that is feeding the site vertically.

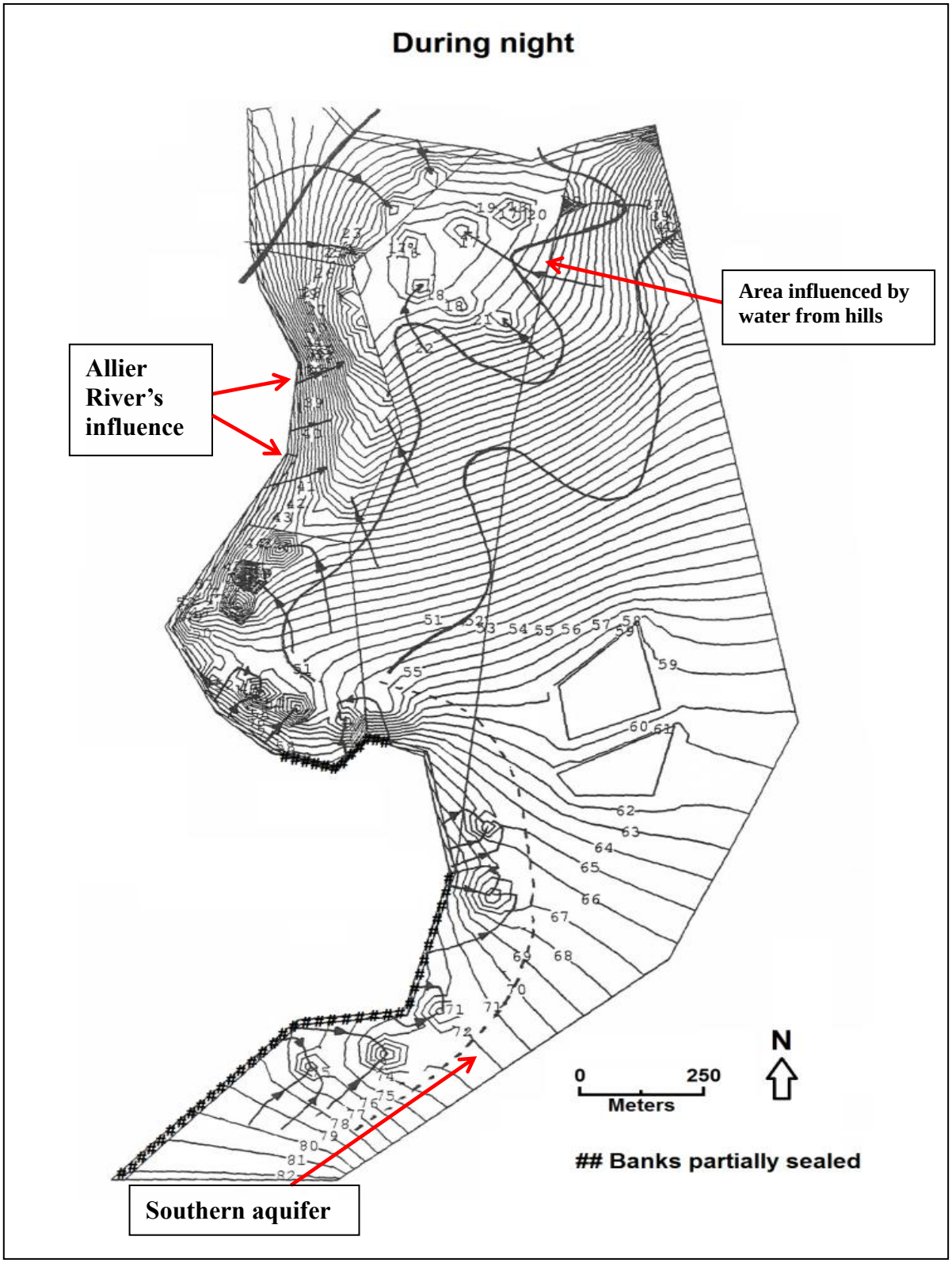

Fig.II-4: Piezometric levels during pumping process (night time) showing the supply of 3 end-members.

2. Geochemical and isotopic characteristics of groundwater

2.1. End-members

2.1.1. Rainfall

During our study, chemical and isotopic composition of rainwater has been investigated. Fifty-three rainwater samples have been collected weekly between 14 February 2011 and 05 November 2012, at Cournon d'Auvergne station, located within the study area. The chemical and isotopic results of rainfall are tabulated in Appendix A and B.

Local precipitation is a natural source of recharge but contains very low amounts of ions. Minimum, maximum, mean, and standard deviation values of each chemical and isotopic parameter of rainfall (Table II-1) highlight the high variability of the mineralization of rainwater. This variability can be due to rain amount (Hicks and Shannon, 1979; Khwaja and Husain, 1990; Al-Momani et al., 1995), to the influence of various chemical sources (Bertrand et al., 2008), or to the diversity in the origins of air masses (Celle-Jeanton et al., 2009). One way to keep out the influence of rain quantity is to use the volume-weighted mean of concentrations to characterize the general features of the precipitation chemistry (Bertrand et al., 2008).

The volume-weighted mean (VWM) pH of rainwater is 6.3, showing a tendency of slight acidity of rainfall. Generally, unpolluted precipitations are known to be weakly acid due to their equilibrium with atmospheric CO_2. Then, the pH of chemically undisturbed rainwater is about 5.7 (Berner and Berner, 1987). The acidic feature is common in industrialized countries and is due to anthropogenic emissions such as SO_x and NO_x (Tost et al., 2007). The VWM concentrations of the major ionic species are in the following order: HCO_3^- >NO_3^- >NH_4^+ > Ca^{2+} > SO_4^{2-} >Na^+ >Cl^- >K^+ >PO_4^{3-} >Mg^+. Rainfalls chemistry seems to be mostly influenced by elements coming from terrestrial and anthropogenic sources. Négrel and Roy (1998) and Bertrand et al. (2008) found similar results at Sainte-Marguerite (9 Km to the south from the study site) and Opme station (15 Km toward west), respectively.

Table II-1: Major ionic constituents (mg/l) and stable isotopes of the 53 sampled rains during the study period (from Feb-2011 to Nov-2012).

	pH	EC	HCO_3^-	Cl^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	$\delta^{18}O$ ‰	δ^2H ‰
Min	5.6	3.1	2.0	<1	<1	0.20	<0.05	0.1	0.01	0.02	<0.02	0.06	–17.5	–133.6
Max	8.5	32.0	43.0	4.0	7.5	2.4	1.3	3.1	0.3	1.7	0.8	3.6	–1.9	–8.2
AV	7.0	14.4	7.3	1.8	2.3	1.3	0.2	0.7	0.1	0.4	0.1	1.0	–6.0	–44.4
SD	0.6	7.2	8.0	1.0	1.4	0.5	0.3	0.7	0.1	0.4	0.2	0.7	3.3	25.5
VWM	**6.3**	**11.0**	**6.8**	**0.14**	**1.3**	**0.44**	**0.04**	**0.5**	**0.04**	**0.15**	**0.05**	**0.78**	**–6.1**	**–44.2**

Concentrations supplied by rainfall to groundwater can be calculated by using the following equation (Appelo and Postma, 1993):

$$\text{Concentration factor} = (P/Peff) * VWM_{ion} \quad (1)$$

where P is the total volume of annual precipitation, Peff refers to the efficient rainfall (Peff= the total volume of annual precipitation – total annual evapotranspiration) and VWM is the volume-weighted mean of each ionic concentration for the period of measurements. The calculations give the major ion concentrations of the local recharge by rainfall (HCO_3^-=17.8 mg/l, Cl^-=4.8 mg/l, NO_3^-=3.5 mg/l, SO_4^{2-}=1.1 mg/l, Ca^+=1.2 mg/l, Mg^{2+}=0.1 mg/l, Na^+=0.4 mg/l, K^+=0.1 mg/l, values are volume-weighted means).

The isotopic composition of rainwater (Fig.II-5) is in the range –17.5 to –1.9‰ for $\delta^{18}O$ and –133.6 to –8.2‰ for δ^2H. The VWM for $\delta^{18}O$ and δ^2H in precipitation are –6.1 and –44.2‰, respectively. The oxygen-18 values are positively correlated to the deuterium values. The physical basis for this correlation lies in the fractionation of isotopes during evaporation-condensation processes (Gourcy et al., 2005). The Mezel Meteoric Water Line (MMWL) is established for the study site. The mathematical regression of MMWL data is the following: $\delta^2H = 7.62\ \delta^{18}O + 1.14$ ($r^2 = 0.98$). It is controlled by local climatic factors i.e. the origin of vapour mass, re-evaporation during rainfall and the seasonality of precipitation (Clark and Fritz, 1997) and then differs from the Global Meteoric Water Line (GMWL; $\delta^2H = 8\ \delta^{18}O + 10$) defined by Craig (1961). Moreover it varies greatly from the one defined by Bertrand et al. ($\delta^2H = 7.9\ \delta^{18}O + 7.3$, 2009) in the Argnat Basin (Chaîne des Puys, mean elevation= 550m), and the one determined by Gal ($\delta^2H = 7.8\ \delta^{18}O + 5.5$, 2005) in Saint-Just-Saint-Rambert (Monts du Forez, elevation= 420m). Such a difference mainly could lie with a secondary evaporation during rainfall (Friedman et al., 1962) as the study site is characterised by very warm summer and generally low intensity rainfall events. Low y-intercept of MMWL may then be due to an increase of evaporation within the air column below the air

masses considering that our sampling site is situated at a lower elevation. Fette et al. (2005) stated that this difference could mainly be due to the altitude and evaporation effect.

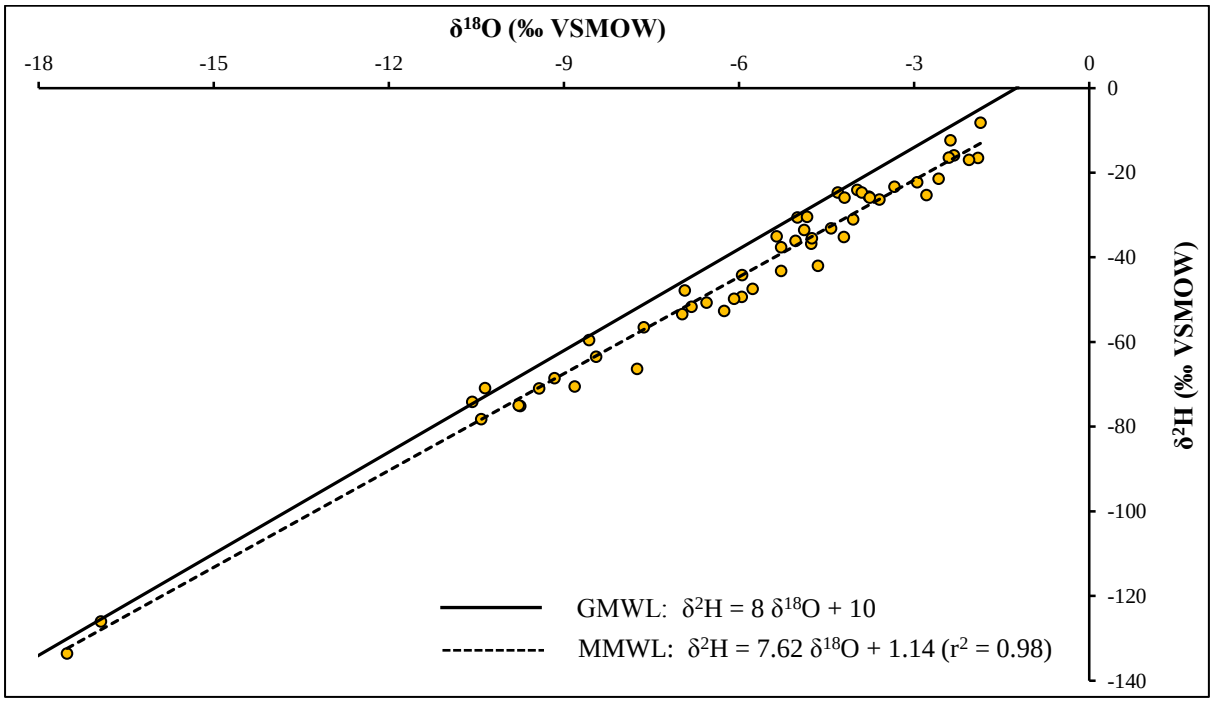

Fig.II-5: Relationship between isotope $\delta^{18}O$ and $\delta^{2}H$ of rainfall during study period determining Mezel meteoric water line (MMWL).

There are several factors that influence the distributions of stable isotopes in rainfall. These effects include altitude effects, latitudinal effects, temperature effects and amount effects (Ingraham, 1998). Temperature is inversely correlated to the isotopic fractionation that occurs during condensation and evaporation (Mook, 2000). As a result, precipitation normally has higher isotopic values during warmer summers and lower values during cooler winters. Fig.II-6 exhibits these typical seasonal variations in isotopic composition and amount effects from the study area. The most depleted sample was collected during March 2011, the 14th ($\delta^{18}O$= –17.5‰, $\delta^{2}H$= –133.6‰) and February 2012, 13th ($\delta^{18}O$= –16.9‰, $\delta^{2}H$= –126.1‰), while the most enriched sample was taken during July 2012, 30th ($\delta^{18}O$= –1.86, $\delta^{2}H$ = –8.2‰).

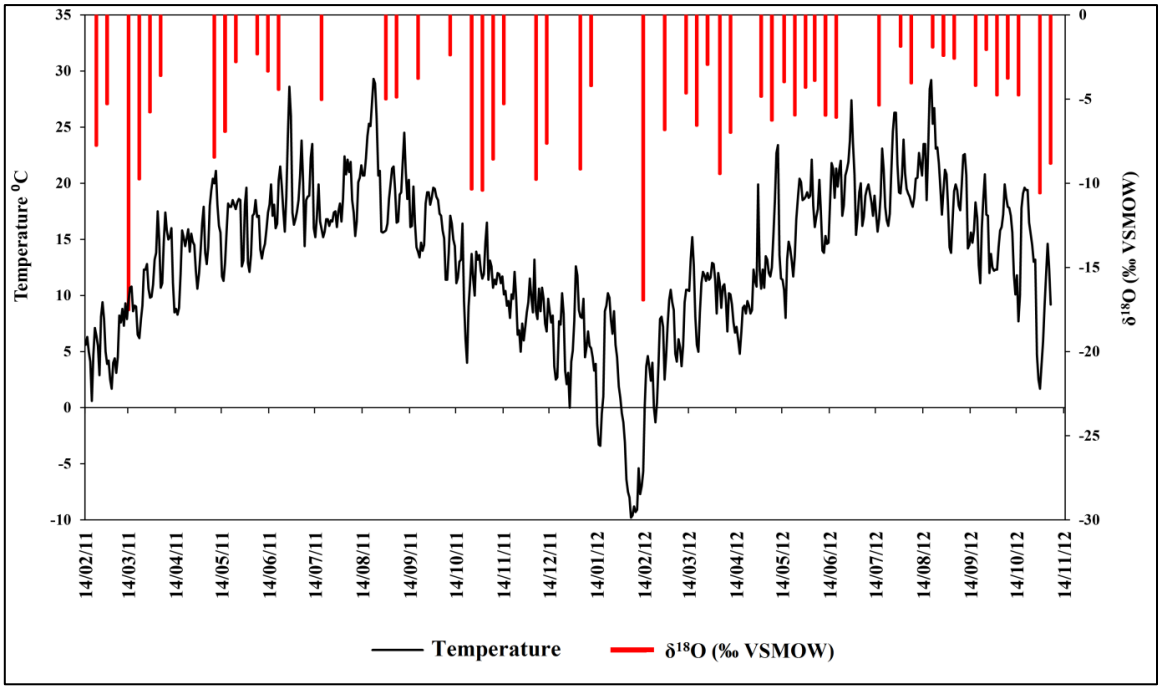

Fig.II-6: Time evolution of isotope $\delta^{18}O$ and daily temperature.

If isotopic content is not correlated to the amount of rainfall, a weak negative correlation is observed with ionic concentrations (Fig.II-7a, b).

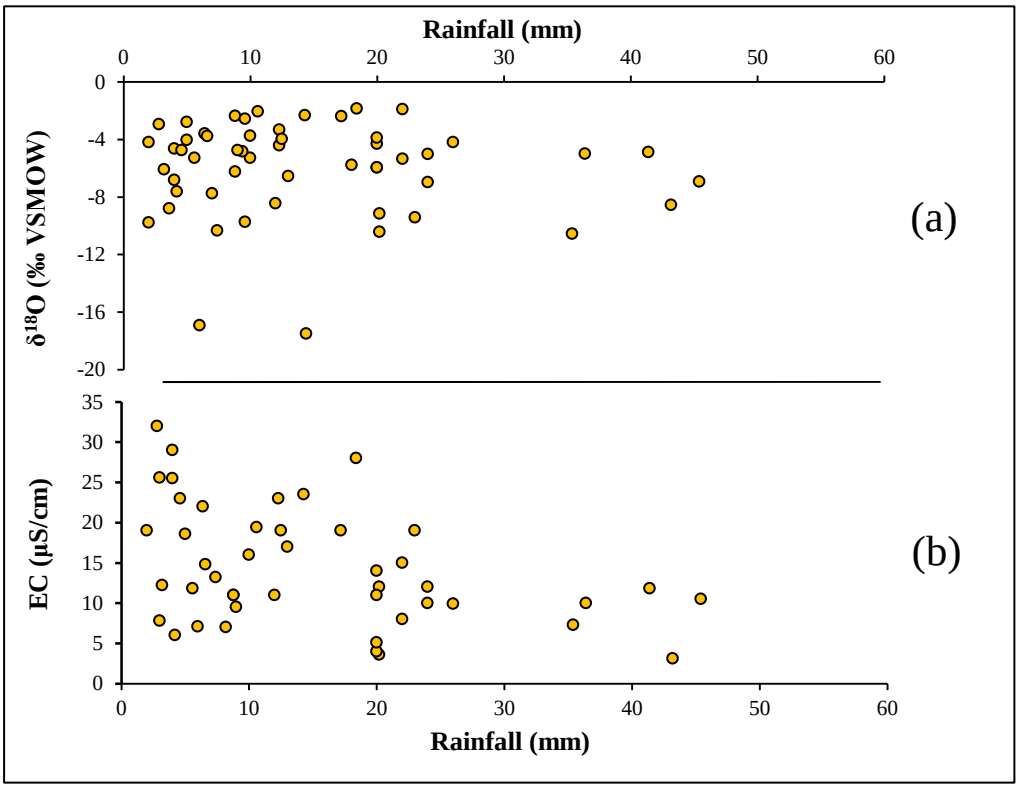

Fig.II-7: Relationship between rainfall high (mm) and oxygen-18 (a), and electrical conductivity of rainwater (b).

2.1.2. Allier River

Direct recharge from Allier River is the main source of groundwater in the pumping area. The statistical results of chemistry and stable isotopes in Allier River are shown in Table II-2.

Table II-2: Statistics on chemical and isotopic results of Allier River.

Parameters	Unit	Min	Max	Av	SD
T	^{0}C	0.6	21.3	13.5	5.8
pH		7.1	7.9	7.5	0.2
EC	µS/cm	79.0	248	180.6	44.9
DO	mg/l	7.8	13.8	9.8	1.6
HCO_3	mg/l	24.0	98.0	69.6	15.2
Cl	mg/l	6.7	21.6	15.4	3.8
NO_3	mg/l	1.9	6.9	4.4	1.1
SO_4^{-2}	mg/l	4.5	10.4	7.9	1.3
Ca^{+2}	mg/l	6.2	20.3	14.3	3.0
Mg^{+2}	mg/l	2.2	6.8	5.0	0.8
Na^+	mg/l	5.6	17.9	12.7	3.1
K^+	mg/l	1.7	6.2	3.4	0.8
$\delta^{18}O$	‰(VSMOW)	-9.4	-6.9	-8.0	0.6
δ^2H	‰(VSMOW)	-65.7	-48.7	-54.8	3.6

The electrical conductivity of the Allier River is generally low (mean for the sampling period = 180.6 µS/cm) and presents temporal variation (standard deviation = 37.4 µS/cm). Generally, high flow rate correspond to low EC (Fig.II-8) in relation with a dilution effect. The dissolved oxygen (DO) in natural water depends on physical, chemical and biological activities of the water body (Neal et al., 1998; Datry et al., 2004). The amount of dissolved oxygen gas depends highly on temperature and somewhat on atmospheric pressure (Fig.II-8). Salinity also influences dissolved oxygen concentrations, such that oxygen is low in highly saline waters and vice versa (Carr and Neary, 2006; Rixen et al., 2010). Since the temperature is inversely correlated with dissolved oxygen (DO) in water, significant seasonal variations of DO is correspondingly noticed with maximum value during winter (13.8 mg/l in 13/02/2012, T° = 0.6°C) and minimum value during summer (7.8 mg/l in 30/07/2012, T° = 21.3°C).

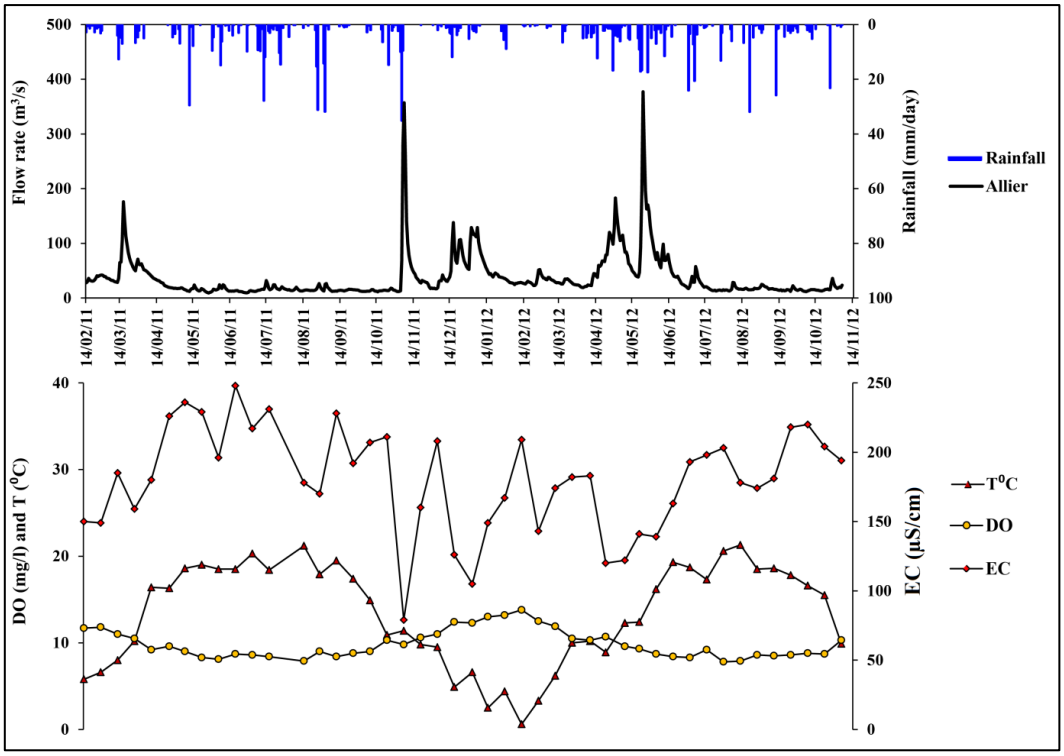

Fig.II-8: Time evolution of rainfall amount, Allier River flow rate, temperature, dissolved oxygen and electrical conductivity (EC) of Allier River during study period: high flow rate correspond to low EC.

The Allier River's water type is Ca-Na-Mg/HCO_3-Cl (Fig.II-9) in accordance with the leaching of the water catchment's basement mainly constituted of granitic and gneissic rocks. One exception concerns the 07/11/2011 analysis characterized by a Ca-Na-Mg/Cl-HCO_3 facies. This particular water has been recorded during a flood event and then corresponds to major dilution effect with an electrical conductivity of 79 µS/cm; the change in water facies could be explained by the low concentration in ions. Likewise EC, all major cations and anions show weak variations with high concentrations during low flow and low concentrations during high flow (Fig.II-10). A similar relationship between river flow rate and ionic concentration was observed in alluvial aquifer of the alpine Rhône River valley in Switzerland (Schürch and Vuataz, 2000).

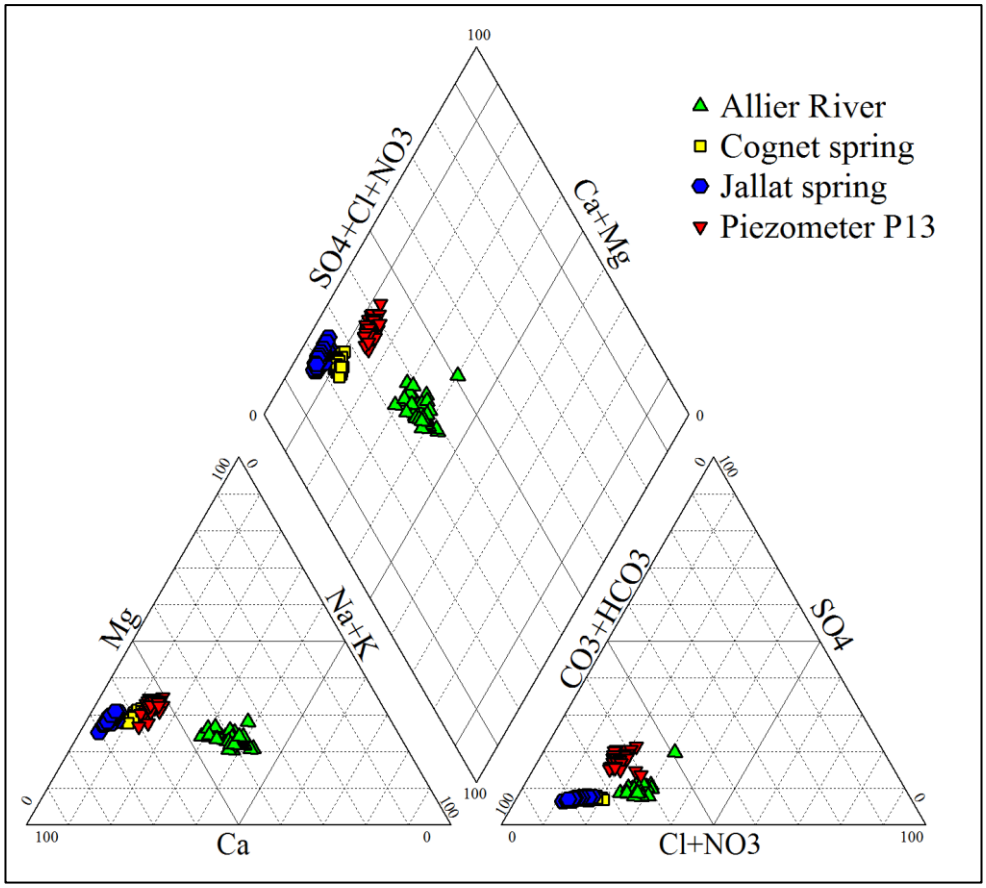

Fig.II-9: Piper diagram showing the chemical water type of the end members

Allier River is the main stream of the region and then collects rainfall and surface flows of the whole watershed. As temperature decreases with altitude, isotopic content of rainfall decreases with altitude. Altitudes of the Allier Basin may exceed 1600 m in some places, then Allier River is characterized by depleted values of stable isotopes with a mean value of -8.02 $\delta^{18}O$‰ and -54.7 $\delta^{2}H$‰ compare to the isotopic signature of local rainfall (–6.1 $\delta^{18}O$‰ and –44.2 $\delta^{2}H$‰). The isotopic values of Allier River measured in this study are in good agreement with those given by Négrel et al. (2003; -7.95‰ for $\delta^{18}O$, -54.95‰ for $\delta^{2}H$). Furthermore, Allier River demonstrates clear temporal variations in $\delta^{18}O$ and $\delta^{2}H$, the maximum value is measured on the 27th of August 2012 (-6.85 $\delta^{18}O$‰ and -48.7 $\delta^{2}H$‰) and minimum value on the 14th of March 2011 (-9.41 $\delta^{18}O$‰ and -65.7 $\delta^{2}H$‰, Fig.II-10). Similar temporal variations in Allier River were observed by Négrel et al. (2003).

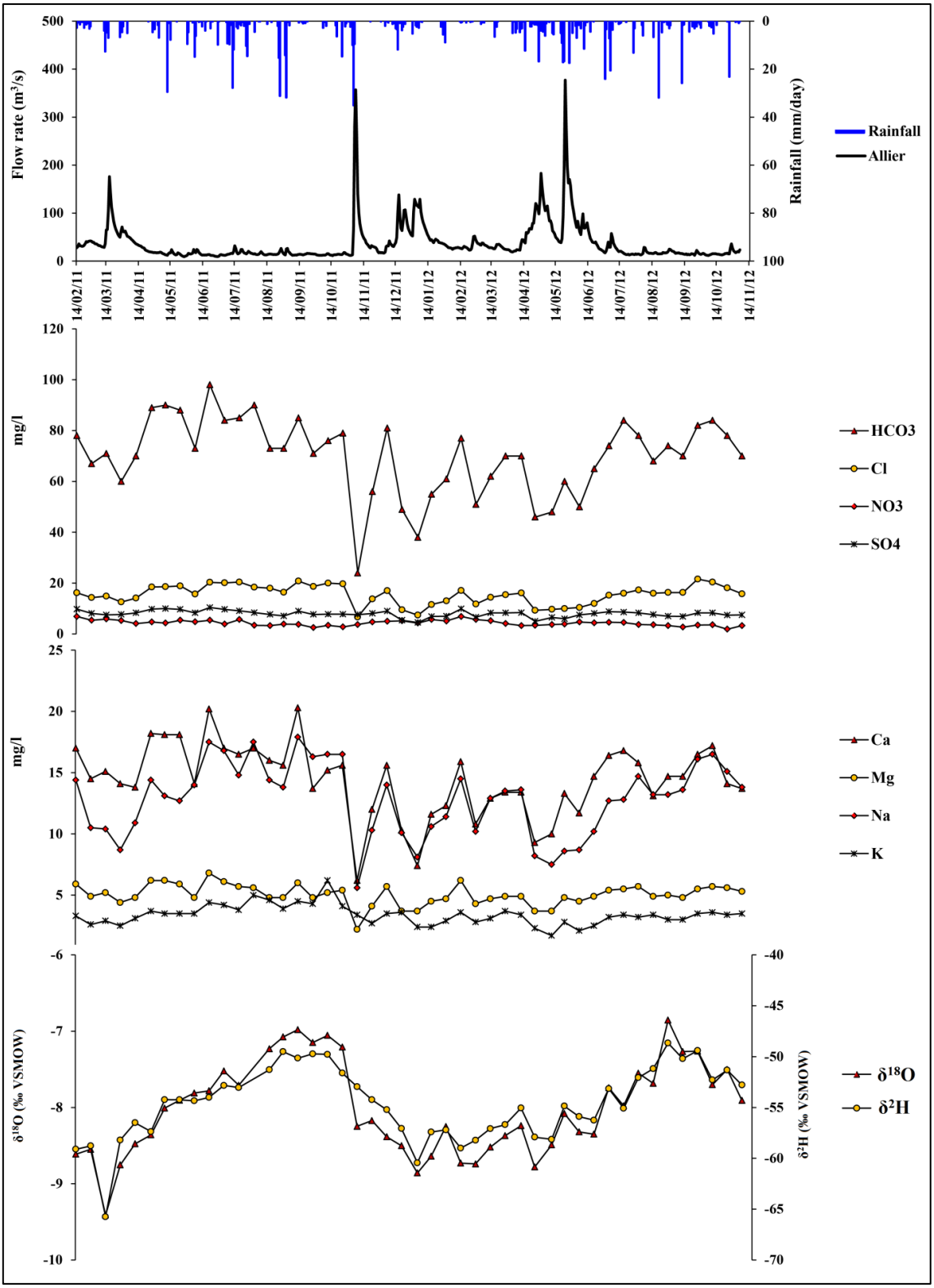

Fig.II-10: Time evolution of rainfall amount, flow rate, major cations, major anions, and stable isotopes of Allier River during study period.

2.1.3. Cognet and Jallat spring

Our investigations mostly concern the eastern shore of the Allier River. Therefore, the water coming from the hills from the eastside of the Allier River may contribute to the natural recharge of the alluvial groundwater. This origin is represented by Cognet and Jallat springs which emerge from an Oligocene aquifer mainly constituted of marls and calcareous rocks (Fig.I-17). They are characterized by high ECs with mean values of 957.6µS/cm and 784.5µS/cm (Table II-3), respectively and display little temporal variations (Fig.II-11).

Table II-3: Statistics on chemical and isotopic results of Cognet and Jallat springs

		Cognet spring				**Jallat spring**			
Parameters	**Units**	**Min**	**Max**	**AV**	**SD**	**Min**	**Max**	**AV**	**SD**
Flow rate	L/min	5.1	32.6	12.5	7.3	1.29	5.57	2.95	1.14
T	^{0}C	9.6	15.2	13.2	1.3	6.5	15.1	12.3	2.4
DO	mg/l	8.5	10.2	9.3	0.4	7.3	9.8	8.5	0.7
pH		6.85	7.66	7.3	0.2	6.8	7.4	7.2	0.1
EC	µS/cm	818	1047	957.6	51.3	715	847	784.5	35.8
HCO_3^-	mg/l	421	527	487.6	23.4	393	448	420.4	11.4
Cl^-	mg/l	29.6	50.2	35.9	5.3	13.7	26.3	19.1	3.4
NO_3^-	mg/l	38.3	55	49.9	3.9	35.5	53.9	42.8	4.6
SO_4^{-2}	mg/l	31.7	41.9	36.7	2.2	25.7	34.4	30.1	2.4
Ca^{+2}	mg/l	102.8	148.4	125.2	10.5	101.1	136.0	114.8	8.6
Mg^{+2}	mg/l	32.3	41.8	38.4	1.8	27.5	34.1	30.5	1.3
Na^+	mg/l	14.3	19.6	15.9	0.9	7.3	11.1	8.7	0.8
K^+	mg/l	14.5	22.9	18.1	1.6	3.1	5.9	4.1	0.6
$\delta^{18}O$	‰(VSMOW)	-7.53	-6.69	-7.03	0.15	-7.2	-6.4	-6.6	0.2
δ^2H	‰(VSMOW)	-52.04	-48.97	-50.42	0.52	-49.7	-46.5	-47.8	0.7

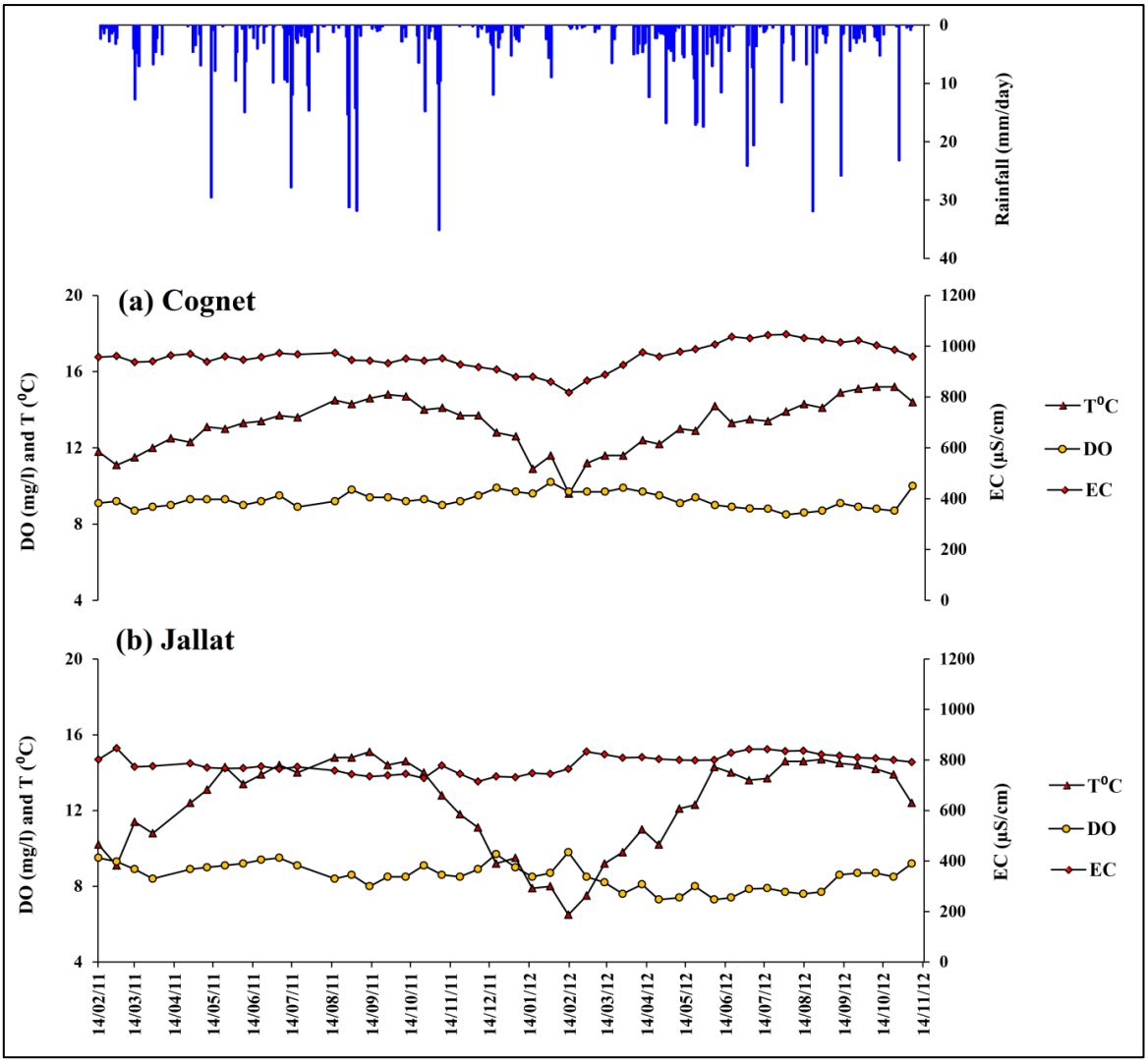

Fig.II-11: Time evolution of rainfall, temperature, dissolved oxygen, and electrical conductivity of (a) Cognet and (b) Jallat.

Similarly, all major cations and anions demonstrate very weak temporal variations and stay almost constant for both springs during the hydrological cycle (Fig.II-12, II-13).

The two springs are characterised by high content of nitrate, sulphate and potassium with a mean concentrations of 49.9 mg/l, 36.7 mg/l and 18.1 mg/l for Cognet and 42.8 mg/l, 30.1 mg/l, and 4.1 mg/l for Jallat, respectively. These ions are primarily of an anthropogenic origin and mainly come from agricultural sources, since the hills are extensively using for agricultural practises. Temperature varies seasonally from 9.6 to 15.2°C for Cognet and 6.5 to 15.1°C for Jallat. These variations are attenuated compare to the high seasonal variations registered in the Allier River. This fact, added to the stability of the concentrations of most of the ions, tends to prove that Cognet and Jallat emerge from a huge reservoir which temporise

the internal variations. Both springs record high contents of dissolved oxygen (DO) with mean values of 9.3 and 8.5 mg/l, respectively. Variations are inverse and concomitant to the ones of temperature. Concentrations in DO are lower than the ones of Allier River mostly because surface waters are in direct contact with air and hence contain more dissolved oxygen and because, in groundwater, DO may be consumed by micro-organisms such as bacteria (e.g. Datry et al., 2004; Rixen et al., 2010).

The dominating water facies for Cognet and Jallat is Ca-Mg/HCO_3 (Fig.II-9) in relation with the circulation within Oligocene sediments.

The stable isotopes signature of both springs (Cognet: -7.0 $\delta^{18}O‰$, -50.4 $\delta^{2}H‰$; Jallat: -6.6 $\delta^{18}O‰$, -47.8 $\delta^{2}H‰$) are comparable to the ones of rainfall (-6.0 $\delta^{18}O‰$, -44.4 $\delta^{2}H‰$), confirming thus the recharge by the local rainfall. They do not demonstrate any temporal variations with corresponding standard deviations of ±0.15 $\delta^{18}O‰$ and ±0.52 $\delta^{2}H‰$ for Cognet, and ±0.2 $\delta^{18}O‰$ and ±0.7 $\delta^{2}H‰$ for Jallat, what confirm the probable existence of a huge reservoir that supply these springs.

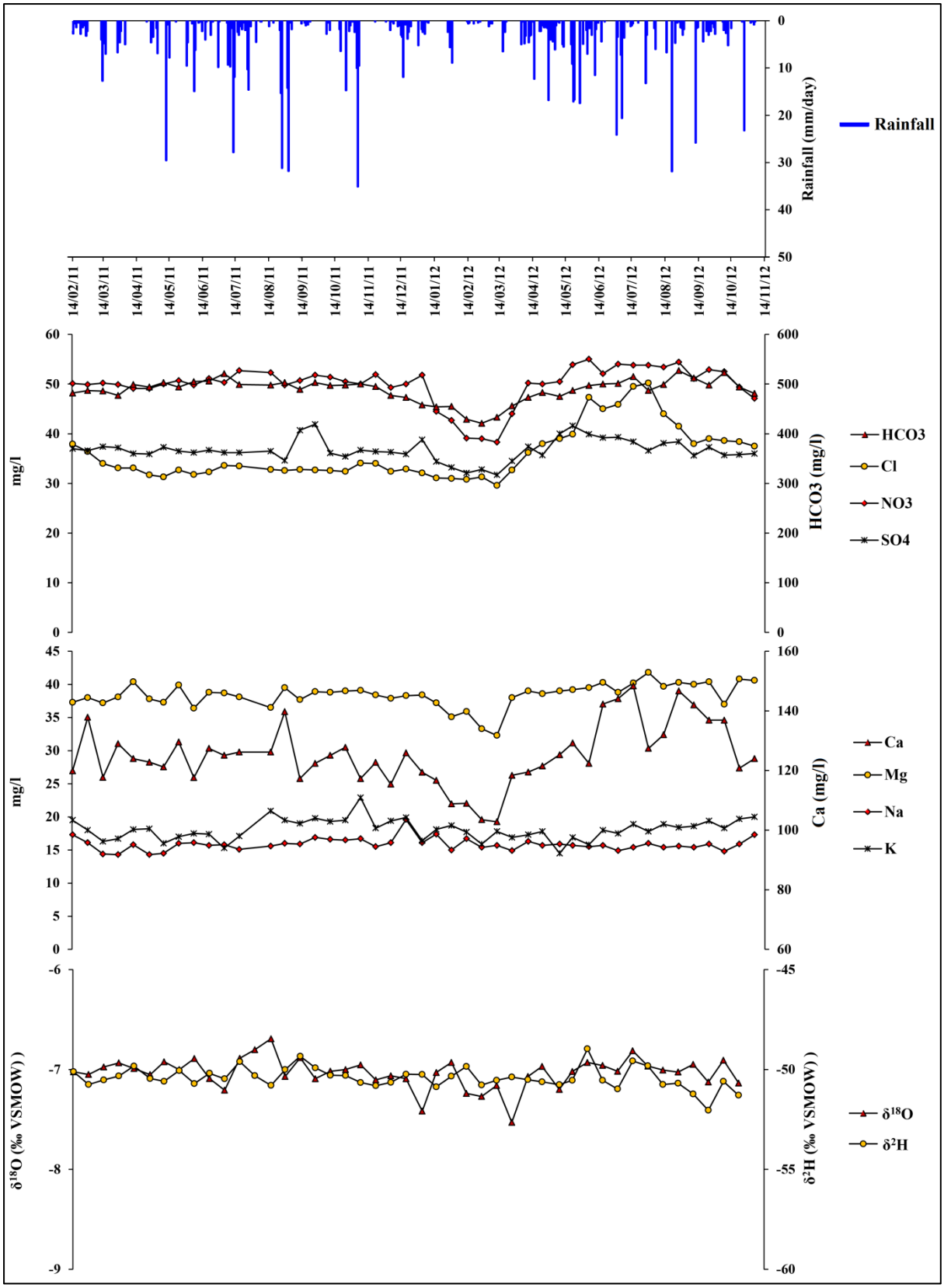

Fig.II-12: Time evolutions in rainfall amount, major cations, major anions, and stable isotopes of Cognet spring during study period.

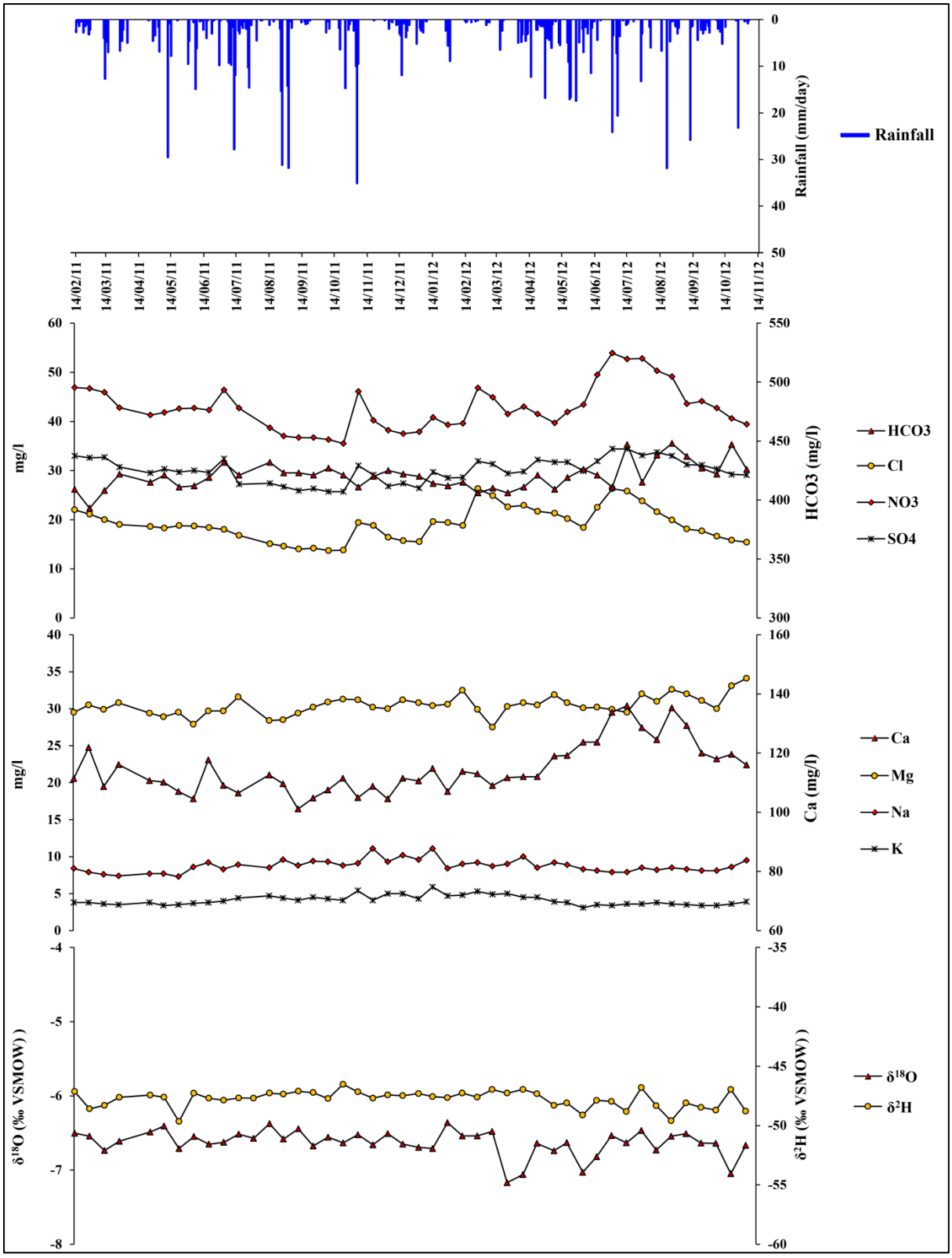

Fig.II-13: Time evolution of rainfall amount, major cations, major anions, and stable isotopes of Jallat spring during study period.

2.1.4. Piezometer P13

The southern alluvial aquifer (non-pumped area) also accounts in the recharge of the alluvial system. This part is represented by piezometer P13 that presents the highest EC (Table II-4) recorded within the site, during the sampling period. EC reaches 1290 µS/cm, what might likely be due to the slow circulation of groundwater in this non-pumping area (mean EC= 1196.3 µS/cm). Excepted the temperature that ranges between 9.1 and 16.2ºC and varies seasonally in relation with the air temperature, all the measured parameters - piezometric levels (range between 316.4 and 317.1 m.a.s.l,), EC (Fig.II-14), DO (Fig.II-14) and major ions (Fig.II-15) - do not show any temporal variations, showing that groundwater may integrate the seasonal variations for a long time and confirming the slow circulation in the alluvial system. P13 contains significant amounts of nitrate and sulphate with mean concentrations of 37.6 mg/l and 114.9 mg/l respectively, highlighting an anthropogenic influence from agriculture since this point is directed located in the agricultural land. P13 presents positive detection of DO due to the possible vertical transport of oxygen in the highly permeable alluvial aquifer (Hamilton and Helsel, 1995; Kraft et al., 1999; Nash and McCall, 1995) which is consequently aerobic throughout its depth. However, P13's content in DO (3.4±0.8 mg/l) is lower than the one of the Allier River in relation with the consumption of DO by soil bacteria. Despite a seasonal variations of temperature of groundwater (from 9.1°C to 16.2°C), DO does not show any evident variations. P13 is featured by Ca-Mg/HCO_3 water types (Fig.II-9).

Table II-4: Statistics on chemical and isotopic results of piezometer P13

Parameters	Units	Min	Max	AV	SD
Water depth	m.a.s.l.	316.4	317.1	316.7	0.2
T	^{0}C	9.1	16.2	12.7	1.7
DO	mg/l	2.0	5.4	3.4	0.8
pH		6.6	7.3	7.1	0.1
EC	µS/cm	1099	1290	1191.6	50.2
HCO_3	mg/l	489	554	516	13.5
Cl	mg/l	57.2	74.8	66.0	4.0
NO_3	mg/l	29.4	51.2	37.6	5.7
SO_4^{-2}	mg/l	91.8	143.8	114.9	13.4
Ca^{+2}	mg/l	129.3	157.8	141.5	6.9
Mg^{+2}	mg/l	44.5	58.5	52.3	2.5
Na^+	mg/l	28.6	44.1	34.2	3.7
K^+	mg/l	9.3	14.3	10.9	1.1
$\delta^{18}O$	‰(VSMOW)	-6.8	-5.8	-6.3	0.3
δ^2H	‰(VSMOW)	-48.8	-44.6	-46.7	1.0

On an isotopic point of view, P13 is characterized by values of δ^2H (-46.7 ‰) and $\delta^{18}O$ (-6.3 ‰) that correspond to local precipitation (-6.0 $\delta^{18}O$‰, -44.4 δ^2H‰). The quite stability of the two isotopes during the year (±0.3 $\delta^{18}O$‰ and ±1.0 δ^2H‰) confirms the integration of the variability of supply.

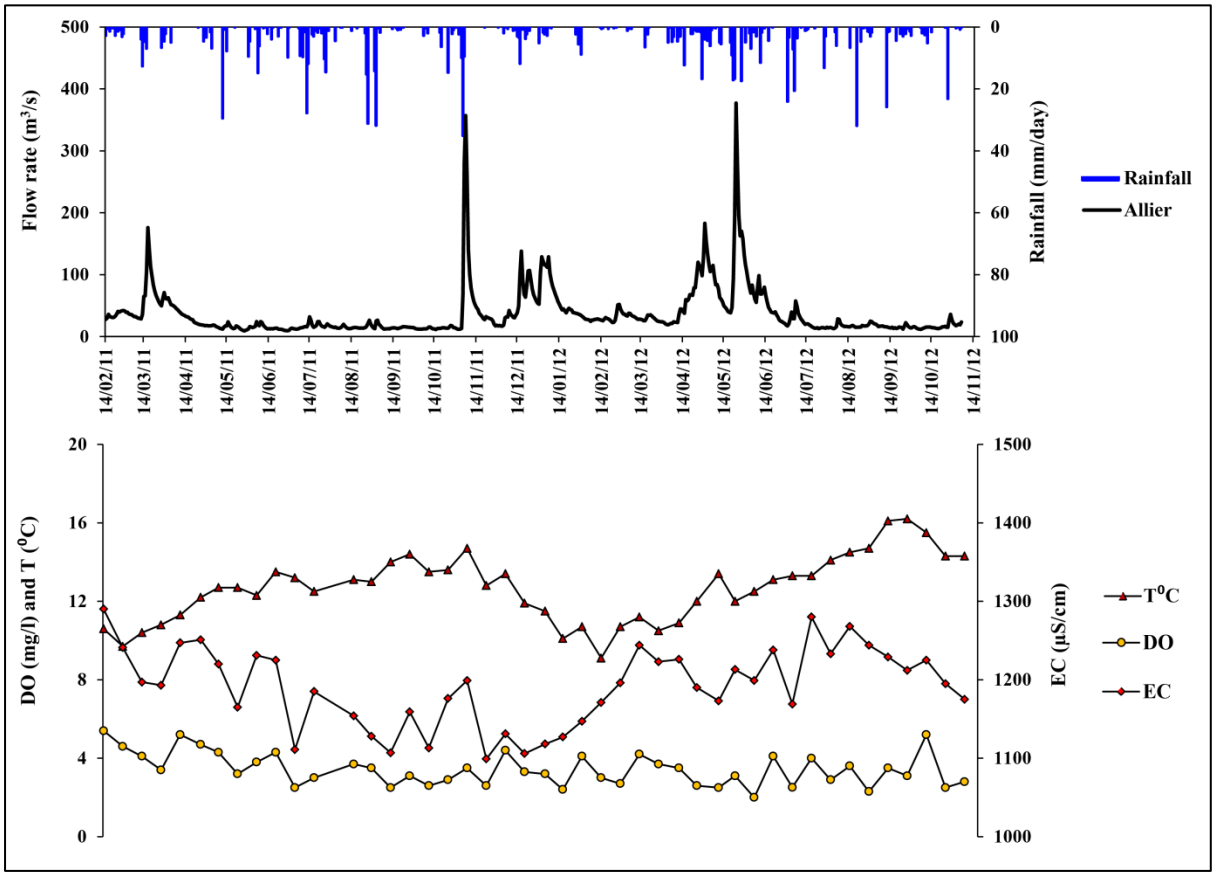

Fig.II-14: Time evolution of rainfall amount, Allier River flow rate, temperature, dissolved oxygen and electrical conductivity (EC) of piezometer P13 during study period.

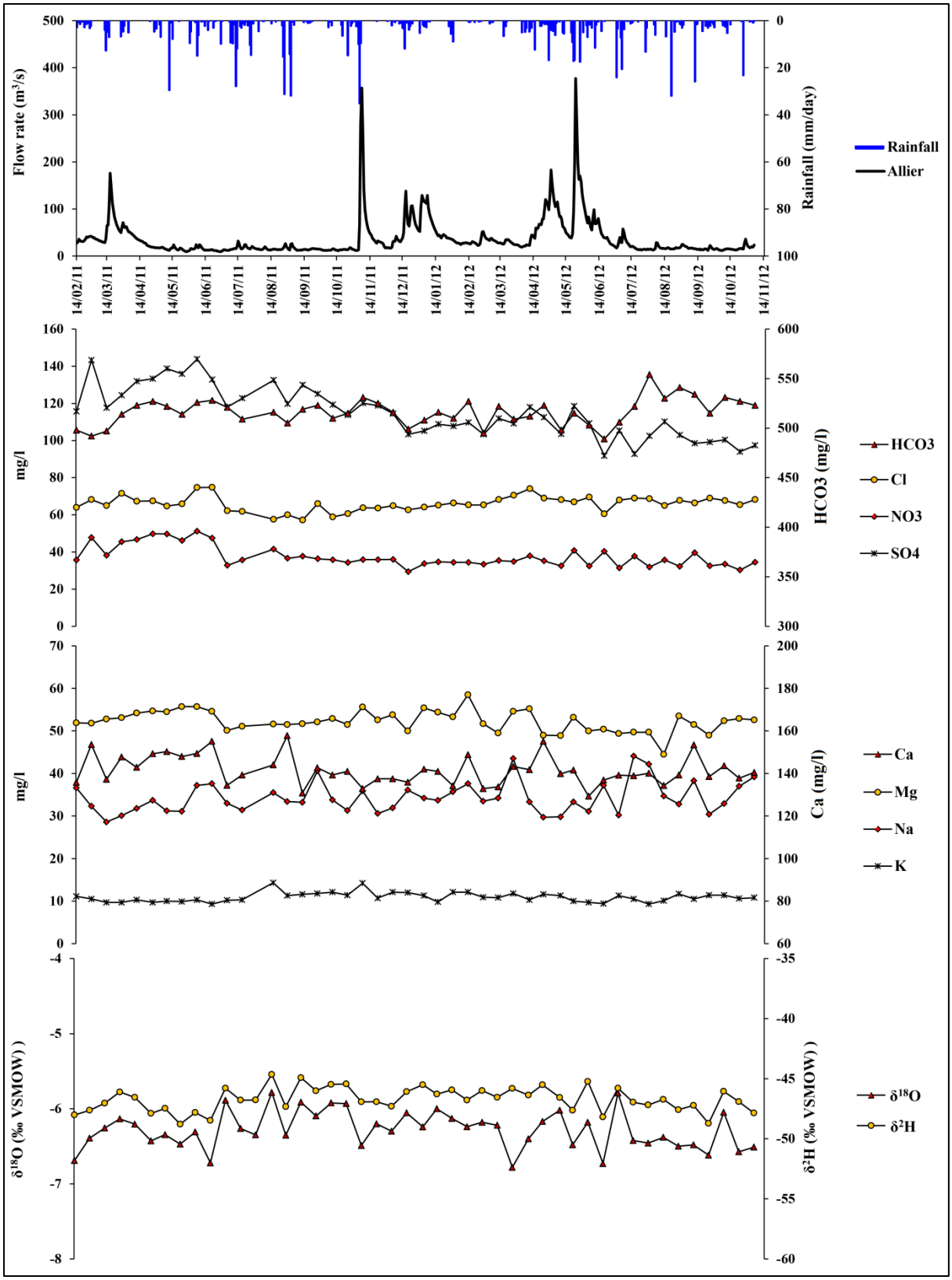

Fig.II-15: Time evolution of rainfall amount, Allier flow rate, major cations, major anions, and stable isotopes of piezometer P13 during study period.

2.2. Groundwater (boreholes)

2.2.1. Physical-chemical parameters (T, pH, EC, and DO)

Spatial distribution of temperature during the two field campaigns (low flow/ Dec-2010 and high flow/ June-2012) shows variations from 8.7 (B50) to 13.1°C (B53) in low flow stage and from 9.7 (B31) to 14.7°C (B60) in high flow stage (Fig.II-16). According to the quite homogeneous water depth within the field, these spatial variations of temperature are most probably related to the origin of groundwater. The boreholes closer to the Allier River such as B26 and B33 show larger seasonal variations in temperature (with standard deviation of ±4.2 and ±4.5°C, respectively), indicating that they could largely be influenced by the Allier River recharge and certainly more than other boreholes.

High temperatures in summer are due to seasonal effect. The average air temperature is of -0.9°C during winter campaign and of 16°C during summer campaign. Air temperature has a direct effect on the shallow alluvial groundwater temperature (Lorite-Herrera and Jiménez-Espinosa, 2008). This is confirming by Fig.II-17 that presents the temporal evolution of air temperature with minimum values recorded in February and maximum temperature measured in August and September. Most of boreholes reveal wide temporal variations in temperature that are comparable to the one of the Allier River, referring to a large influence of Allier on these boreholes. While 5 boreholes (B10, B23, B27, B29 and B65) show slight temporal variations compare to Allier River, signifying that these boreholes could be affected by water from other sources of recharge.

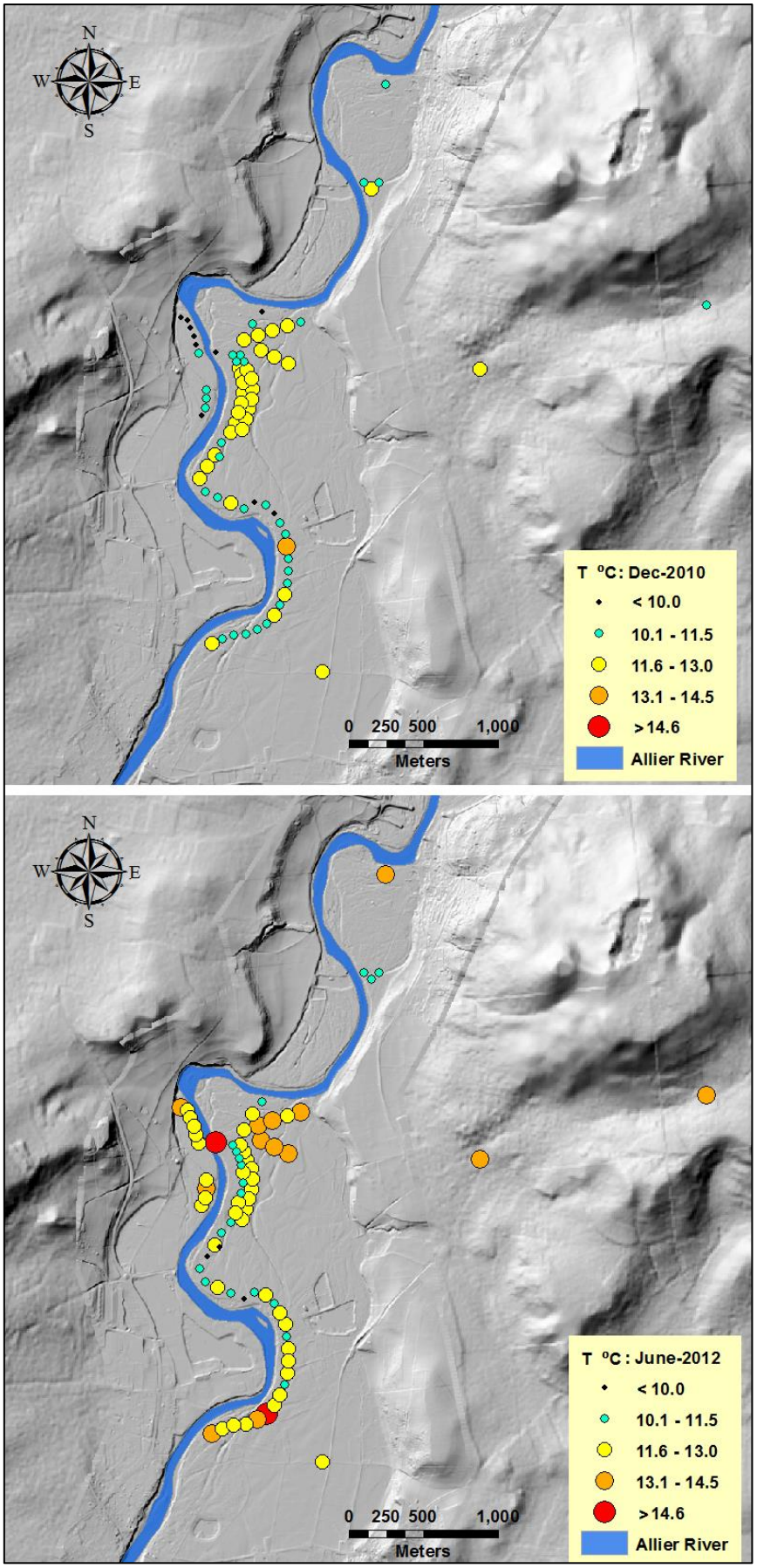

Fig.II-16: Spatial distribution of temperature (T°C) of Allier River during the two field campaigns of low flow (Dec-2010) and high flow stage (June-2012).

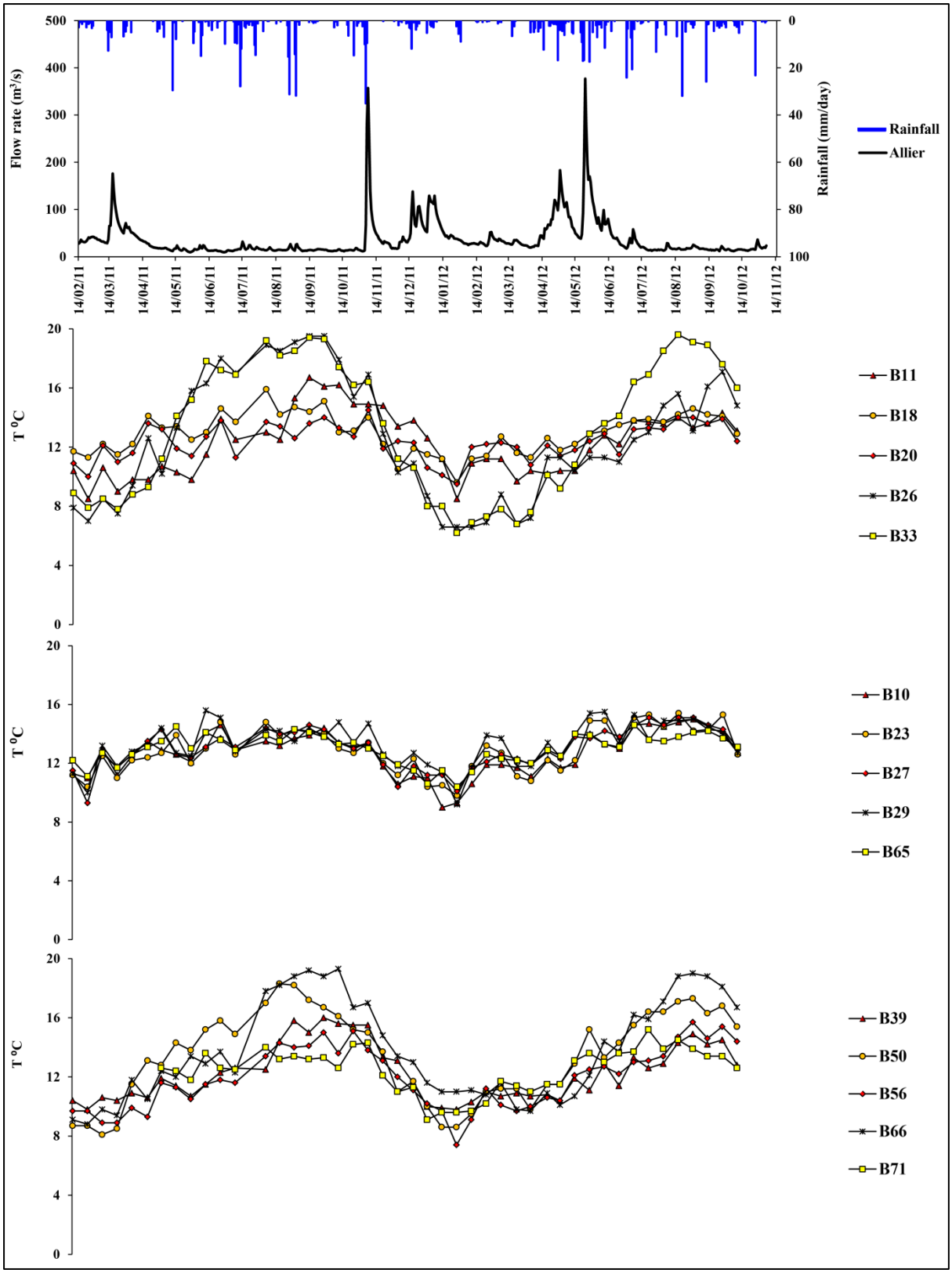

Fig.II-17: Time evolution of rainfall amount, Allier River flow rate, and water temperature of the investigated boreholes during the study period.

pH measurement is one of the most frequently used tests in water chemistry (Hem, 1985). The results of the spatial analyses show that pH is slightly basic, close to neutrality, with a mean value of 7.26±0.16 in low flow [range from 6.92 (B01) to 7.73(B40)] and 7.17±0.16 in high flow stage [range from 6.85 (B31) to 7.72 (B25)]. The spatial distribution of pH values during the two campaigns carried out in Dec-2010 and June-2012 are displayed in Fig.II-18. The recorded pH values are within the range of desirable limit of pH in water prescribed for drinking purpose by WHO (2006) and European Communities (1998) which is between 6.5 and 9.5. The reason of the pH value around 7 is that the water within the alluvial aquifer is weakly mineralized and the water equilibrates immediately (Chkirbene et al., 2009).

The temporal variations in pH values are illustrated in Fig.II-19. The pH of groundwater measured in the boreholes presents small variations with a maximum standard deviation of ±0.21 determined at B26. Three periods of high values of pH could be noticed, from February to April 2011, from October 2011 to January 2012 and from September to November 2012. They are separated by periods of low pH measurements from June to September 2011 and from February to August 2012. A slight shift could exist from one borehole to another. Spring and autumn are the periods during which the pH is the highest and summer and winter are the periods in which the pH is the lowest. In summer, the lower pH can be attributed to high production of CO_2 in the soil, due to intense biological activities (Jaunat, 2012). In winter, the increase in CO_2 partial pressure in response to precipitation is responsible for the low pH values. During spring and fall, despite the significant rainfall, biological activities in the soil is reduced compare to the summer and the production of CO_2 is low, resulting in higher pH values.

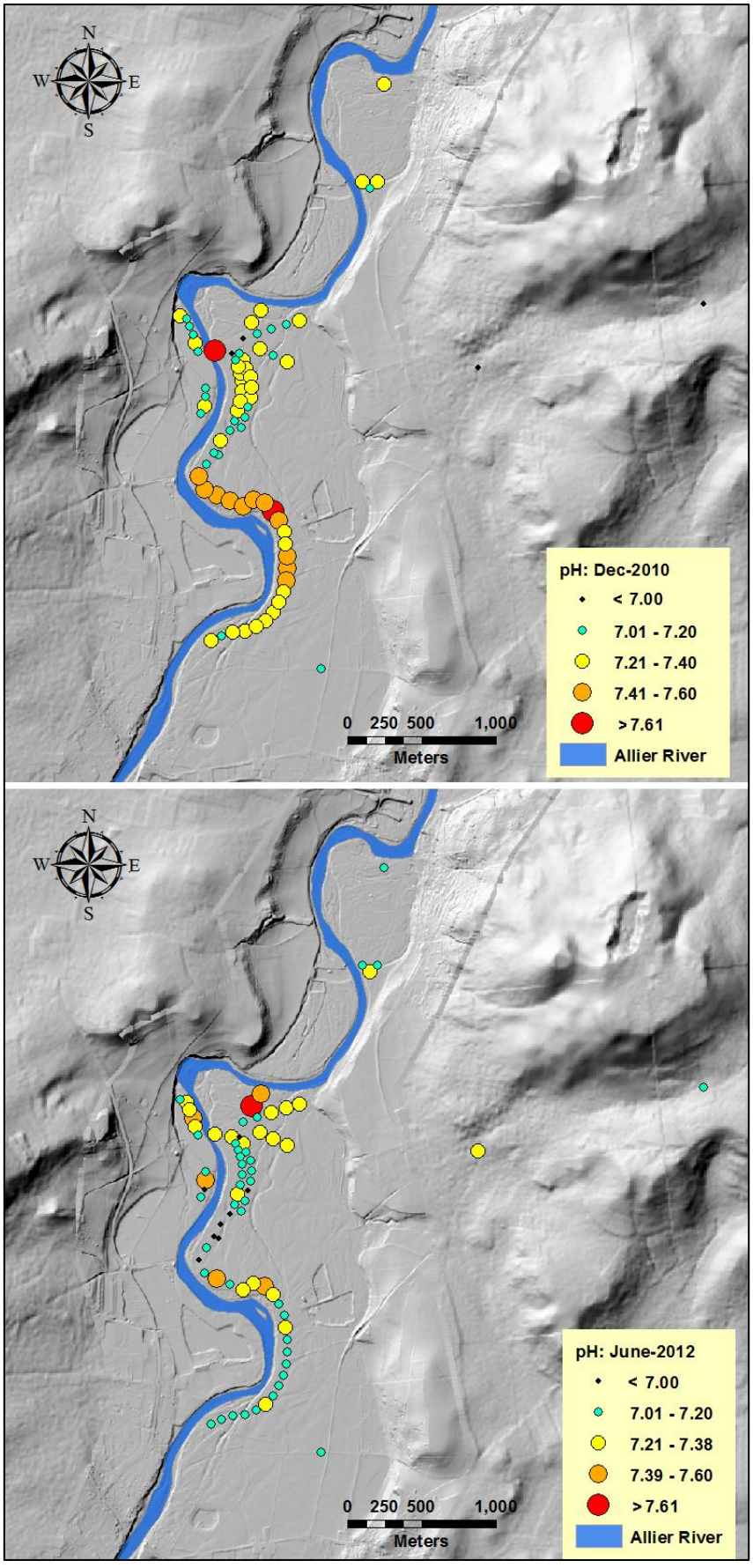

Fig.II-18: Spatial distribution of pH during the two intensive field campaigns (Dec-2010/low flow, June-2012/high flow).

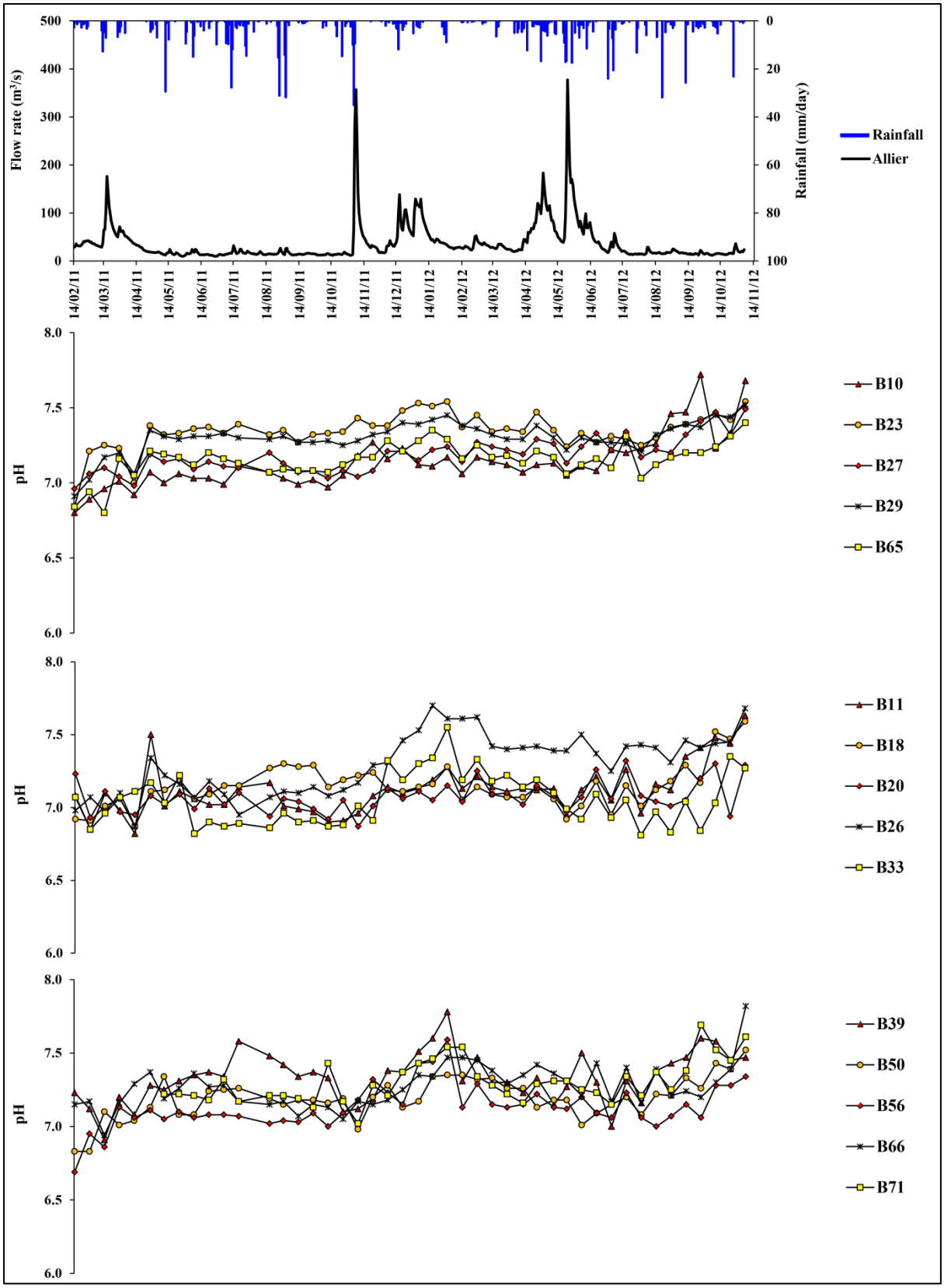

Fig.II-19: Time evolution of rainfall amount, Allier River flow rate, and water pH of investigated boreholes during the study period.

Electrical conductivity (EC) is widely used as a valuable indicator of the dissolved solids or salts in groundwater (Olajire and Imeokaria, 2001), and potable water should have electrical conductivity of less than 2500 µS/cm (WHO, 2008; European communities, 1998). In boreholes, EC values range from 168 (B52) to 955 µS/cm (B23) during low flow stage (Dec-2010) against 151(B52) to 989 µS/cm (B29) during high flow stage (June-2012) with corresponding averages of 276 and 274 µS/cm. Values found for the boreholes are in agreement with the measurement carried out on one alluvial aquifer in Australia by Timms and Acworth (2001) with EC values that range between 157 and 890 µS/cm. Higher EC has been recorded in the alluvial aquifer of alpine Rhône River valley in Switzerland by Schürch and Vuataz (2000) with EC value of 2940 µS/cm. However, lower EC values have been measured in the alluvial aquifer of Kurokawa, Japan by Chkirbene et al. (2009) with EC values between 59.4 and 113.5 µS/cm. These values are in relation with the composition of the rocks constituting the alluvial aquifer and with the residence time of groundwater within the system. The spatial distributions of EC during the two flow stages in the study zone are presented in Fig.II-20. This figure highlights the spatial variability of EC with an increase of the values from the river side toward east, in the area close to the hills.

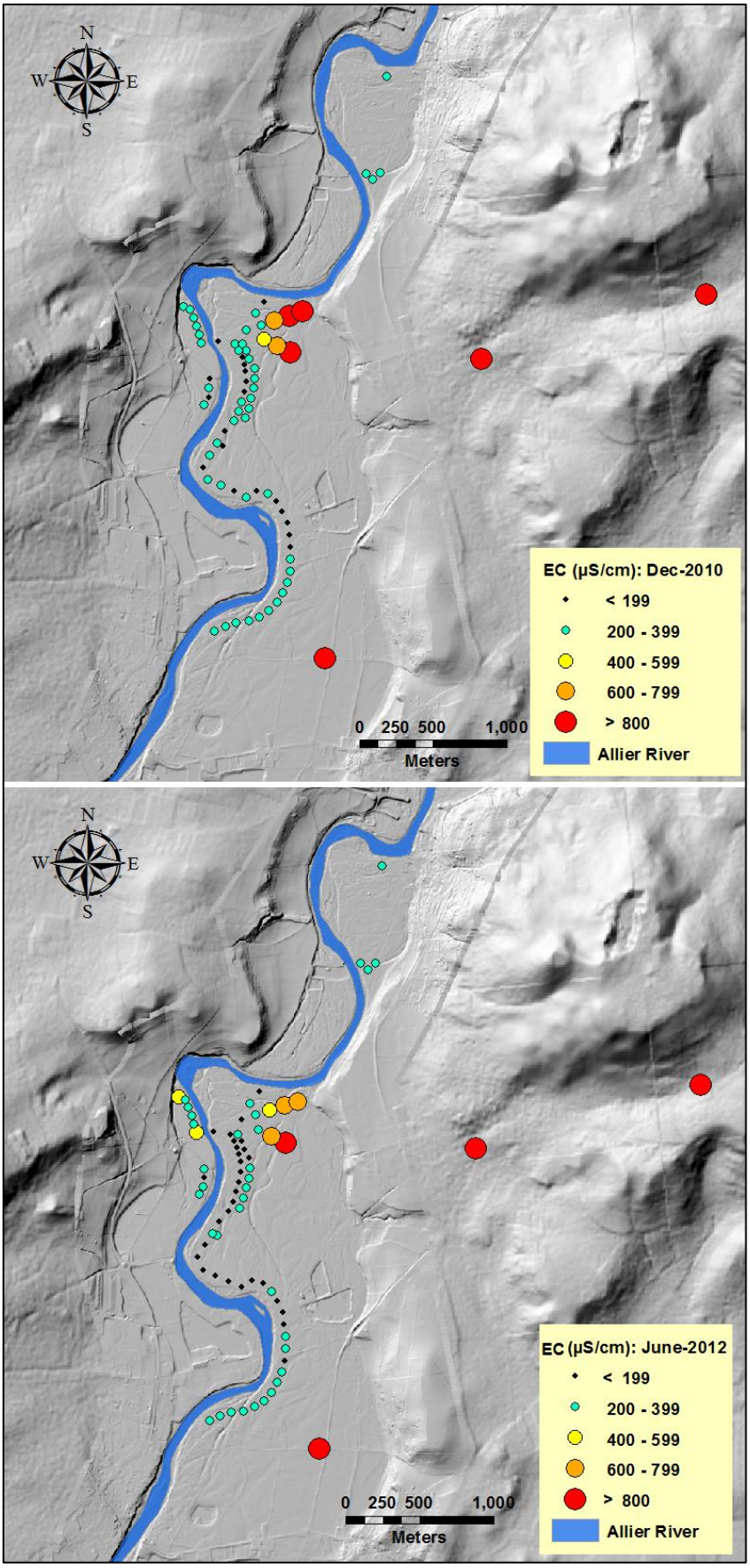

Fig.II-20: Spatial distribution of Electrical Conductivity (EC) during the two intensive field campaigns (Dec-2010/low flow, June-2012/high flow).

The temporal variations in EC values of the selected boreholes are presented in Fig.II-21. The electrical conductivity shows great variability in temporal variation in boreholes and can be divided to three categories:

- Boreholes B11, B18, B20, B26, B33, B39, B66, and B71 are characterized by low EC contents (150 – 300 µS/cm) and exhibit small temporal variations parallel to the ones of the Allier River.
- Boreholes B10, B27, B50, B56, and B65 present high EC contents (up to 700 µS/cm) and display temporal variations. B10 and B27 are located in the middle part of study and seem to be influenced by the Allier River as well as other sources of recharge. B50 shows temporal fluctuations that differ significantly from the ones of the Allier River, although this borehole is located close to the Allier River in the western side. B50 could also be under the influence of groundwater coming from the hills in this western part (no measurements have been realized in this area). B56 and B65 are both located in the area characterized by partially sealed banks of Allier River and show temporal variations, particularly B56.
- Boreholes with high EC (up to 1000 µS/cm) such as B23 and B29. These boreholes are placed in the eastern part of the Allier and are close to hills. B23 displays great temporal variations (between 384 µS/cm in the 27th of November 2011 and 1001 µS/cm in the 16th of August 2011). The lowest value is recorded during a high flow of the Allier River, attesting that a part of the incoming water flows from the Allier River. B29 is characterized by the highest EC but does not show any temporal variations (values between 912 - 1009 µS/cm).

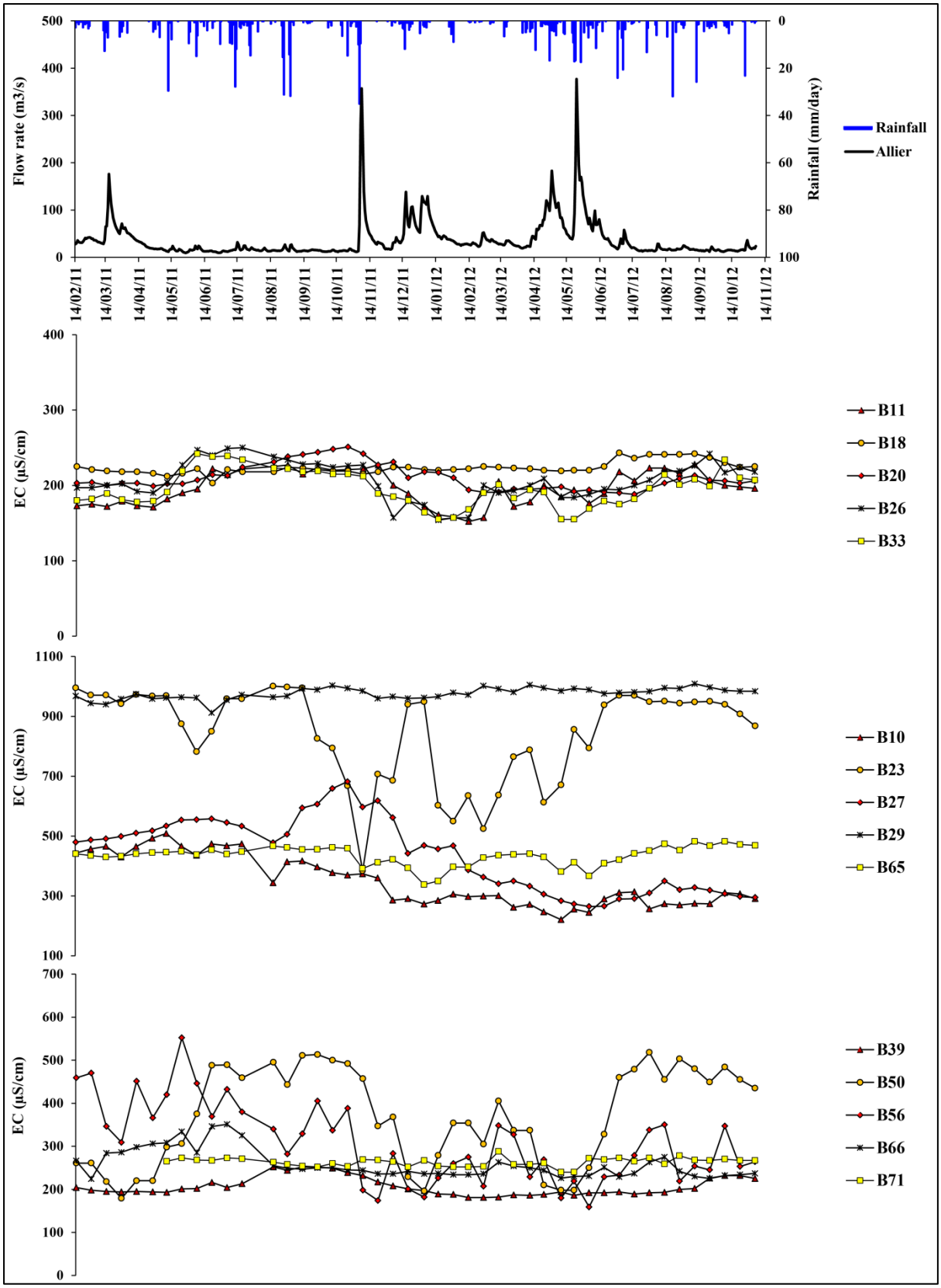

Fig.II-21: Time evolution of rainfall amount, Allier River flow rate, and electrical conductivity of investigated boreholes during the study period.

The spatial distribution of DO is shown in Fig.II-22. The content of dissolved oxygen during low flow stage campaign spreads between 2.4(B57) and 8.1(B50) mg/l with an average value of 5.6±1.4 mg/l, and during high flow stage the values range from 1.0(B40) to 8.4(B19) mg/l with an average value of 5±1.8 mg/l. Similar results are reported for the Mondego River basin in Portugal by Andrade and Stigter (2011) with values varying from 1.03 to 9.6 mg/l and an average value of 4.8 mg/l. Higher concentrations have been detected from the Quaternary alluvial aquifer of the Guadalquivir River in Spain by Lorite-Herrera et al. (2008) with an average value of 8.04 mg/l. Whereas lesser amounts of DO have been reported from the alluvial aquifer of Keum River in South Korea by Chae et al. (2004, mean value of 2.8 mg/l), probably in relation with the variability of physical, chemical and biological activities of the water body (Neal et al., 1998; Datry et al., 2004). All sampling points exhibit seasonal variations of DO Fig.II-23 due most probably to temperature variations affecting this unconfined shallow alluvial aquifer.

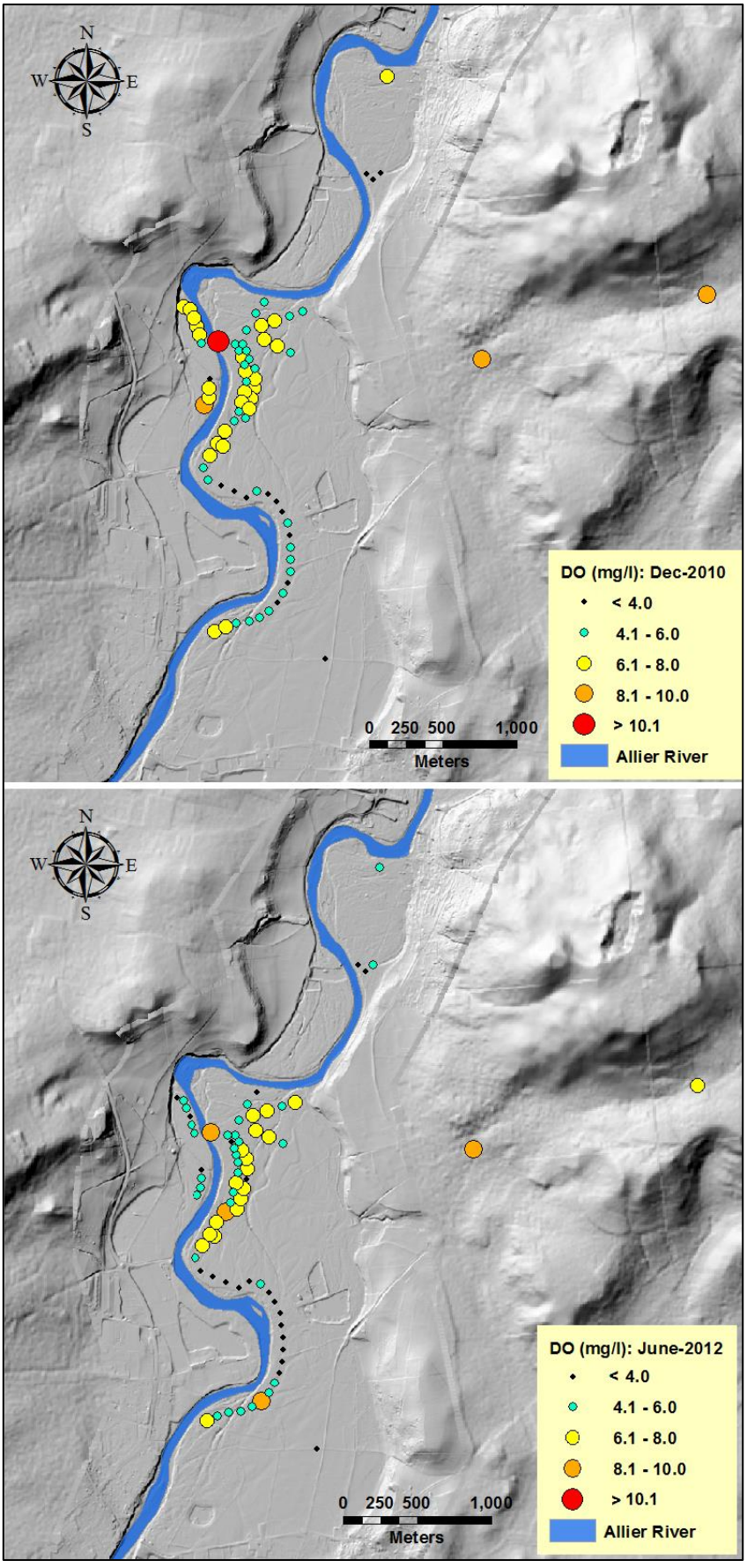

Fig.II-22: Spatial distribution of Dissolved Oxygen (DO) during the two intensive field campaigns (Dec-2010/low flow, June-2012/high flow).

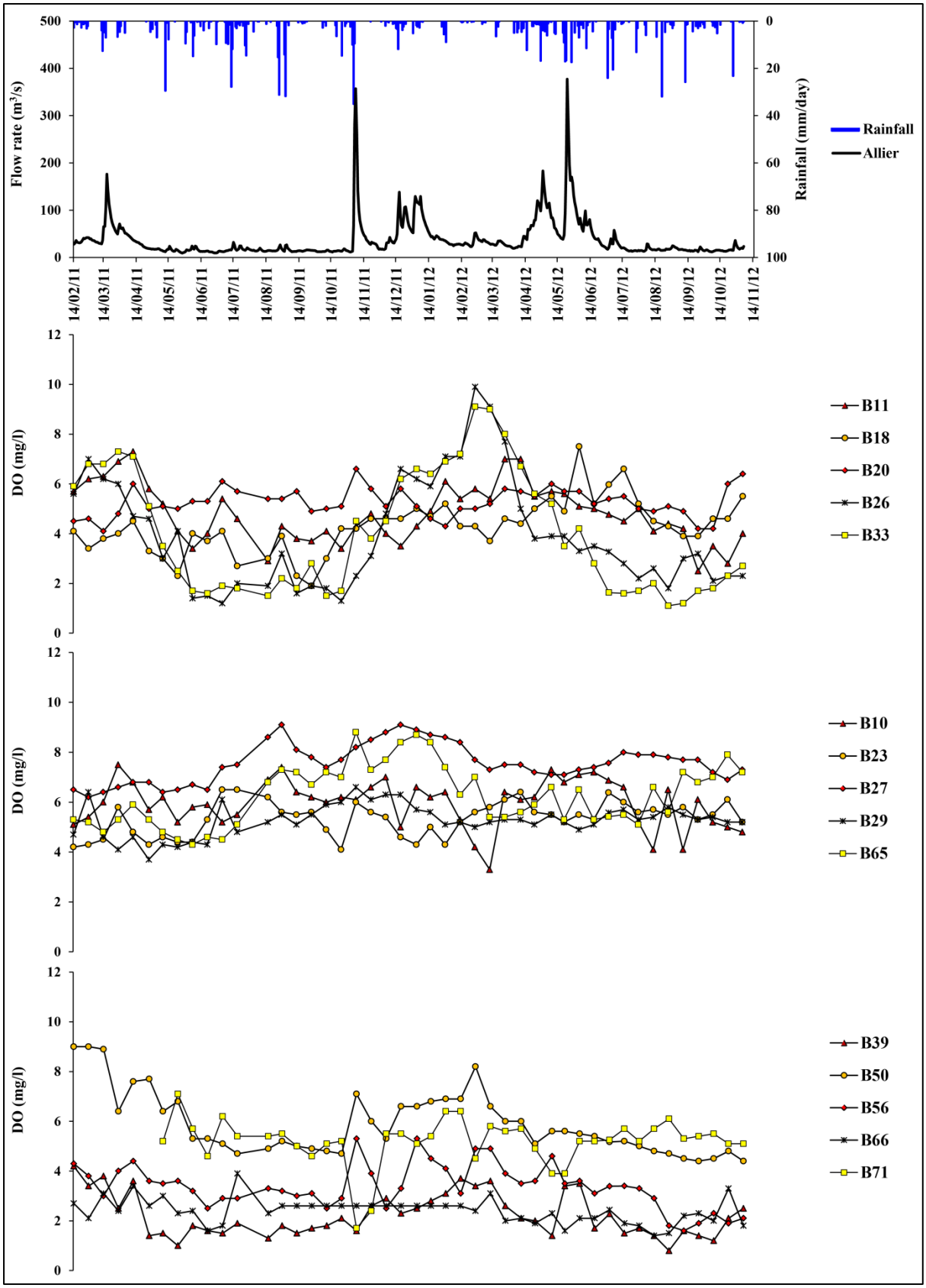

Fig.II-23: Time evolution of rainfall amount, Allier River flow rate, and dissolved oxygen concentrations of investigated boreholes during the study period.

2.2.2. Chemical characteristics of groundwater

Groundwater from all boreholes sampled during the study present a Ca/HCO_3 facies due to both lithology and the dissolution ability of the minerals. This type is recognized in many alluvial systems around the world (in Europe: e.g. Andrade and Stigter, 2011, in Asia: e.g. Chkirbene et al., 2008). Based on secondary cations, the water type evolves from Ca-Na-Mg/HCO_3-Cl, Ca-Mg-Na/HCO_3-Cl recorded in the closest boreholes from the riverbanks to Ca-Mg/HCO_3 for the boreholes located in the eastern part of the site (Fig.II-24). This evolution could be due to the dissolution of Na-feldspar in alluvial sediment for boreholes close to the Allier River compare to the dissolution of carbonate Mg-rich from hills in the eastern side.

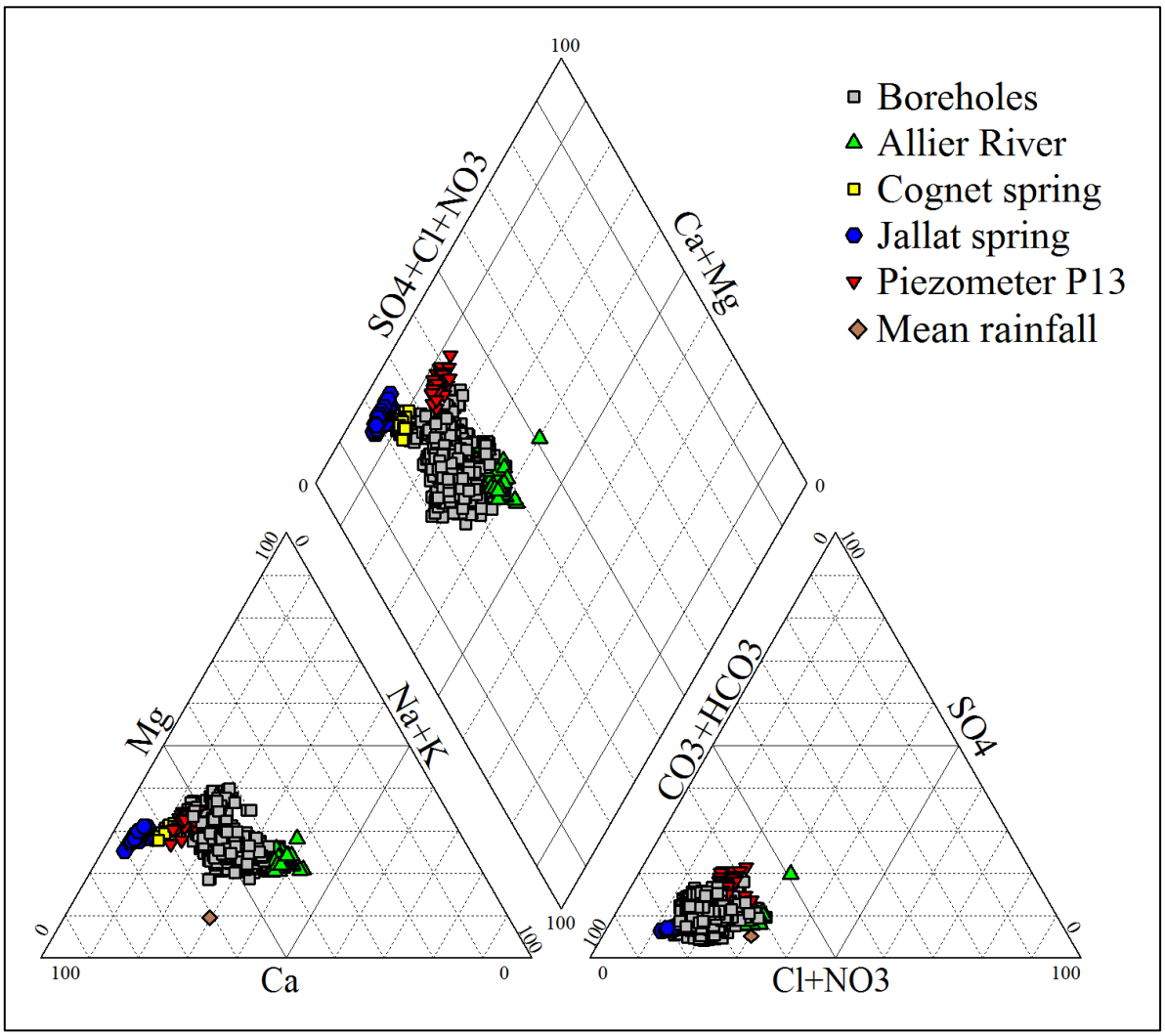

Fig.II-24: Piper diagram showing the chemical water type of the sampling points.

2.2.2.1. Spatial variations of major ions

Major ions constitute a significant part of the total dissolved solids present in ground water. Concentrations of these ions in groundwater depend primarily on the hydrogeochemical processes that take place in the aquifer system. These processes occur when the groundwater moves toward equilibrium in major ion concentration. Hence, the study of concentrations of various major ions present in groundwater is used in the identification of geochemical processes (Appelo and Postma, 1993; Evangelou, 1998). The analytical results of major ions are presented in Appendix A.

Calcium (Ca^{2+}) is the predominant cation in boreholes groundwater which accounts for 50.9%. The spatial distribution of calcium is shown by Fig.II-25. During low flow stage campaign (Dec-2010), content of Ca^{2+} in boreholes spreads between 15.1 (B58) and 112 (B23) mg/l with an average value of 27.2 mg/l. During high flow stage (June-2012), the values range from 12.7 (B52) to 100.8 mg/l (B29) with an average value of 24.6 mg/l. These values are consistent with the ones observed in the alluvial aquifer of Keum River in Korea (3.9–110 mg/l; Chae et al., 2004). While, these values are generally lower than the values detected in the alluvial aquifer of Allier River near Vichy, France (70–733 mg/l in Négrel et al., 2004) or in other countries like Switzerland (514.8–533.2 mg/l, Schürch and Vuataz, 2000), and China (51.1–256.5 mg/l, Han et al., 2009). Smaller concentrations comparable to the ones of our study have been reported by Choi et al. (2008) for the alluvial aquifer of Mankyeong watershed in Korea. Such elevated Ca^{2+} concentrations observed in the study area result probably to the reaction of carbonate and silicate minerals with carbonic acid derived from the respiration of organic matter (Appelo and Postma, 1995).

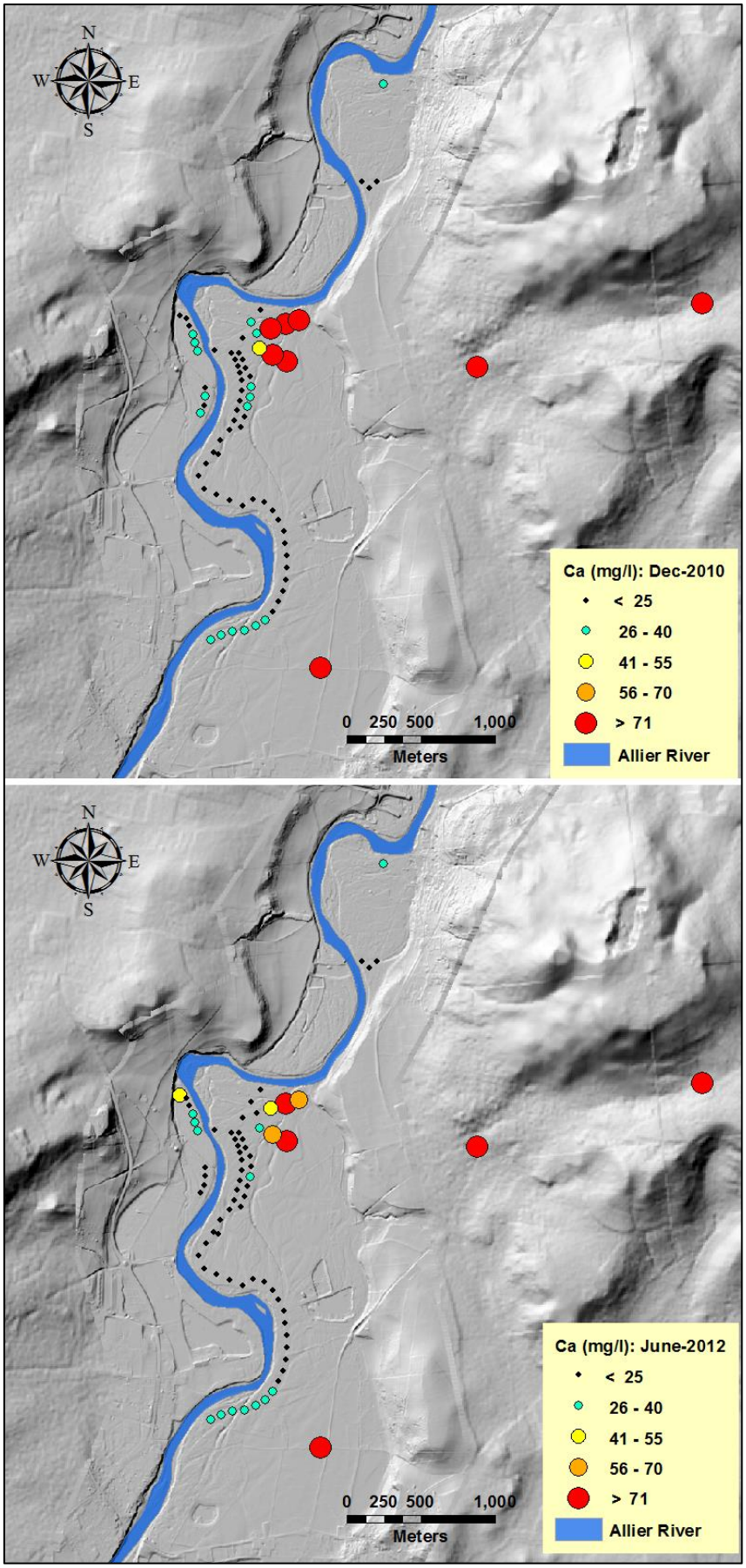

Fig.II-25: Spatial distribution of Ca (mg/l) during the two intensive field campaigns (Dec-2010/low flow, June-2012/high flow).

Magnesium (Mg^{2+}) is also found in considerable amounts and varies in groundwater from 4.5 (B05) to 47.9 mg/l (B29) with an average of 9.2 mg/l during low flow stage, and from 4.3 (B48) to 49.5 mg/l (B29) with an average of 9.1 mg/l during high flow stage (Fig.II-26). These values are in agreement with data reported by Bhattacharya et al. (2006) for Rio Dulce alluvial aquifers (Santiago del Estero Province, Argentina) that range between 0.5 and 51.1 mg/l, and Chae et al. (2009) for Keum River watershed (Korea) that range from 11.3 to18.6 mg/l. Concentrations evaluated for the boreholes are lower than those reported in China (20.4–81.5 mg/l; Han et al. (2009), Yangwu River alluvial fan), and Australia (0.5–223 mg/l, Vanderzalm et al. (2011), Todd River alluvial aquifer).

Sodium (Na^{+}) is one of the important naturally occurring cations and is the dominant cation next to calcium in the study site with 23.6%. Sodium's spatial distribution in the study area is shown in Fig.II-27. Na^{+} concentrations in boreholes vary between 9.3 (B49) and 38.4 mg/l (B29) with an average value of 13.3 mg/l during low flow stage and between 9.2 (B56) and 37.6 mg/l (B29) with an average value of 13.4 mg/l during high flow stage. The alluvial sediment is considered as the main source of sodium since it contains significant amounts of feldspar which comprise large quantities of sodium ion. These results are in agreement with those observed in Loire Alluvial aquifer, France by Négrel et al. (2003) that measured a Na^{+} mean value of 13.1 mg/l, and Rhône River alluvial aquifer, Switzerland by Schürch and Vuataz (2000) with a mean value of 14.0 mg/l. The Na^{+} measurements are much lower than those recorded in Australia [performed in the alluvial aquifer of Todd River with a mean value of 862 mg/l by Vanderzalm et al. (2011)], and Portugal [achieved in alluvial river basin of the Mondego with a mean value of 27.4 mg/l by Andrade and Stigter (2011)]. Lower values of Na^{+} than Allier alluvial aquifer have been reported in Japan by Chkirbene et al. (2009) for the Kurokawa alluvial aquifer with values range between 2.4 and 9.6 mg/l and in Bolivia (average of 10.3 mg/l) for the alluvial system of Cochabamba valley by Stimson et al. (2001).

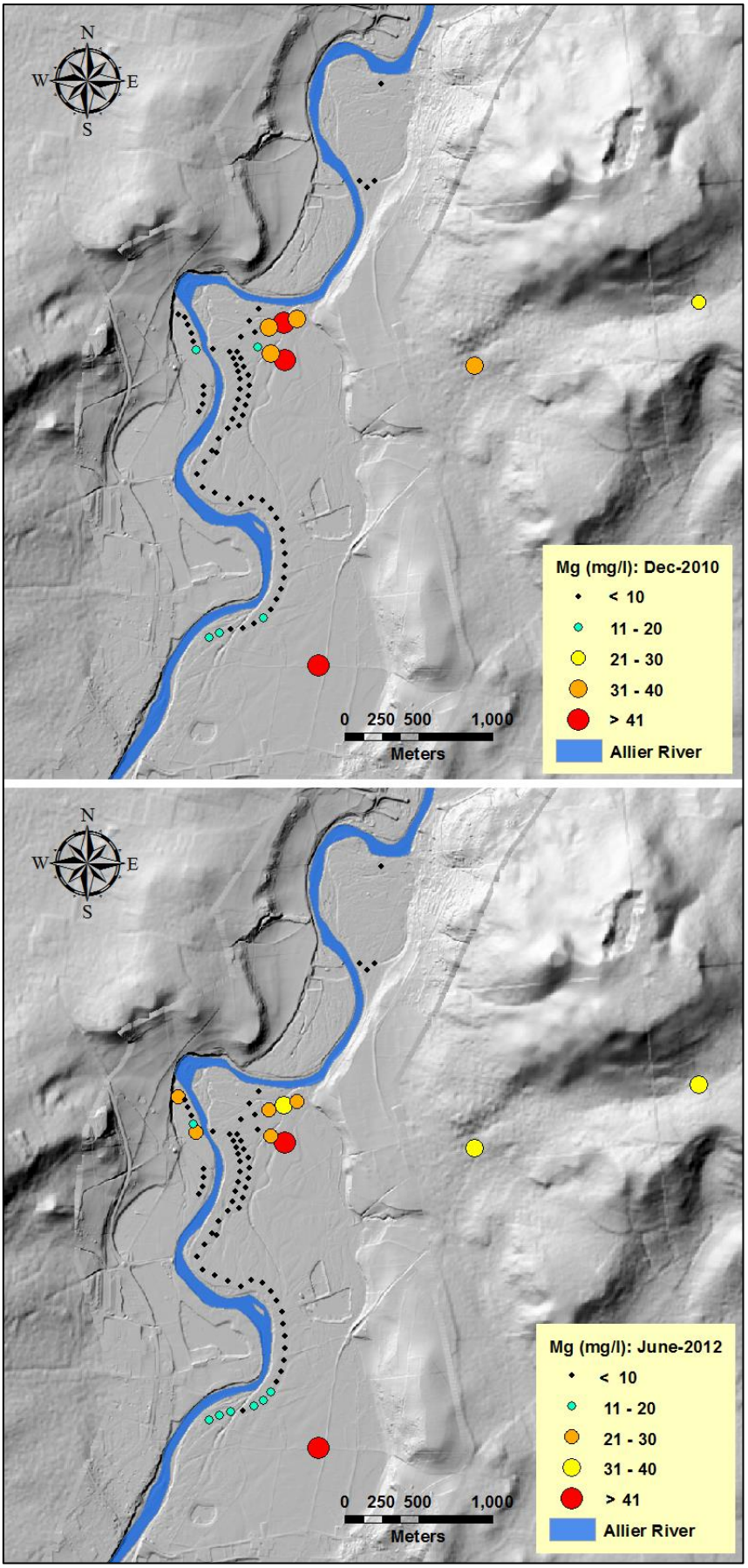

Fig.II-26: Spatial distribution of Mg (mg/l) during the two intensive field campaigns (Dec-2010/low flow, June-2012/high flow).

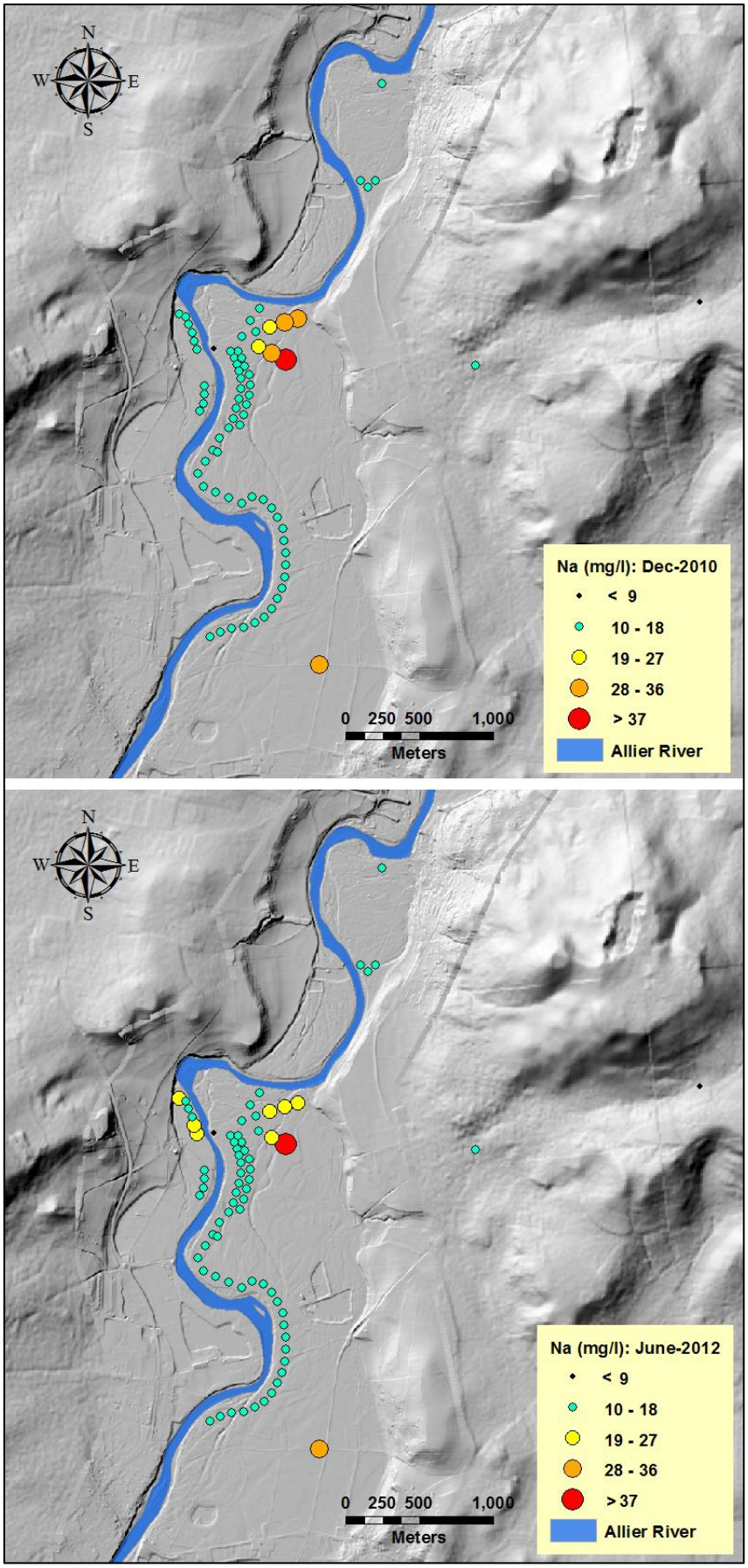

Fig.II-27: Spatial distribution of Na (mg/l) during the two intensive field campaigns (Dec-2010/low flow, June-2012/high flow).

Among the anions, bicarbonate (HCO_3^-) is the predominant ion in the investigated boreholes, accounting for 76.7% of the anions. It ranges from 61(B52) to 473(B23) mg/l for low flow stage (Dec-2010) and from 62(B52) to 460 mg/l (B29) for high flow stage (June-2012). The corresponding means are of 119 and 116 mg/l, respectively. Spatial distributions of bicarbonate in the study area during the two flow stages are shown in Fig.II-28. Boreholes close to Allier River contained lower amounts of bicarbonate compare to boreholes close to the hills in the eastern side due to the short residence time of water. These results coincide with those of Négrel et al. (2003) implemented in alluvial aquifer of Loire River, France (values range between 99 and 360 mg/l), and of Schürch and Vuataz (2000) performed in alluvial aquifer of Rhône River, Switzerland (range from 137 to 381 mg/l). Higher values were recorded by Vanderzalm et al. (2011) in Todd River's alluvial aquifer and were comprised from 240 to 800 mg/l (mean of 472 mg/l), and by Andrade and Stigter (2011) within the Mondego alluvial basin, Portugal with a mean value of 331 mg/l. Nevertheless, other authors have recorded lower values in alluvial aquifers of different regions: Kim et al. (2009) in Osong area, South Korea with the mean value of 72 mg/l, and Chkirbene et al. (2009) in Kurokawa alluvial aquifer, Japan with concentrations range between 11 and 48 mg/l.

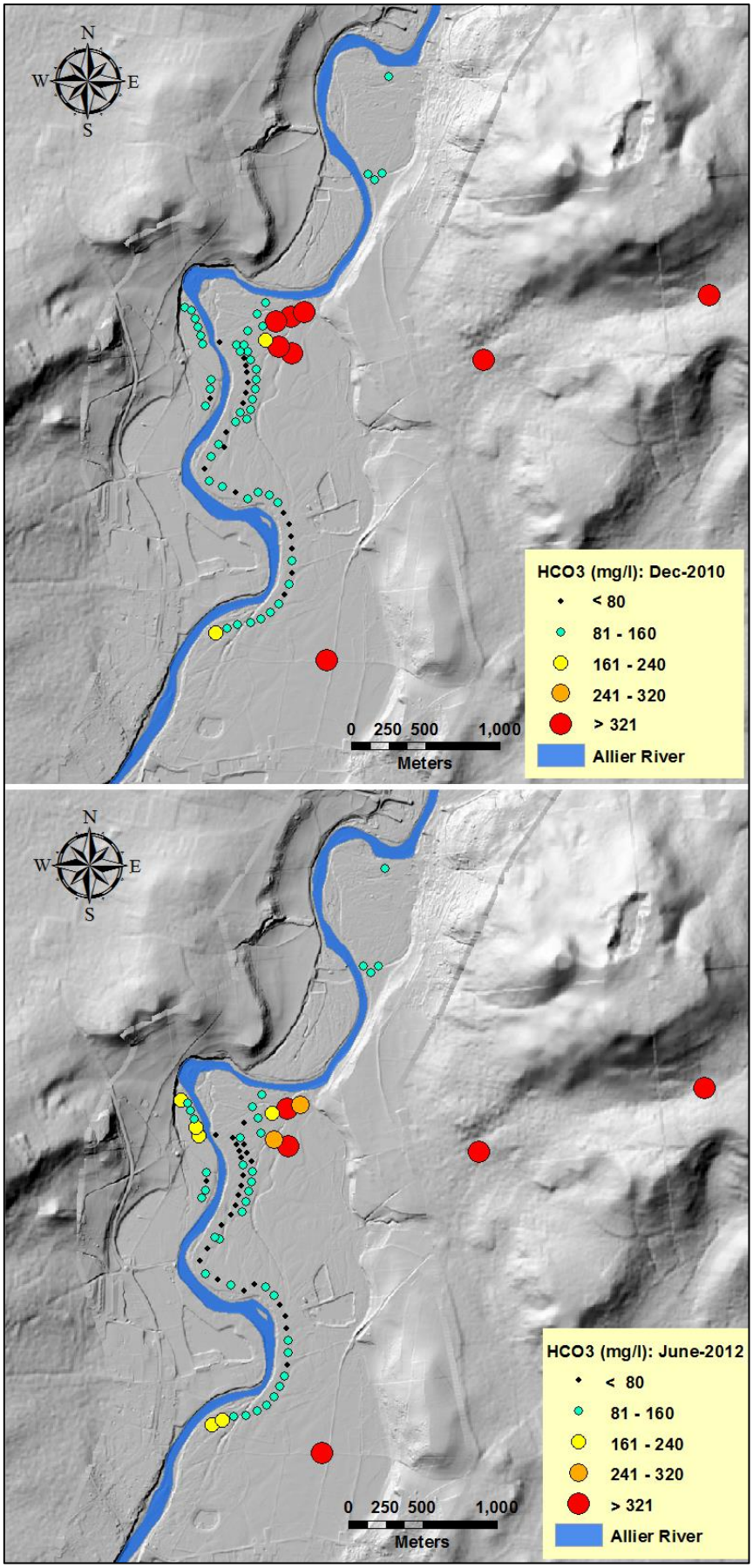

Fig.II-28: Spatial distribution of HCO_3 (mg/l) during the two intensive field campaigns (Dec-2010/low flow, June-2012/high flow).

Chloride (Cl^-) occurs naturally in all types of waters. Spatial distributions of chloride during two flow stages are displayed in Fig.II-29. Chloride contents during low flow stage in boreholes vary between 12(B49) and 49 mg/l (B29), while during high flow stage they fluctuate from 9(B52) to 50.4 mg/l (B29) with corresponding means of 17 and 15.4 mg/l, respectively. These results are in agreement with those of Négrel et al. (1997) for Allier River alluvial aquifer in Vichy with a mean value of 18 mg/l, Négrel et al. (2003) in Loire's alluvial aquifer with an average value of 15.2 mg/l, and Schürch and Vuataz (2000) in Rhône's alluvial aquifer with a value range between 3.9 and 14.6 mg/l. Greater concentrations have been detected in various alluvial aquifer worldwide, such as: Australia [average of 755 mg/l in Todd River alluvial aquifer, Vanderzalm et al. (2011)], Spain [14–592 mg/l in Guadalquivir River's Quaternary alluvial aquifer, Lorite-Herrera et al. (2008)], Portugal [average of 35.6 mg/l in Mondego's river basin, Andrade and Stigter (2011)], and South Korea [13.6 – 82.7 mg/l in alluvial aquifer of Keum River, Chae et al. (2004)]. However, Chkirbene et al. (2008) have measured lower Cl^- concentration from Kurokawa's alluvial aquifer (Japan) with values ranging between 2.2 and 7.6 mg/l. Chloride ions do not participate in the weathering reactions since local lithologies do not contain any evaporite deposits. Cl^- in groundwater, therefore, comes from sea salt (Meybeck, 1983; Négrel, 1999) and/or human activities (domestic sewage, fertilizers, de-icing salt, etc.)

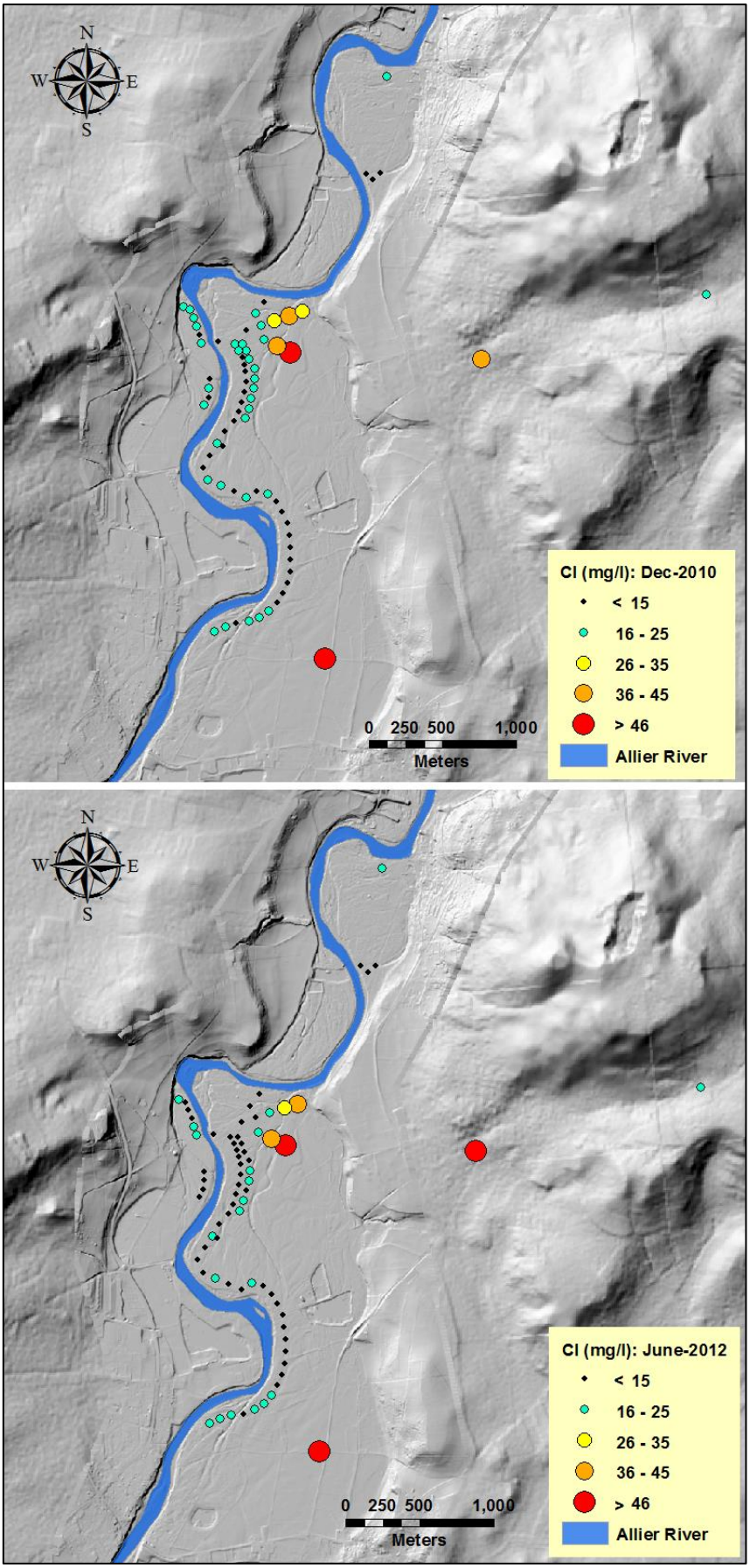

Fig.II-29: Spatial distribution of Cl (mg/l) during the two intensive field campaigns (Dec-2010/low flow, June-2012/high flow).

Sulphate (SO_4^{2-}) concentrations vary spatially as shown in the Fig.II-30. Generally, SO_4^{2-} concentrations in boreholes are less than 100 mg/l. In low flow stage campaign (Dec-2010), the lowest SO_4^{2-} concentration is recorded in B39 (5.9 mg/l) and the highest concentration is recorded in B29 (80.2 mg/l) with an average value of 15.4 mg/l. While during high flow rate (June-2012), the minimum concentration of SO_4^{2-} is recorded in B40 (6.7 mg/l) and the maximum concentration in B29 (82 mg/l) with an average of 14.5 mg/l. Parallel results have been gathered from France: in Allier River's alluvial aquifer close to Vichy by Négrel et al. (2004) with a range from 25 to 33 mg/l, in Loire alluvial aquifer by Négrel et al. (2003) with values between 15.9 and 60.2 mg/l. Elsewhere, similar findings have been recorded such as in South Korea by Chae et al. (2004) in Keum River watershed that present values between 0.3 and 93.5 mg/l. Chkirbene et al. (2008) measured lower Cl^- concentrations in Kurokawa's alluvial aquifer (Japan) with values ranging between 3.8 and 12.7 mg/l. Nonetheless, much greater concentrations have been noticed by: Vanderzalm et al. (2011) in Todd River's alluvial aquifer (Australia) with an average value of 1260 mg/l, Schürch and Vuataz (2000) in the Rhône's alluvial aquifer whith values ranging from 1492 to 1808 mg/l, and Lorite-Herrera et al. (2008) in Guadalquivir River (Southern Spain) with a range from 37 to 844 mg/l.

The sulphate contents in groundwater are, most possibly, coming from agricultural fertilizers which are applied to enhance crop productions that surrounded the study area. Piezometer P13 is the only point directly drilled in agricultural land and shows the maximum concentration of SO_4^{2-}. The spatial distribution of SO_4^{2-} shows that the concentration of this ion increases from the Allier River toward the eastern side.

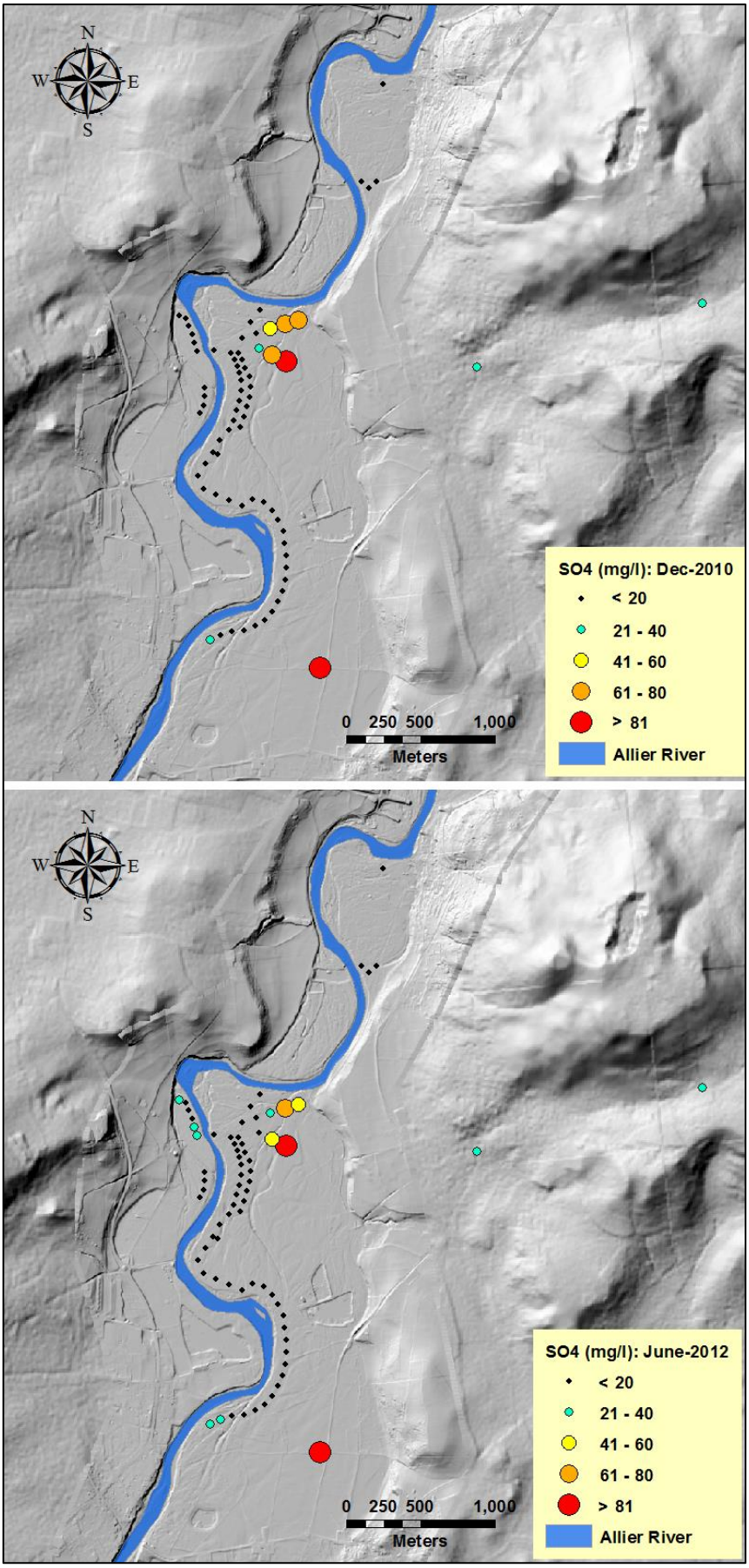

Fig.II-30: Spatial distribution of SO_4 (mg/l) during the two intensive field campaigns (Dec-2010/low flow, June-2012/high flow).

Nitrate (NO_3^-) depends also on anthropogenic activities and largely on agriculture. Chemical analyses of NO_3^- show that none of the water sample exceeds the maximum contamination level of 50 mg/l (WHO, 2008). From Fig.II-31, it is clear that the high levels of nitrate are recorded in the boreholes close to the hill side which are surrounded by agricultural lands. In this part of the study area, moreover, waste waters are poorly treated and may supply NO_3^-. Concentrations of nitrate vary between 0(B40&B69) to 22.2 mg/l (B24) during low flow stage (Dec-2010) and between 0(B40) and 21.3 mg/l (B23) during high flow stage (June-2012), with the corresponding averages of 5.7 and 5.8 mg/l, respectively. Identical results have been detected in Kurokawa's alluvial aquifer, Japan (4.2–21.5 mg/l, Chkirbene et al. (2008)). Weaker concentrations comparable to this study have been reported by Vanderzalm et al. (2011) for the Todd River watershed with an average of 0.8 mg/l, as well as Schurch and Vuataz (2000) for the Rhône River's alluvial aquifer (0.1–3.3 mg/l). Higher values have been found by Négrel et al. (2003) for the Loire River's alluvial aquifer (0.9–55 mg/l), and Lorite-Herrera et al. (2008) for Guadalquivir River's alluvial aquifer, Spain (0.3–72.5 mg/l).

Nitrate concentrations are mainly controlled by the application of fertilizers in the agricultural lands (Spalding and Exner, 1993; Chowdary et al., 2005). Denitrification can also cause variations of nitrate concentrations (Torrento et al., 2010). The boreholes with high nitrate content are located in the eastern side of the Allier River close to the hills and agricultural fields hence they could be recharged by water of high nitrate content from agricultural fields. Moreover, waste waters from water treatment plants also contain high nitrate contents and hence enter both surface and groundwater (Spalding and Exner, 1993).

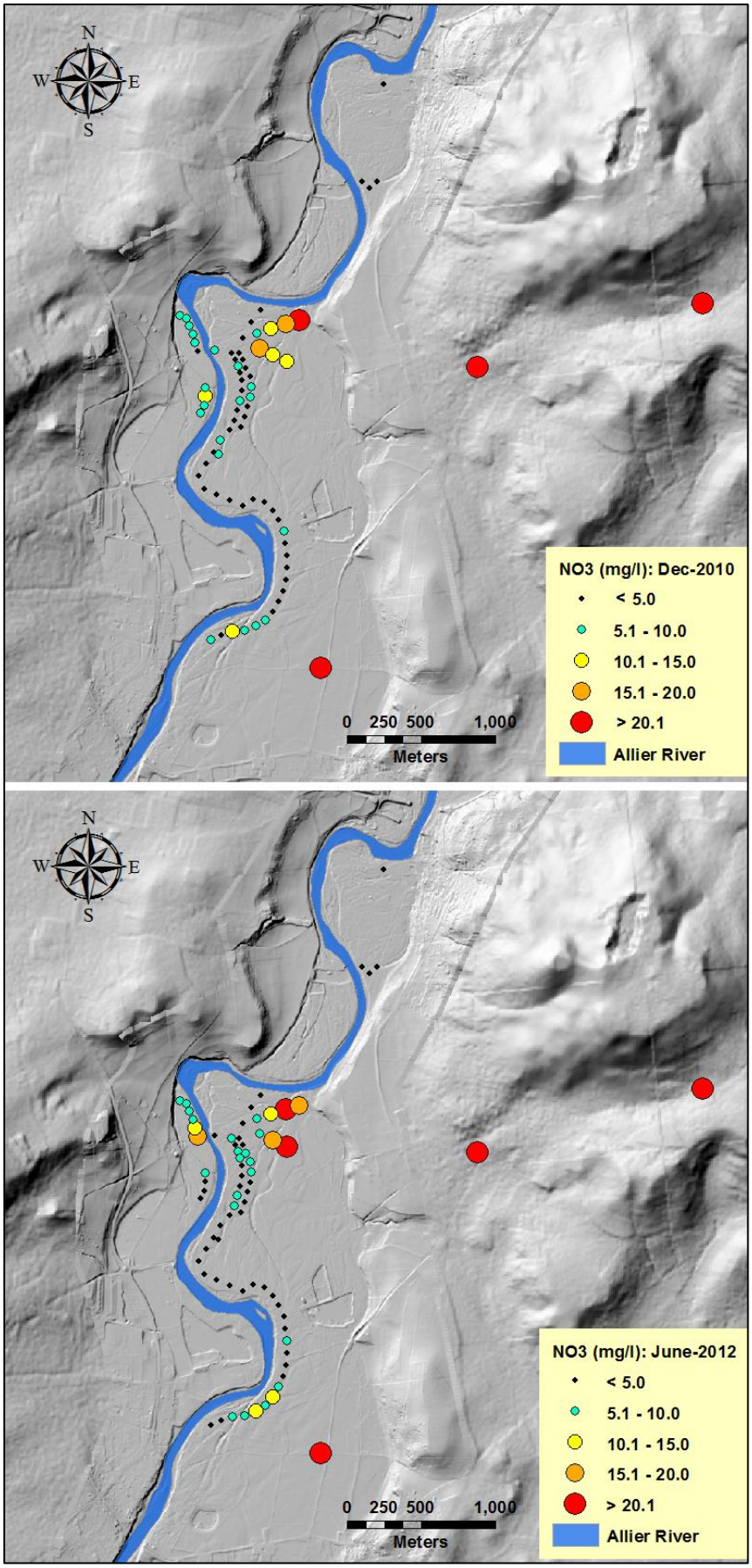

Fig.II-31: Spatial distribution of NO_3 (mg/l) during the two intensive field campaigns (Dec-2010/low flow, June-2012/high flow).

2.2.2.2. Temporal variations of major ions

In order to better illustrate the overall temporal variations of water chemistry, five boreholes (B10, B29, B33, B39, and B65) among the 15 studied have been selected to represent the whole study zone, depending on their locations, behavior and ionic contents. Temporal variations of major ions of each selected boreholes are discussed below.

Borehole B33 is characterized by low EC value (average of 196 µS/cm) and represents the boreholes close to the Allier River that behave likewise the Allier River. During the study period, significant temporal variations have been observed in all ions in parallel with water temperature of this borehole. Time evolutions of major ions are compared to water level and temperature of B33 (Fig.II-32). The highest value of each parameter is recorded during summer time and the lowest value is recorded during winter time, excluding nitrate which presents the highest value during spring. Time evolutions of the parameters measured at B33 are in good agreement with that of Allier River confirming the strong connection between surface and groundwater. Groundwater fluctuations do not seem to have any correlation with ionic concentration variation. The best example is quoted on the 7th of November 2011 when water level reaches a maximum value (317.58 m.a.s.l.) that does not correspond to any chemical variation. Also, a couple of sharp declines in water level, due to pumping, do not cause any change in water chemistry. Although B33 is far from agricultural practices, nitrate levels vary between 1.6 – 6.8 mg/l. Allier River is considered as the main source of nitrate in this borehole and presents very close values ranged between 1.9 – 6.9 mg/l. When detailed groundwater nitrate monitoring is conducted in shallow aquifers, significant temporal variations are usually observed (Postma et al., 1991; Steinheimer et al., 1998). Where it occurs, denitrification can increase this variability (Montgomery et al., 1997).

Fig.II-32: Time evolution of major ion concentrations, water level and temperature of B33 during the study period.

Borehole B10 is representing the boreholes located in the middle part of the study zone (in the edge of one of the old Allier channel) and is believed to be influenced both by Allier River and other sources of recharge. The average electrical conductivity of this sampling point is 348 µS/cm which is higher almost twice than the Allier Rive's one. All major ions display significant temporal variation (except sodium and potassium) as shown in Fig.II-33. Maximum concentrations of these ions are measured during spring and summer 2011, and minimum values measured during winter 2012, with a possible relation with rainfall amount. Groundwater concentrations of this borehole decrease almost double in the year 2012 compare to 2011 for most of ions (HCO_3^- from 203 to 90 mg/l; Cl^- from 29.5 to 15.7 mg/l; SO_4^{+2} from 46.3 to 10.1 mg/l; NO_3^- from 20.7 to 4.3 mg/l; Ca^{+2} from 56 to 21.7 mg/l; Mg^{+2} from 18 to 7.2 mg/l; Na^+ from 20.1 to 11.9 mg/l; and K^+ from 6 to 2.6 mg/l). This borehole is

affected by the anthropogenic inputs since it contains high amount of nitrate (up to 20.7 mg/l) which originate from agricultural practices.

A few sharp declines in some major ion concentrations can be noted and are positively associated with the groundwater level fluctuations. This input is certainly caused by rapid transfer of weakly mineralized waters from Allier River, through the alluvial sediments, via pumping process during day time, that cause dilution of major ions.

Seasonal variations in groundwater chemistry and piezometric levels reflect fluctuation in groundwater recharge (Schürch and Vuataz, 2000). Therefore, temporal variation in water chemistry of B10 could also be influenced (partially) by the fluctuations of the Allier River flow rate. B10 may only be recharged by the Allier River during high water flow periods, in winter and spring, which could result in a decrease of ionic content. In summer, however, the flow rate of Allier River decreases and B10 could be recharged by other sources characterized by high ionic content (hills and/or southern aquifer) that mix with the Allier River origin. Moreover, the old Allier River channel could modify the chemical signature of B10.

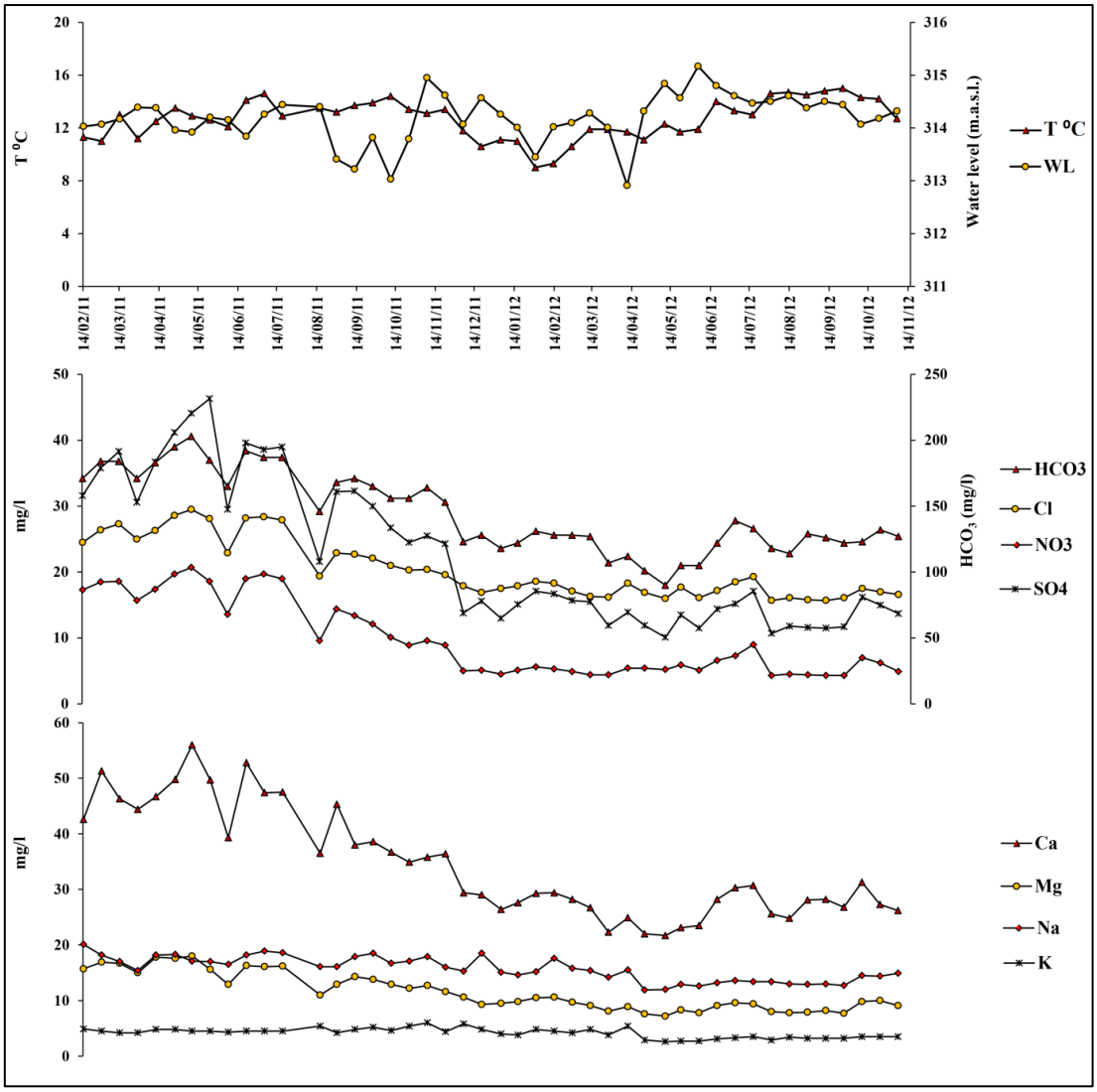

Fig.II-33: Time evolution of major ion concentrations, water level and temperature of B10 during the study period

Borehole B29 can be distinguished for it presents the highest EC value (average of 977 µS/cm). It is located far from the Allier River, in the eastern side, close to the hills. All major ions are remarkably constant (Fig.II-34) and do not show any temporal variations throughout the course of the study, except bicarbonate (HCO_3^-). Significant temporal variations in bicarbonate are noticed: a maximum value is recorded during summer (503 mg/l in 24/10/2011) and a minimum value is recorded during winter and spring (459 mg/l in 26/04/2011). The availability of bicarbonate in groundwater is mainly due to the dissolution of carbon dioxide (CO_2), which is influenced by biological process in the soil and temperature (Appelo and Postma, 1993). During summer the biological processes and temperature increase and enhance the production of CO_2 in the soil. Therefore, bicarbonate in groundwater is high during summer and low during winter. The recharge source of B29 could

be the water from hills and/or the water from southern alluvial aquifer which both present high ionic content.

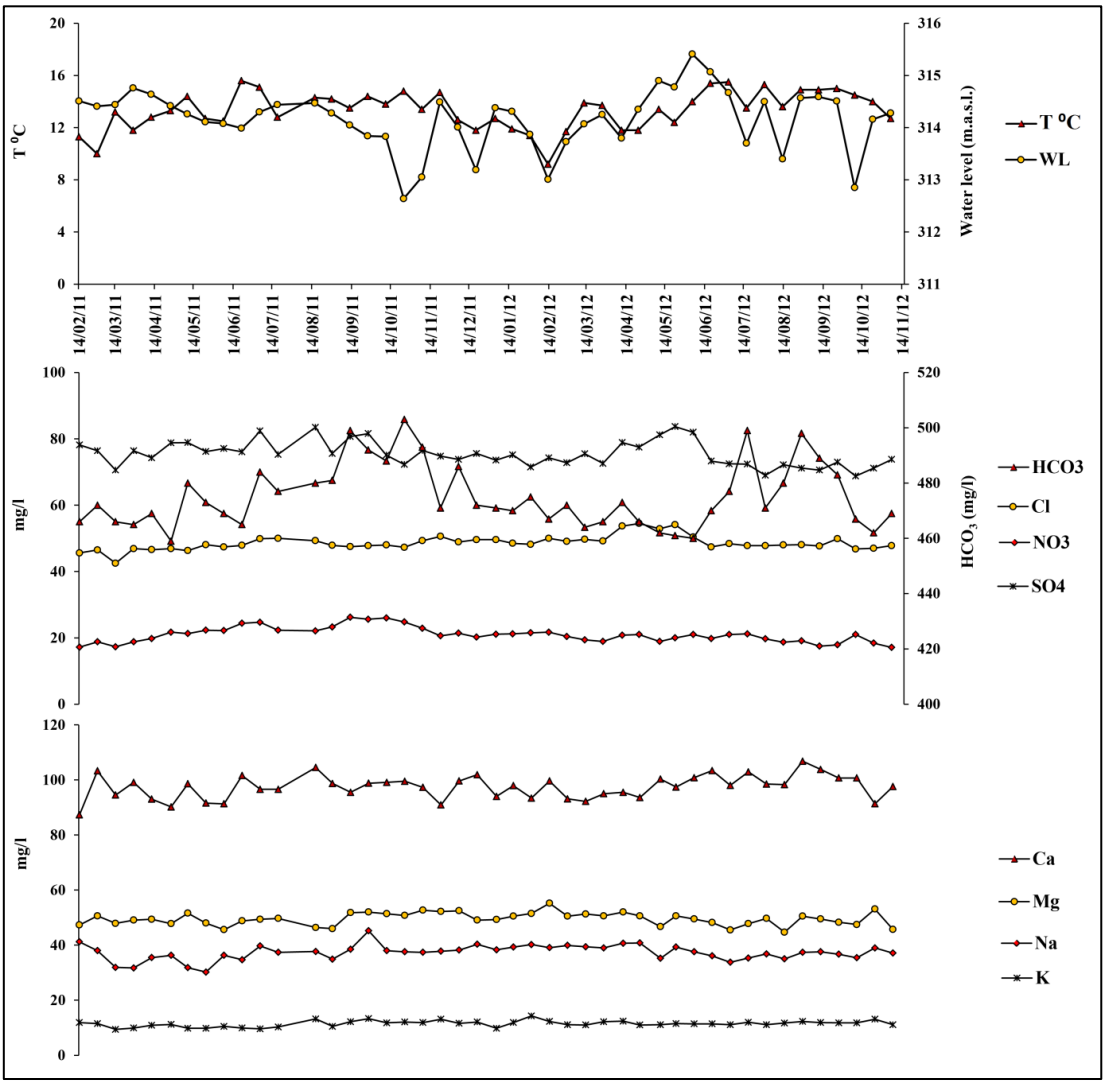

Fig.II-34: Time evolution of major ion concentrations, water level and temperature of B10 during the study period

Borehole B39 is different than other boreholes. This borehole is the only one which is not pumped, in the study zone, due to the high content of manganese ion, above drinking water level. B39 is situated close to the Allier River and is characterized by a low EC value (average value of 209 µS/cm). Fig.II-35 displays the time evolution of major ions, temperature and water level measured during the study period. The results show significant temporal variations in water mineralization. The higher ionic contents are noticed during summer campaigns and the lower ones appear during winter and spring. This temporal variation corresponds to the ones of the Allier River, indicating the strong connection

between B39 and surface water. Water level of B39 is fluctuating in accordance with the Allier River flow rate; the highest water levels are measured in the 7th of November 2011 and the 4th of June 2012, during flood periods of the Allier River. Nitrate is the only ion that displays no temporal variations and remains at very low concentration (average value of 0.66 mg/l) during the study period. Denitrification could be the main cause of nitrate depletion in this borehole.

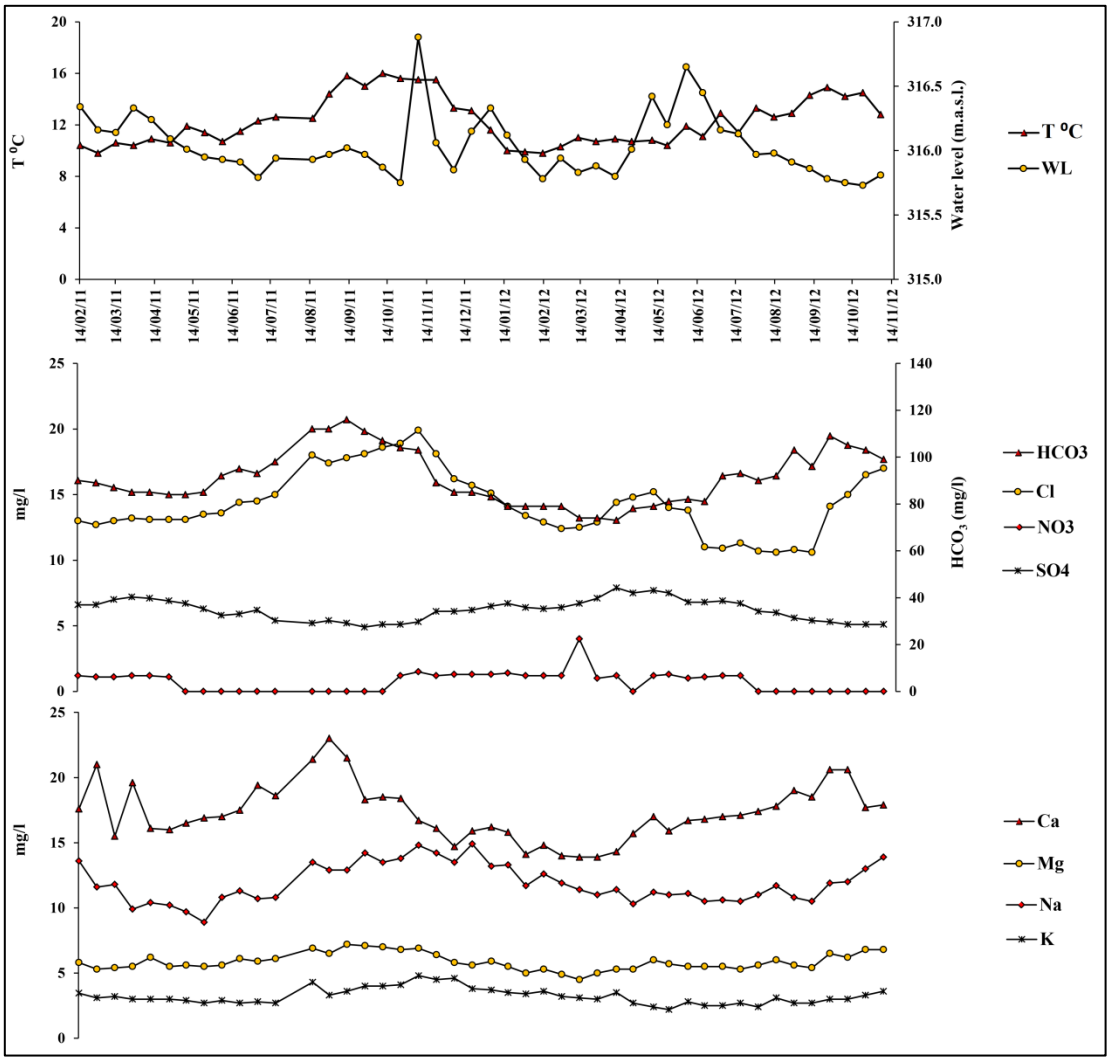

Fig.II-35: Time evolution of major ion concentrations, water level and temperature of B39 during the study period

Borehole B65 is located near the sealed banks of the Allier River, in the southern part of the study zone. It is characterized by high EC compare to the Allier River's one (average value of 434 µS/cm). It behaves unlike the rest of boreholes. Water temperature in this borehole shows weak seasonal variations [range between 10.4 (13/02/2012) and 14.6°C (30/07//2012)] compare to the boreholes close to the Allier River, such as B33 (range between 6.2–19.6°C) and B39 (9.8–16.0°C), indicating an additional source of water. Some major ions display temporal variations while some others remain constant (Fig.II-36). These variations are negatively correlated to the water level fluctuations. A high water level (7/11/2011 for example) is followed by a decrease of the concentrations of the majority of ions, referring to that B65 is, to some extent, influenced by the Allier River, particularly during flood periods. Nitrate levels in this borehole are very low (average value of 1.5 mg/l) but display slight temporal variations and reach a peak of 10.1 mg/l during the high flow record on the 07th of November 2011. Very weak temporal variations can be quoted for magnesium, sodium and potassium, indicating that these ions are not affected by any physical (water level) or chemical changes. Therefore, B65 presents an unique behavior and differs from the other boreholes.

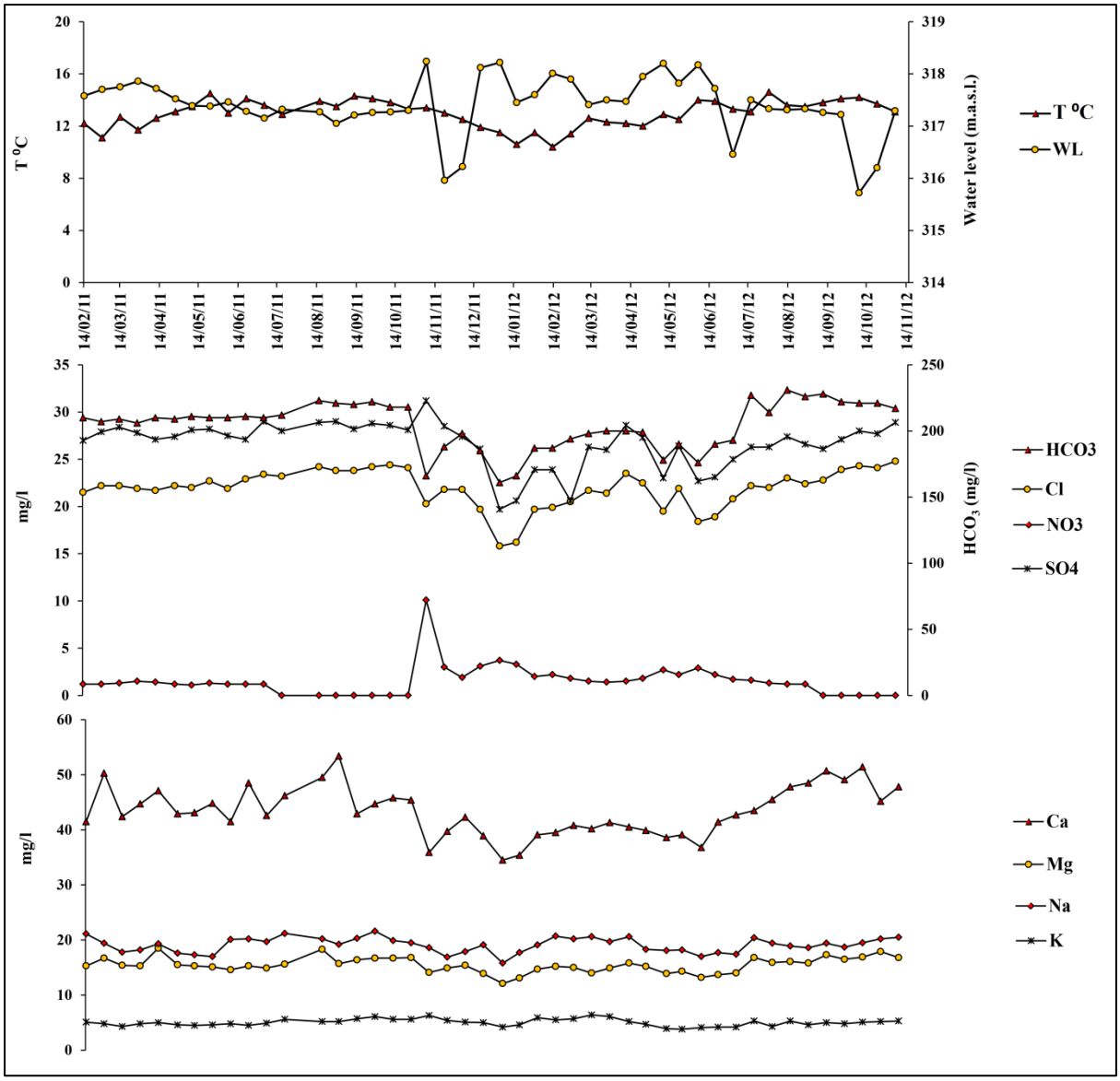

Fig.II-36: Time evolution of major ion concentrations, water level and temperature of B65 during the study period

2.2.2.3. Water-rock interactions

The plot of Na/Ca vs HCO_3^- for the 15 selected boreholes reflects the geology of the water basin (Fig.II-37a). The Allier River that totalises the influences of the whole watershed clearly presents enrichment in Na^+ in relation with the crystalline nature of the basement. Boreholes samples present a progressive enrichment in Ca^{2+} and HCO_3^- between Allier River end-member and a pole represented by Cognet spring/P13. This evolution is confirmed by Fig.II-37b plotting Ca+Mg vs HCO_3^-. A progressive enrichment in Ca^{2+}, Mg^{2+} and HCO_3^- is registered from the Allier River to the hills/southern aquifer that suggests an increase in the residence time within the aquifer and might reflect carbonate dissolution as the presence of

significant proportion of carbonates in the basin has already been reported (Négrel et al., 2004). A mixing with water that circulates in carbonates is also possible as the abundance of Ca^{2+}, Mg^{2+} and Na^{+} ions can be associated with minerals available in the alluvial terraces in the study area such as augite, green and brown hornblende, olivine, mica and opaque (Pelletier, 1971; Pastre, 1986; Tourenq, 1986). The presence of H_4SiO_4 in Cognet spring, boreholes, P13 and surface water suggests that crystalline rock fragments form a major component of aquifer matrix. H_4SiO_4 is present in all water samples at high concentrations but Cognet spring has the maximum concentration with a mean value of 38.8 mg/l, higher than the mean value of 17.7 mg/l recorded in boreholes.

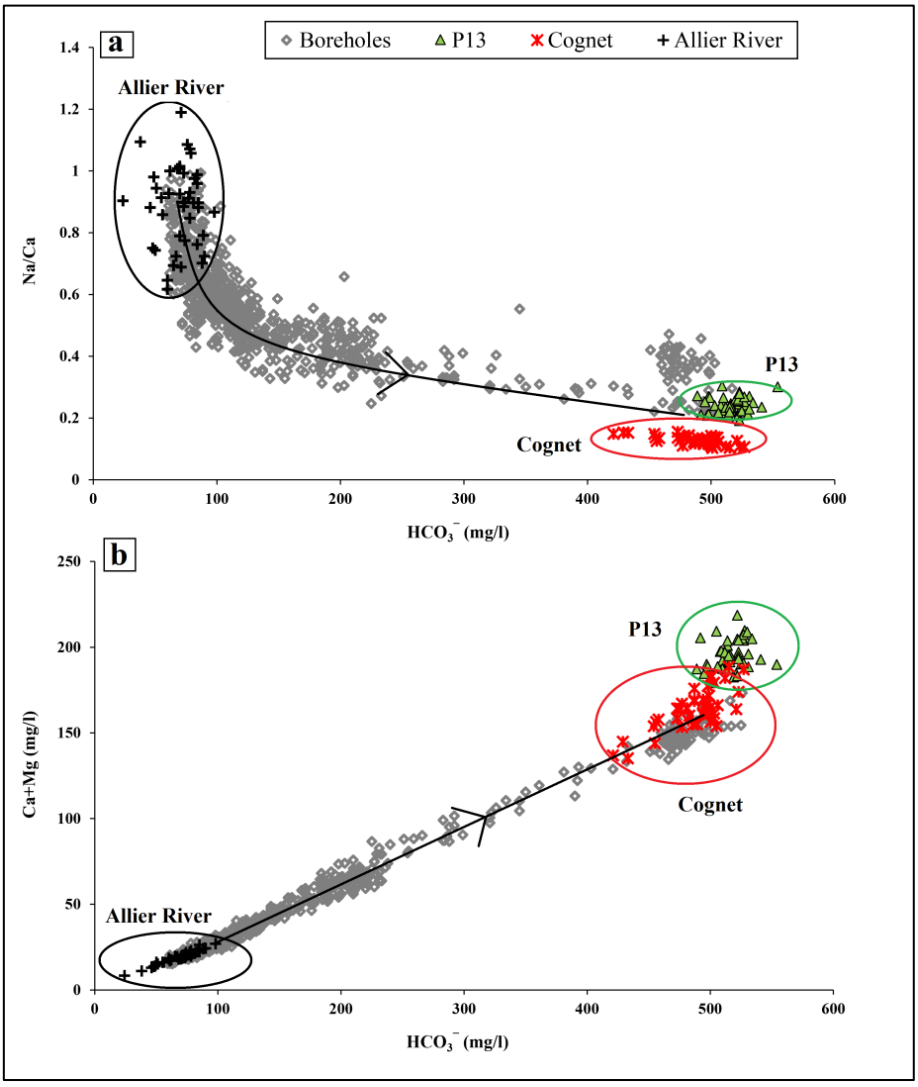

Fig.II-37: (a) Na^{+}/Ca^{2+} vs HCO_3^{-} and (b) $Ca^{2+}+Mg^{2+}$ vs HCO_3^{-} plot.

Thus, weathering and erosion of rocks or soil, and chemical reactions beneath the land surface control the natural composition of groundwater (Bullen et al., 1996; Kim, 2002). Saturation indices (SI) of carbonate minerals (calcite and dolomite), and siliceous minerals (quartz and chalcedony) are calculated by using PHREEQC program (Parkhurst and Appelo, 2003). The summary statistics of saturation indices of some common mineral phases is presented in Table II-5 and Fig.II-38. All the samples are saturated with respect to quartz and/or chalcedony confirming the crystalline nature of the basin basement. Boreholes close to the Allier River (e.g. B33) are undersaturated with respect to carbonate minerals indicating either that the groundwater originates from an environment where carbonate minerals are poorly available or/and due possibly to the short residence time of groundwater within this borehole, so that there is inadequate time for mineral phases to react to reach equilibrium. While, water samples from Cognet spring, P13 as well as both boreholes B23 and B29 are shown oversaturated with respect to carbonate and siliceous minerals, suggesting that waters involved in their chemical composition have possibly longer residence time and consequently have dissolved more minerals.

Table II-5: The average values with standard deviation of saturation indexes (SI) for carbonate and siliceous minerals.

Sample ID	SI Calcite	SI Dolomite	SI Chalcedony	SI Quartz
Allier	-0.9 ±0.3	-1.9 ±0.6	-0.2 ±0.1	0.3 ±0.1
Cognet	0.5 ±0.1	0.9 ±0.3	0.4 ±0.1	0.8 ±0.1
Jallat	0.3 ±0.1	0.4 ±0.2	0.4 ±0.0	0.9 ±0.0
P13	0.4 ±0.1	0.6 ±0.3	0.3 ±0.1	0.7 ±0.1
B10	-0.7 ±0.2	-1.4 ±0.3	0.1 ±0.1	0.5 ±0.1
B11	-1.2 ±0.2	-2.6 ±0.3	-0.1 ±0.1	0.4 ±0.1
B18	-1.0 ±0.1	-2.1 ±0.2	0.0 ±0.1	0.4 ±0.1
B20	-1.1 ±0.1	-2.4 ±0.2	-0.0 ±0.1	0.4 ±0.1
B23	0.3 ±0.2	0.6 ±0.3	0.1 ±0.1	0.5 ±0.1
B26	-0.9 ±0.2	-2.1 ±0.3	-0.1 ±0.1	0.3 ±0.1
B27	-0.4 ±0.2	-0.8 ±0.4	0.3 ±0.1	0.5 ±0.1
B29	0.4 ±0.1	0.8 ±0.2	0.2 ±0.1	0.6 ±0.1
B33	-1.3 ±0.1	-2.6 ±0.3	-0.1 ±0.1	0.4 ±0.1
B39	-0.9 ±0.2	-1.9 ±0.4	0.0 ±0.1	0.4 ±0.1
B50	-0.6 ±0.4	-1.3 ±0.7	-0.0 ±0.1	0.4 ±0.1
B56	-0.7 ±0.2	-1.6 ±0.5	0.0 ±0.1	0.5 ±0.1
B65	-0.4 ±0.1	-0.9 ±0.2	0.1 ±0.1	0.5 ±0.1
B66	-0.7 ±0.2	-1.5 ±0.3	-0.0 ±0.1	0.4 ±0.1
B71	-0.6 ±0.1	-1.4 ±0.3	0.1 ±0.1	0.5 ±0.1

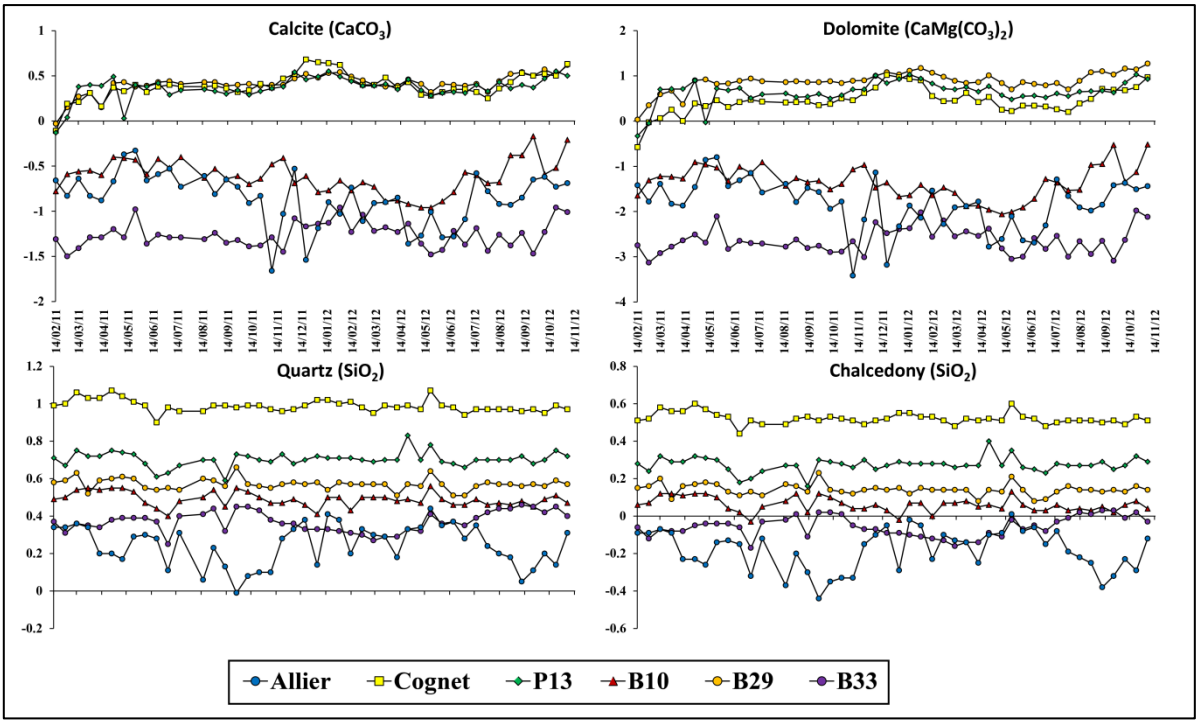

Fig.II-38: Plot of saturation indexes (SI) for Allier River, Cognet spring, P13, B33, B10 and B29

The results show a progressive increase in the SI with respect to chalcedony and quartz from the Allier River to Cognet (B33-B10-B29) in relation with the dissolution of alluviums of crystalline origin (siliceous pebbles, sands, silts) and the volcano-sedimentary nature of the hills. This could suggest that the increase in the residence time is a major process in the chemical composition of waters. Regarding the evolution of SI with respect to dolomite and calcite, B33 and B10 are clearly undersaturated and show the same variations compared to the Allier River indicating to rapid recharge by water from Allier River, since these points located very close to the Allier River. Whereas, B29 and P13 are oversaturated with carbonate minerals and present a trend similar to Cognet spring demonstrating that these points are recharged partly or mostly by water from hills rather than Allier. This implies a mixing of the alluvial groundwater with groundwater coming from the hills or from the southern part of the alluvial aquifer.

2.2.3. Isotopical characteristics of groundwater ($\delta^{18}O$ and $\delta^{2}H$)

Stable oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$) isotopes are regarded as conservative tracers since they are part of the water molecule and are therefore unaffected by chemical reactions. Once water has been recharged into an aquifer, there are only two means by which its $\delta^{18}O$ or $\delta^{2}H$

content can be altered. Evaporation from the water table is the first way that the isotopic content of water may be altered as lighter isotopes are driven off and the water shifts toward a heavier isotopic composition. Mixing of two waters with different isotopic signatures is another means by which the $\delta^{18}O$ or $\delta^{2}H$ value of water can be altered after recharge into an aquifer (Clark and Fritz, 1997).

In order to confirm these first hypotheses on the sources of recharge, stable isotopes of the water molecule have been used (Fontes, 1980; Gonfiantini, 1986; Nativ and Riggio, 1989; Wood and Sanford, 1995; Clark and Fritz, 1997). The relationships between $\delta^{2}H$ (‰VSMOW) and $\delta^{18}O$ (‰VSMOW) are shown in Fig.II-39 for water collected from the 19 sampling points. The analytical results are presented in Appendix B.

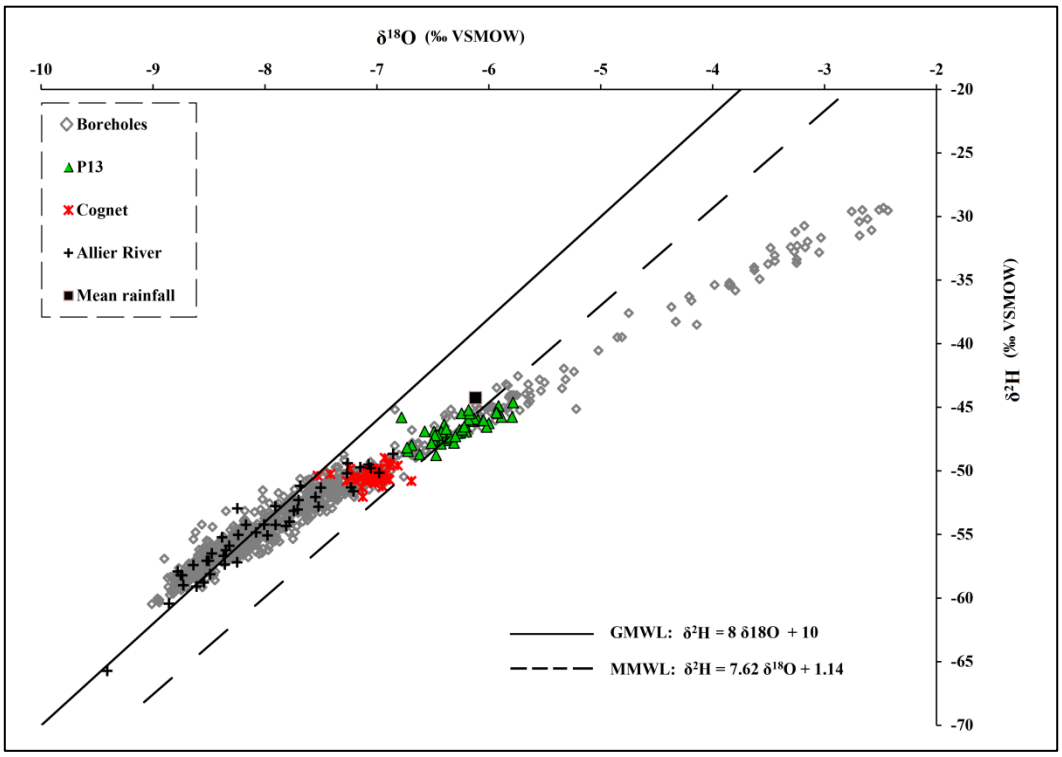

Fig.II-39: $\delta^{18}O$ versus $\delta^{2}H$ (‰ SMOW) of all boreholes and end members for spatial and temporal followings

In the 15 selected boreholes, $\delta^{18}O$ varies from -9.0‰ to -2.4‰ with an average value of -7.5‰ (*n*=680); $\delta^{2}H$ varies between -60.5‰ and -29.3‰ with an average value of -52.4‰. The mean isotopic content of the Allier River (-8.1 $\delta^{18}O$‰ and -55.5 $\delta^{2}H$‰) which represents the input signal of the whole upstream watershed (altitude from 305 to 1423 m.a.s.l.), falls on the GMWL, in agreement with Négrel et al. (2003). P13 and Cognet spring present values close to the MMWL (Mezel Meteoric Water Line), testifying of a recharge by local

precipitation. The isotopic signatures of most of the boreholes fall on, or close to the GMWL and behave similarly to the Allier River, demonstrating a strong interaction with the Allier River. Few boreholes (B23, B27, and B29) present more enriched values, close to the values of Cognet and P13 and drop into MMWL, indicating that these points could partly or highly be recharged by other sources than the Allier River. Likewise, waters from boreholes are distributed along a line with a smaller slope than the MMWL that may indicate either evaporation or mixing trend between the two poles defined by Allier River and local recharge. This last hypothesis is consistent with the fact that the isotopic content of groundwater varies along with the distance from the two end-members. In contrast to this general trend, borehole B65, harbouring the most enriched $\delta^{18}O$ and $\delta^{2}H$, (ranging from -5.9‰ to -2.4‰ and from -44.1‰ to -29.3‰, respectively), shows evidence of some additional isotopic enrichment by either stronger evaporative process or mixing with geothermal water. Indeed, the Allier basin is characterized by the availability of localized geothermal springs (Rihs et al., 2000; Bertrand et al., 2013). Measurements in carbon-13 of total dissolved inorganic carbon show that this geothermal effect cannot be implied as the values of B65 are comprised between -16.3 $\delta^{13}C$‰ and -8.3 $\delta^{13}C$‰ PDB far from the local signature of mantellic CO_2 degassed in the Chaîne des Puys (-6.6±0.8 $\delta^{13}C$‰) determined by Batard et al. (1982).

From the temporal monitoring of selected points in the plain, a clear simultaneous seasonal evolution of $\delta^{18}O$ can be quoted for Allier River and B33 with a little delay in B33 peaks, highlighting this borehole is mainly supplied by the Allier River (Fig.II-40). B29, Cognet spring and P13 present enriched and more stable values, demonstrating the absence of a rapid supply to the system for these points. The particular borehole B65 seems to be disconnected from the variations of rainfall height, but is however related to the fluctuations of the Allier River flow rate. Recorded isotopic values of B65 decrease during high flow periods and increase during low flow; this could imply a sealing of a part of the banks of the river near B65. The water infiltrated from the Allier River or coming from the southern part of the aquifer evaporates during the low flow periods and is mixed with new water coming from a reconnection of the Allier River during the high flow periods.

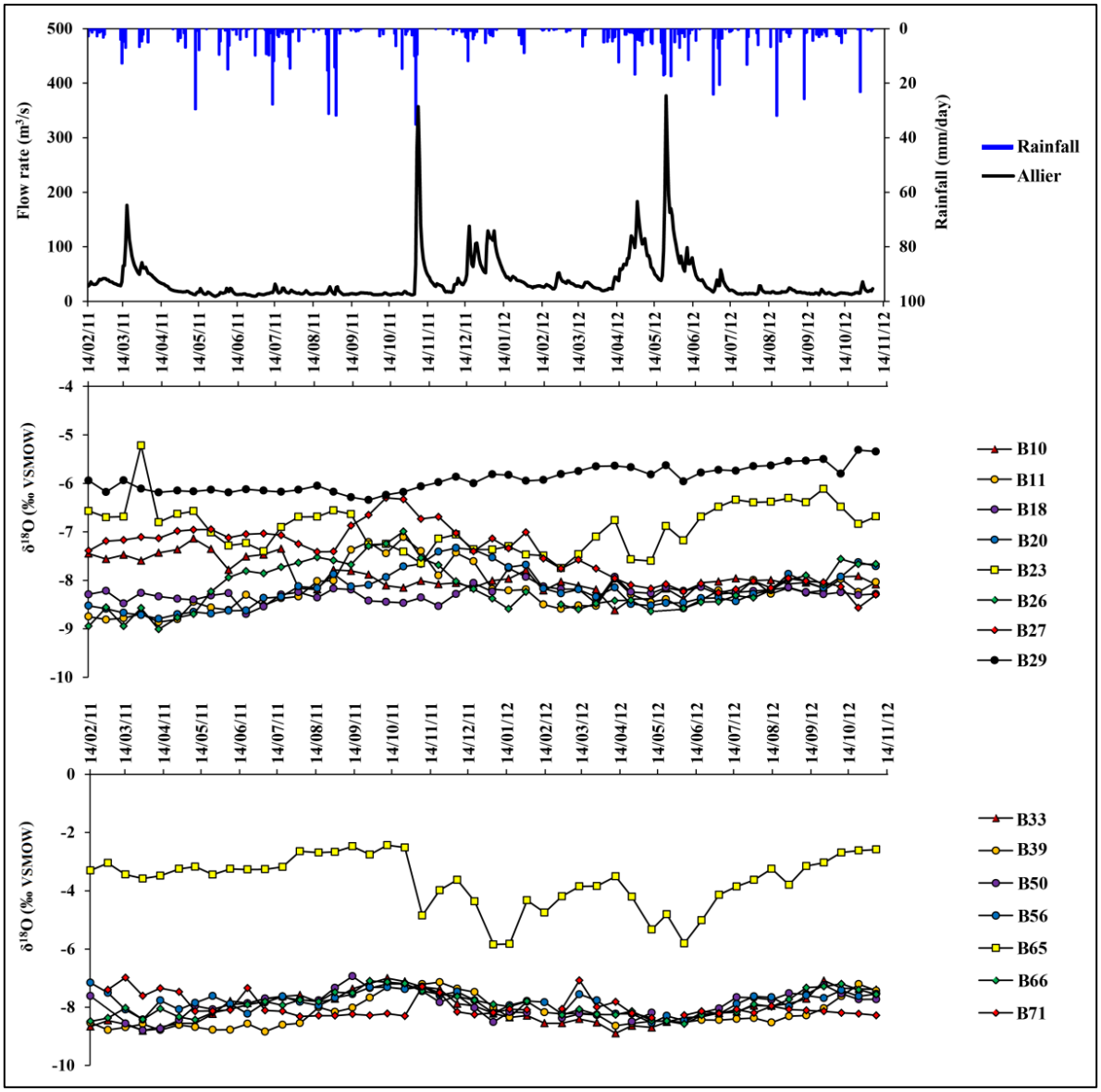

Fig.II-40: Time evolution of rainfall amount, Allier River flow rate, and oxygen-18 ($\delta^{18}O$) of sampling points during the study period.

The spatial distribution of stable isotope of $\delta^{18}O$ of the 75 sampling points during the two campaigns is shown in the Fig.II-41.

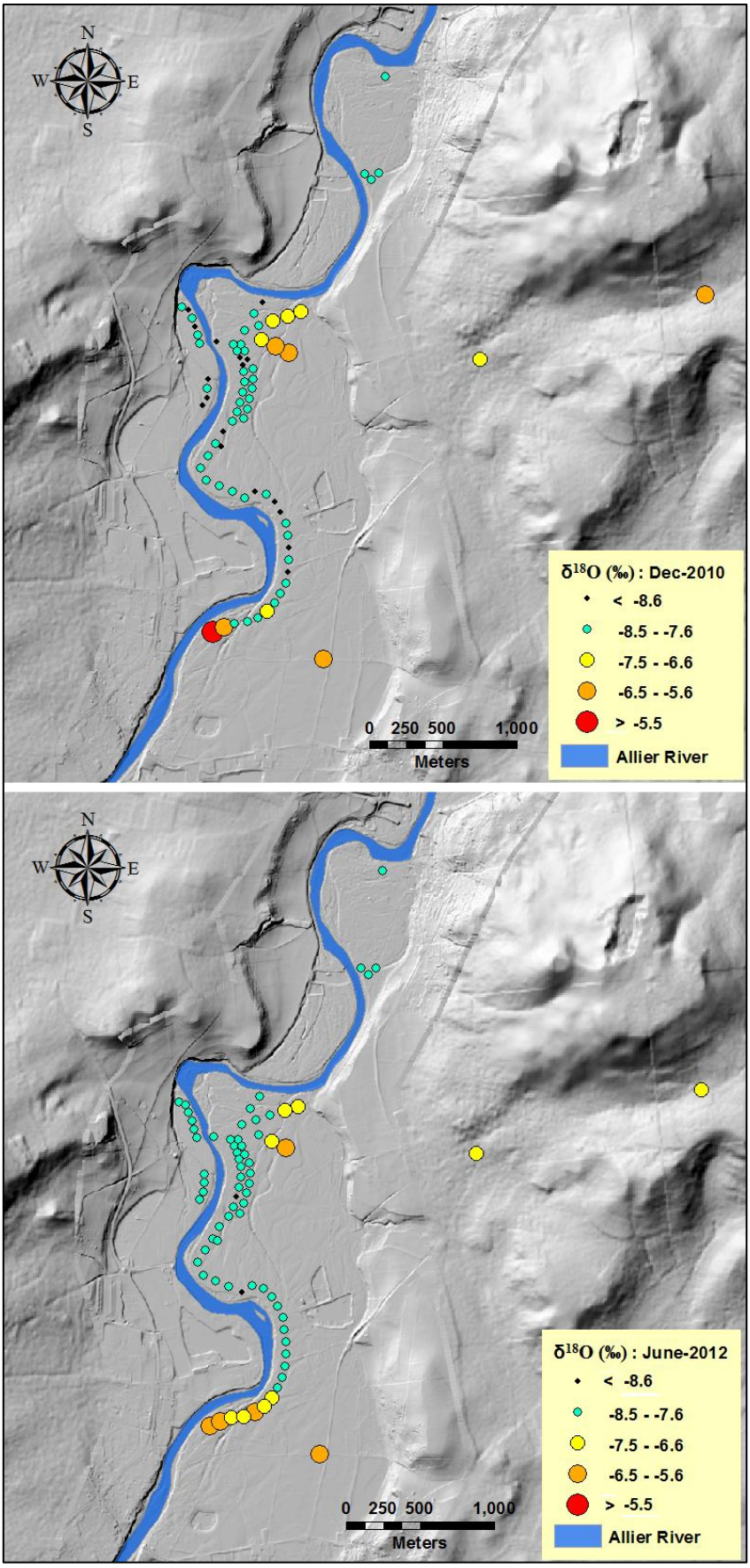

Fig.II-41: Spatial distribution of oxygen-18 during two field campaigns of low flow (Dec-2010) and high flow (June-2012) stage of Allier River

The results based on isotopic analysis confirm the hypothesis formulated thanks to physico-chemical parameters, with an implication either of a possible increase of the residence time within the shallow alluvial aquifer that leads to evaporation (Mook, 2000) or the mixing with a secondary supply isotopically enriched.

3. Mixing between different sources of recharge

Chloride, nitrate and sulphate ions cannot be related to the dissolution of minerals from the bedrock. Moreover, for these 3 elements, the calculated groundwater concentrations due to rainfall (Cl^- = 4.8 mg/l, NO_3^- = 3.5 mg/l, SO_4^{-2}=1.1 mg/l) are largely lower than the measured concentrations. These 3 elements could then be attributed to an anthropogenic origin: fertilizers can be implied for Cl^-, NO_3^- and SO_4^{-2} in association with K^+ (Widory et al., 2005), waste waters for NO_3^- and de-icing salt for Cl^- (Meybeck, 1983; Négrel, 1999). According to the boreholes' concentrations in Cl^-, SO_4^{2-} and K^+ falling into the range of the ones of the determined end-members and to the independence of these parameters from the lithology, Cl^-, SO_4^{2-} and K^+ can be used to estimate the participation rate of each end-member to the chemistry of boreholes within the alluvial system (Fig.II-42).

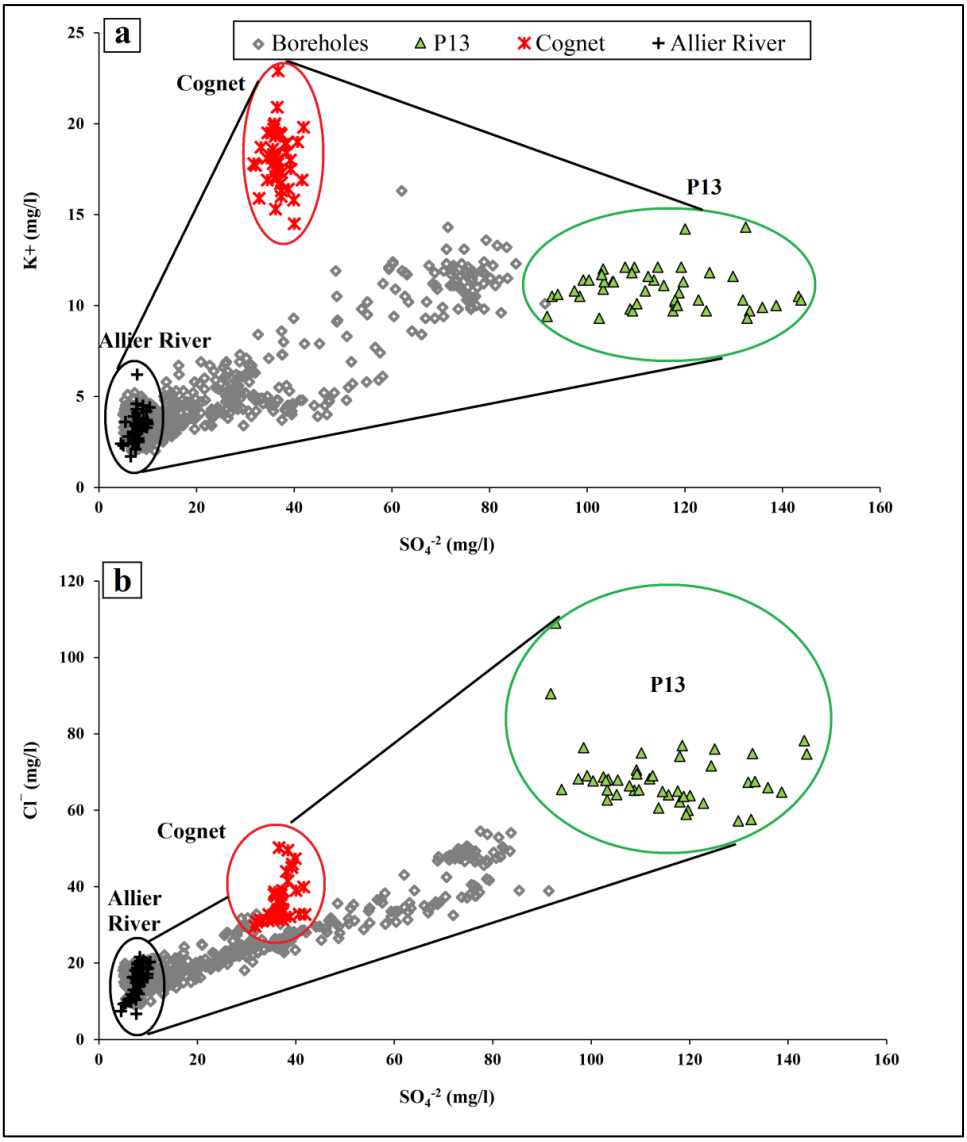

Fig.II-42: (a) SO_4^{2-} vs K^+ and (b) SO_4^{2-} vs Cl^- plot.

The mathematical resolution of the 3 equations system with 3 unknown values (Jeuken, 2004) leads to the mean participation percentages of each end-member to the chemical composition of the boreholes selected for the following time investigation (Table II-6). The used mathematical equations can be written as:

$$X_B = F_aX_a + F_hX_h + F_{sa}X_{sa}$$

$$Y_B = F_aY_a + F_hY_h + F_{sa}Y_{sa}$$

$$Z_B = F_a Z_a + F_h Z_h + F_{sa}Z_{sa}$$

where X, Y, and Z are the concentrations of Cl^-, SO_4^{2-} and K^+, respectively for each borehole (B) and end-member: Allier River (a), hills' aquifer (h) and southern aquifer (sa); F is the function of each end-member in borehole.

Table II-6: Contributions percentage of the 3 end-members

Borehole ID	Recharge % by Allier River			Recharge % by Hills (Cognet)			Recharge % by South alluvial aquifer (P13)		
	K^+/SO_4^{2-}	K^+/Cl^-	mean	K^+/SO_4^{2-}	K^+/Cl^-	mean	K^+/SO_4^{2-}	K^+/Cl^-	mean
B10	87	82	84	0	0	0	13	18	16
B11	100	95	97	0	0	0	0	5	3
B18	100	95	97	0	0	0	0	5	3
B20	100	94	97	0	0	0	0	6	3
B23	33	41	37	23	32	27	44	27	36
B26	100	95	97	0	0	0	0	5	3
B27	79	76	77	0	0	0	21	24	23
B29	17	18	17	27	27	27	56	55	56
B33	100	94	96	0	0	1	0	6	3
B39	100	94	96	0	0	1	0	6	3
B56	90	85	87	2	0	1	8	15	12
B65	81	78	79	3	0	2	16	22	19
B66	98	91	94	0	0	0	2	9	6
B71	98	91	94	0	0	0	2	9	6

Based on our dataset that includes only the hills' aquifer and the southern aquifer in the right bank of the Allier River, the contribution of end-members has not been calculated for B50. The results of recharge calculations show that eight boreholes are only recharged by the Allier River (Fig.II-43). In parallel, B27, B56 and B65 are mainly supplied by the Allier River, but present a secondary supply from the southern part of the alluvial aquifer. This latter varies from 11% for B56 to 22% for B27 and is consistent with the location of the boreholes; the lower percentage corresponds to B56 closer to the Allier River than B27. High contribution of southern aquifer for B65 (19%) may be due to the sealing of the river banks during low flow period; the contribution of the Allier River to B56 suggests that the bank is not sealed in this part of the river. Concerning B23 and B29, results of calculations involve the participation of the three possible origins. As these two boreholes are in the same distance from the hills, the participation of the volcano-sedimentary aquifer seems to be the same and is evaluated to 27%. The participation of the southern part of aquifer versus Allier River evolved with the increasing distance from the river. Thus B29 presents a higher contribution of the southern part of the alluvial system (56%) whereas B23 displays higher income from the Allier River (37%)

Overall, the contribution of Allier River recharge is significant in the majority of groundwater samples within the alluvial aquifer, contributing up to 100% in boreholes adjacent to it. As expected, the effect of Allier River recharge declines with distance from the river and thus the points far from the river are influenced by either incoming waters from the hills or from the southern part of the alluvial aquifer that modify both their chemical and isotopic signatures.

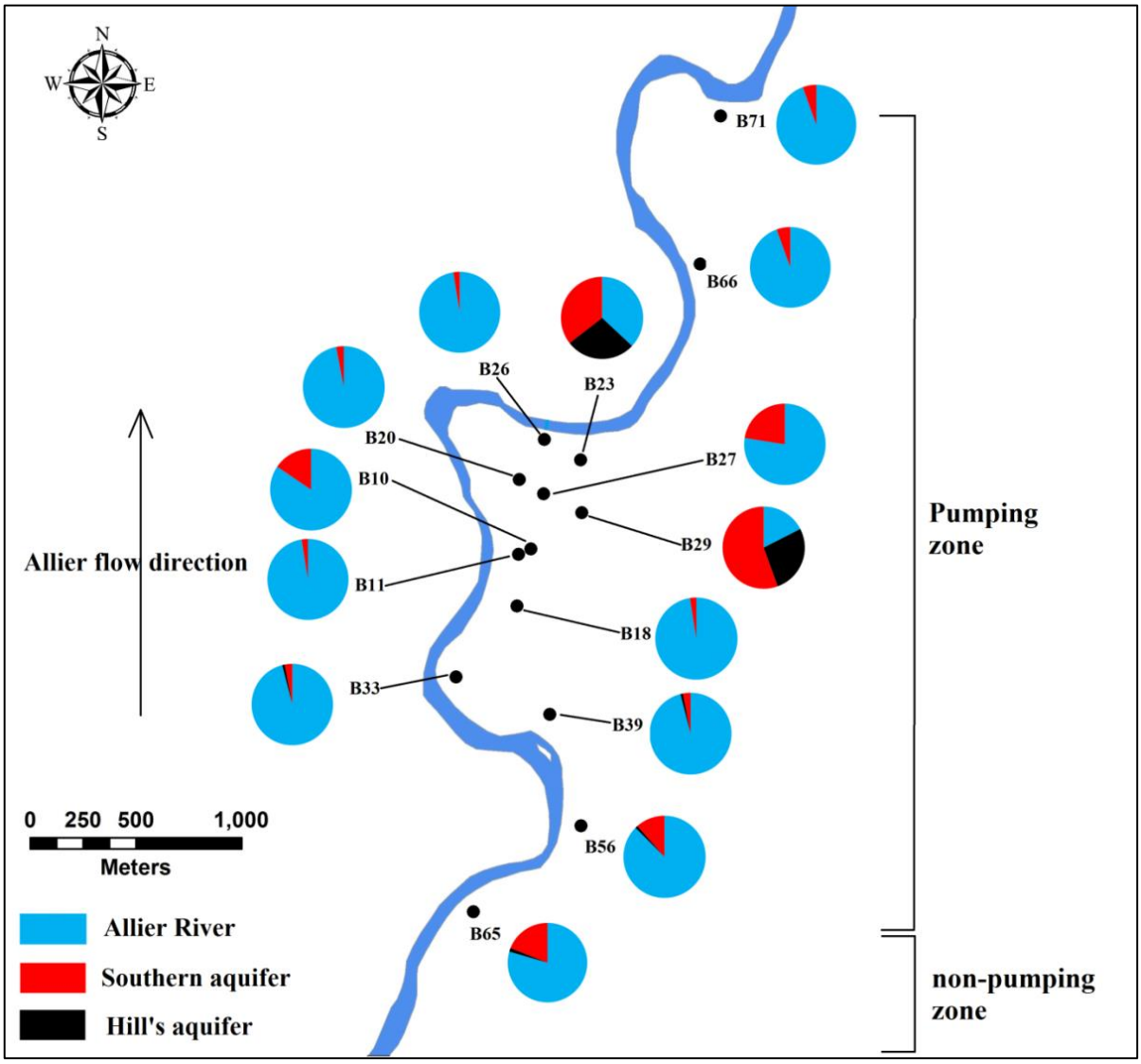

Fig.II-43: Calculated contribution percentage of end-members to groundwater samples

4. Summary

Groundwater circulates generally from south to north, with a natural alimentation from the hills in the non-pumped part of the alluvial aquifer. Four end-members have been determined for the recharge of the alluvial groundwater: rainfall, Allier River, surrounding hills' aquifer and the southern part of the alluvial system. Isotopes of the water molecule show that water of the Allier Basin is recharged by rainwater with an evolution from a pole defined by the GMWL and the Allier River, which integrates the influence of the whole watershed to a more local pole defined by the MMWL (δ^2H= (7.6±0.2) $\delta^{18}O$ + (1.14±1.1)). However, autochthonous recharge by rainfall seems contributing a few to the geochemistry of the alluvial aquifer feeding as only 38% of the total precipitation infiltrate and that effective precipitation harbours major ion concentrations largely below the groundwater contents. Then the chemical content of the investigated boreholes of the alluvial system depends mainly on the contribution of the 3 other end-members. The main recharge is assumed by the Allier River, and then thanks to the water movement generated by the pumping, the water move towards east where the chemistry of boreholes is affected by water/rock interactions and evaporation. On the eastern and southern alluvial aquifer borders, a mixing with waters coming from the hills' aquifer or the southern non-pumped part of the system is shown, notably by the anthropogenic elements such as nitrates, sulphates (associated with potassium) and chloride. The contribution of the 3 end-members to the boreholes' chemistry has been calculated and shows that Allier River could participate up to 100% in boreholes adjacent to it; this recharge declines with distance from the river. Boreholes located on the eastern and southern borders are then affected by either incoming waters from the hills or from the southern part of the alluvial aquifer that modify their chemical and isotopic signatures. Locally a probable sealing of the river banks has been highlighted for B65.

CHAPTER III

EMERGING POLLUTANTS

Introduction

When contaminants spread in the environment, the measure of the potential impacts requires considering at the same time the concerned zone and the evolution of compounds in the environment. The notions of behaviour, physico-chemical characteristics and potential toxicity are parameters to be taken into account to plan the vulnerable zones with determined pollutions. Groundwater pollutions can be diffuse (fertilizers, pesticides,…), punctual (e.g. industrial) or linear (along a river, a road,…). They can have a permanent or accidental character. We distinguish furthermore contamination of a natural origin, connected to the circulation within the soil or the aquifer or the substratum and pollutions of an anthropological origin. Independently of the mechanisms involved in the transfers, it is essential to determine the spatial origin of the pollution to know if it can contaminate the groundwater and in which ways. In a general way, the distribution of a pollutant depends on the nature of the pollutant, on physical properties of the environment, on possible interactions between the pollutant and the solid environment (adsorption, dilution) or other present components in the water, degradation by microbiology and mixtures of waters of different origins (dilution).

Over the past century, a large number of anthropogenic substances have been widely dispersed into the environment (Selborne, 2012) from carbon dioxide, radioactivity and oil pollution to arsenic and polychlorinated biphenyls (PCBs) and now occupy a central place in social, economic and politic debates and developments worldwide. Concerns about chemical in the environment date back to the 1920s, but really increase since the 1960s with the consideration of the damage caused to the environment by pesticides (Plant et al., 2012). However many other environmental chemical contaminants are now on concerns beside pesticides and include a vast range of synthetic and natural substances: heavy metals (from industrial products, fertilisers, …), organic substances (phytosanitaries, …), inorganic substances (fertilisers), pathogenic microbiology, etc. The potentially additive or synergistic effects of such chemicals, as mixtures, or chemical combinations are now of a major concern, as are the chronic effects of exposure, even at low or very low levels.

Moreover, some substances are highly persistent and remained in the environment long time after the restrictions on their use. This has led to the development of studies in ecotoxicology and environmental chemistry that considerably improve the knowledge of the sources, behaviour, fate and health effects of the pollutants in the environment (Plant et al., 2012) and that are accompanied by great improvements in analytical methods. The quality of fresh water is affected by many factors (Ohandja et al., 2012) including run-off from mining, agriculture, sediments and landfill, influx from sewage and treated wastewater, and atmospheric depositions (Chon-Ohandja et al., 2009). This contamination is peculiarly important in surface water.

This chapter gives an overview of several groups of substances that may affect the quality of the alluvial aquifer of the Allier River: toxic tracers, synthetic organic agricultural chemicals and pharmaceuticals. This problem is of major concerns as alluvial aquifers can be extremely important source of water supplies nevertheless their shallow nature could generally be susceptible to contamination by various pollutants. Intrinsic factors such as high rainfall, shallow water table, and sandy soils with organic matter content may contribute to the high potential concentrations of different contaminants such as toxic metallic elements, pharmaceuticals, and pesticides (Novak et al., 1998).

1. Trace elements: occurrences and concentrations

Trace elements are distributed in groundwater and surface water from a variety of natural and anthropogenic sources (Mondal et al., 2010). Various anthropogenic activities (urbanisation, industrial and agriculture) introduced the groundwater system to high concentration of trace elements. Generally, trace elements are characterized by concentrations lower than 1 mg/l in natural waters, due to their low mobility at the earth's surface. Knowledge of the spatial and temporal distribution of trace elements plays an important role in understanding the impact of agriculture and other anthropogenic activities on a certain area (Alpers et al., 2000a; Gaillardet et al., 2003). Two categories of elements can be distinguished on sanitary criteria (OMS, 1996): 1) toxic elements for which there is an important sanitary risk; 2) unwanted elements which may generate complaints on behalf of the consumers.

A set of 28 trace elements comprised of Al, As, B, Ba, Be, Br, Cd, Co, Cr, Cu, F, Fe, Gd, Hg, Li, Mn, Mo, Nd, Ni, Pb, Rb, Sb, Se, Sn, Sr, V, U, Zn have been analysed to investigate the alluvial aquifer of the Allier River; the results of trace elements exhibit significant spatial and temporal variations along the study area and during the study period. The analytical results are presented in Appendix C.

Cumulative frequency curves (Fig.III-1), showing the distribution of concentrations in a log-scale, help to discriminate different populations, more or less affected by anthropogenic contribution. Distribution is also the result of several geochemical reactions including sorption processes, redox reactions and saturation with respect to minerals phases that could limit solubility (Potot et al., 2012). Most of elements present an unimodal distribution with a sharp slope tending to a normal distribution. Cu, F, Mn, Sn, U plots display softened slopes (wide distribution of concentrations) or irregular curves (multimodal distribution), maybe as a consequence of contamination or various reactions.

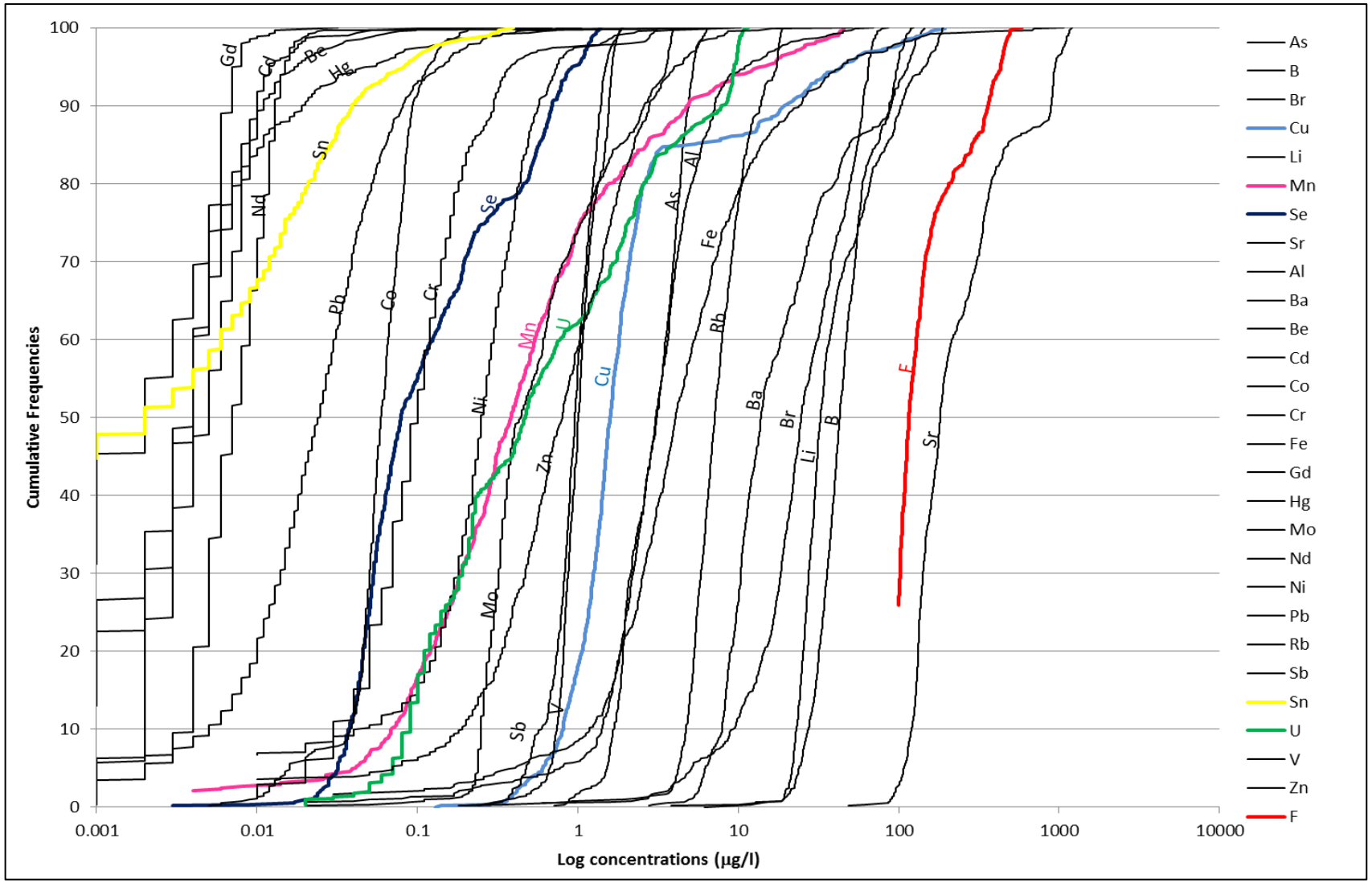

Fig.III-1: Cumulative frequencies for traces

Among the analysed traces, six (As, Mn, Cu, F, Se and Cd) have been selected for they belong to the priority list of unwanted or toxic elements (Directive 98/83/CE) and present an interesting spatial distribution or temporal evolution in boreholes (Table III-1).

Table III-1: Average (AV) and standard deviation (SD) of selected trace elements of sampling points during the study period.

	Sample ID		As (µg/l)	Mn (µg/l)	Cu (µg/l)	F (µg/l)	Se (µg/l)	Cd (µg/l)
1	**B10**	AV	1.82	2.58	30.30	107.9	0.316	0.003
		SD	0.17	3.78	31.87	5.7	0.188	0.002
2	**B11**	AV	2.19	1.20	63.47	108.6	0.058	0.002
		SD	0.56	2.19	46.95	9.5	0.016	0.001
3	**B18**	AV	1.47	7.50	1.22	105	0.042	0.002
		SD	0.35	12.39	0.93	4.6	0.012	0.002
4	**B20**	AV	1.97	0.21	1.75	107.2	0.053	0.003
		SD	0.12	0.16	0.48	5.8	0.013	0.002
5	**B23**	AV	4.98	0.27	1.44	355.7	1.022	0.165
		SD	0.39	0.73	0.37	31.3	0.245	1.050
6	**B26**	AV	4.37	0.55	2.18	112.3	0.050	0.007
		SD	0.41	0.55	0.93	10.5	0.015	0.004
7	**B27**	AV	2.03	0.38	1.36	126.3	0.450	0.005
		SD	0.34	0.39	0.50	15.8	0.260	0.003
8	**B29**	AV	4.22	0.20	1.23	446.7	0.631	0.106
		SD	0.30	0.14	0.36	43.9	0.100	0.657
9	**B33**	AV	3.14	1.50	1.69	111.4	0.049	0.003
		SD	0.49	1.26	0.42	9.6	0.011	0.002
10	**B39**	AV	13.65	725.01	0.52	117.1	0.027	0.005
		SD	10.01	643.44	0.33	11.7	0.010	0.007
11	**B50**	AV	3.51	0.60	1.54	124.4	0.174	0.013
		SD	0.87	1.30	0.49	16.7	0.094	0.042
12	**B56**	AV	3.06	0.80	2.07	162.4	0.166	0.008
		SD	0.68	0.99	0.55	23.1	0.138	0.005
13	**B65**	AV	3.85	0.16	0.62	239.8	0.125	0.004
		SD	0.62	0.15	0.28	39.4	0.037	0.003
14	**B66**	AV	5.08	17.32	2.10	133.4	0.056	0.010
		SD	0.87	14.95	0.54	14.4	0.025	0.007
15	**B71**	AV	2.80	2.33	1.33	125.5	0.091	0.004
		SD	0.57	3.36	0.60	18.5	0.069	0.003
16	**Allier**	AV	3.91	6.75	2.20	114.9	0.062	0.010
		SD	1.29	2.82	1.13	11.9	0.014	0.008
17	**Cognet**	AV	33.93	0.09	2.04	406.9	0.990	0.004
		SD	2.08	0.12	0.90	20.4	0.137	0.004
18	**Jallat**	AV	94.79	0.14	0.64	613.6	1.051	0.004
		SD	4.73	0.11	0.27	46.6	0.192	0.005
19	**P13**	AV	5.01	4.24	1.30	535.7	1.356	0.007
		SD	0.98	4.39	1.32	55.9	0.330	0.004

1.1 Arsenic, Manganese and Iron : detected concentrations above the guidelines values (98/83/CE)

Arsenic occurs naturally in rocks and soils and is especially concentrated in certain types of mineral deposits. It can be released into the environment both naturally and through human activities. The dominant Arsenic species in water depends on pH and redox potential. Arsenate (As^{5+}) is predominant under oxidizing conditions and is less toxic than arsenite (As^{3+}). The relatively small amount of As released into stream waters during weathering is mobile only if pH and Eh (Plant et al., 2012) are sufficiently low to favor its persistence in its trivalent form (As^{3+}). Then surface waters indicate generally low As concentrations that rarely exceed a few μg/l (1 to 2 μg/l; WHO, 2011) except in acid and anoxic conditions. Various mechanisms responsible for arsenic mobilization in aquifers are reported in the literature (Smedley and Kinniburgh, 2012; Stuyfzand et al., 2006) which can be divided in three main groups (Bonte et al., 2013): oxidation of pyrite, reduction of metallic (hydro)oxydes or desorption from charged surfaces such as Fe, Al and Mn Oxydes. Natural concentrations in rock and soils have been reported in (Plant et al., 2012): 3.4 mg/kg in continental crust, 1.5 mg/kg in granite, 4.3 mg/kg in gneiss, 1.5 mg/kg in basalt (Wedepohl, 1991) and values from 4.4 to 9.3 mg/kg in soil (Kabata-Pendias and Pendias, 1992). Beside this natural origin, Arsenic can be released in the environment notably through pesticides, especially herbicides and insecticides, mining, smelting and fossil-fuel combustion. Arsenic is a toxic element with guideline value of 10 μg/l (98/83/CE). Acute exposure can cause many problems from gastrointestinal effects to death and chronic exposure may generate cancer and neurological problems.

Manganese is one of the most abundant metals in the earth's crust and is ubiquitous in the environment. Abundance varies from the type of rocks: 0.07% in continental crust, 0.0035% in granite, 0.14% in basalt and 0.07% in sedimentary rocks. It is a minor component of most rock types and it is also present in soils from weathering and aerial deposition but may also be generate by underground pollution sources (Homoncik et al., 2010). Manganese is naturally occurring in many surface and groundwater and in soils that may erode into these waters. Anaerobic groundwater often contains elevated levels of dissolved manganese (WHO, 2011). As a nutrient, Mn is essential for human health at low concentrations (Keen and Zidenberg-Cherr, 1994) although chronic exposure to high doses may be harmful (guideline value of 50 μg/l, 98/83/CE). There are substantial data supporting the neurological effects of inhaled

manganese in both humans and animals, however, there are little data for the association between oral exposure to manganese and toxic effects (USEPA, 2004). The World Health Organization (WHO) and Directive 98/3/CE have set guideline values of 0.4 mg /l (WHO, 2008) and 50 µg/l, respectively. Concentrations up to 0.15 mg/l may generate undesirable effects like coloration of the water, metallic taste, neutralization of disinfectants, formation of black deposits and, as a result, the reduction of the diameter of the water pipes. As arsenic and iron, manganese species depend on pH/Eh conditions; mobilization of Mn is favored by low Eh and/or acid pH. Fe^{2+} and Mn^{2+} are stable in anaerobic conditions. Two processes of reduction may be observed: 1) a permanent one connected to the presence of organic matter buried in recent sediments or deposited on the bottom of streams, peculiarly in quiet zones, 2) a seasonal one related to the presence of dissolved organic matter in the water; the mineralization of the organic matter leads to the consumption of dissolved oxygen then nitrates and thus generates a reduction of the redox potential. The mobilization of Mn is favored by an increase of temperature.

High content of manganese has been observed by a lot of authors in alluvial systems comparable to the one of the Allier River (Recoulès, 1984; Verjus, 1984; Haroux, 1986, …). In the study site, high concentrations of manganese have been detected (in B39; stop of pumping in 1990) and are still of great concerns in the study site for Mn generates deposit in the water pipes used for the supply of drinking water and because, sometimes, Mn concentrations are above the guideline values imposed by Directive 98/83/CE (Fig.III-2).

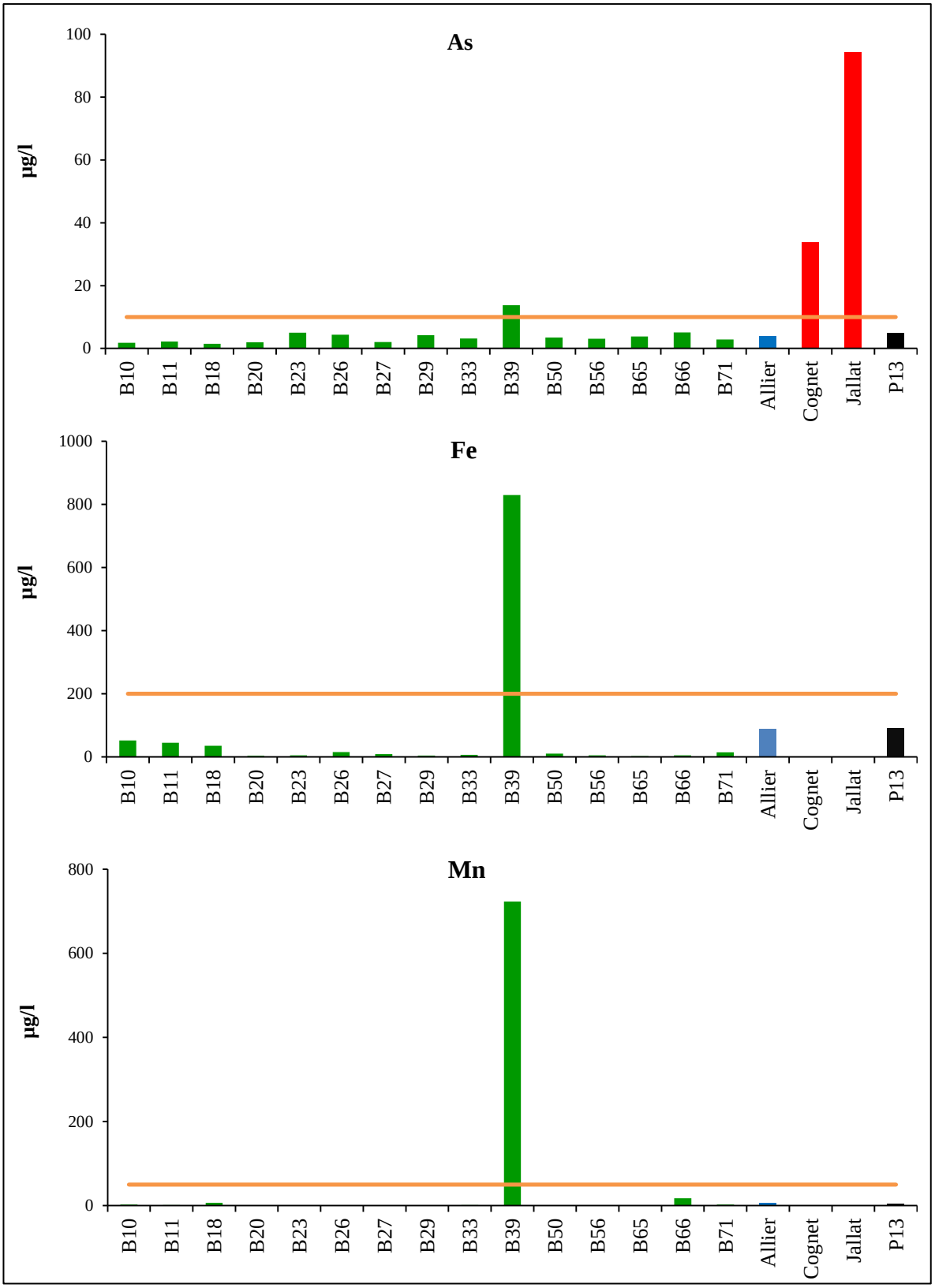

Fig.III-2: Arsenic, Iron and Managanese mean values for each selected borehole and the determined poles of variation: Allier River, hills (Jallat and Cognet'springs) and southern aquifer (P13). The red line indicates the guideline values imposed by Directive 98/83/CE.

All the pumping boreholes present concentrations of arsenic, iron and manganese below the maximum acceptable concentration for drinking waters (Directive 98/83/CE) with mean values of 3.2±1.3 µg/l, 15.4±63 µg/l, 2.4±6.6 µg/l, respectively (Fig.III-2). B39 (non-pumping borehole), Cognet and Jallat exhibit the highest As concentrations with mean values of 13.7±10, 33.9±2.1 µg/l and 94.8±4.7 µg/l, respectively. Fig.III-3 highlights the relative stability of As concentration in hills' springs. Coupled with the relatively high concentrations in all elements observed for these points, it suggests that As is of a natural origin in relation with the circulation of groundwater in rocks that contain arsenic.

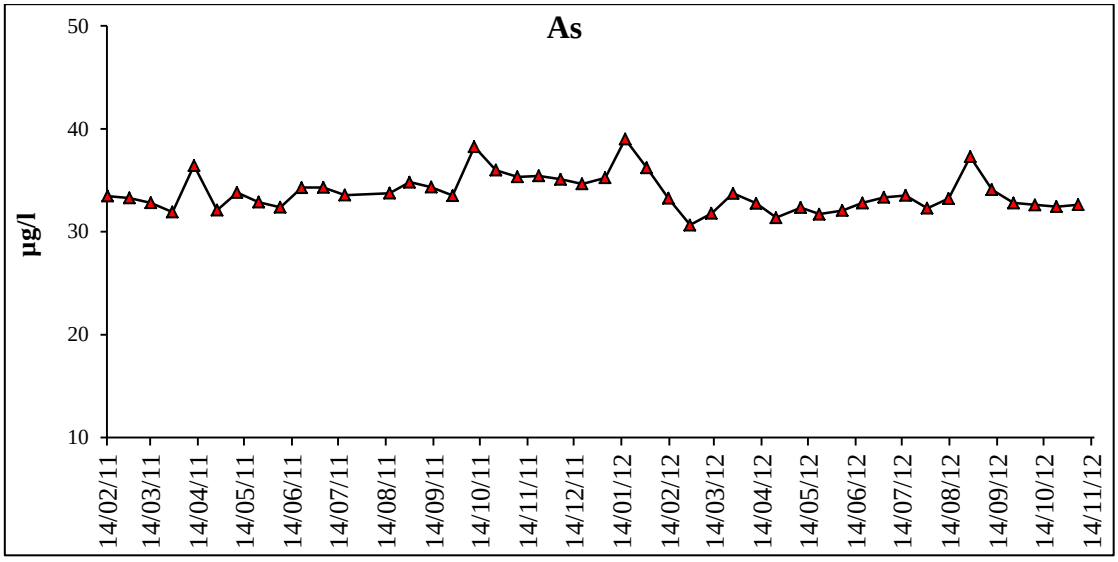

Figure III-3: Variation of arsenic concentrations in Cognet spring highlighting the stability of this component.

B39 presents a different behavior. This borehole has not been pumped for more than twenty years due to its high content in manganese. Its particular location in one of the meander of Allier River, affected by an oxbow, may generate this Mn high content as Mn is peculiarly observed in quiet and meander areas of Rivers (Recoulès, 1984; Verjus, 1984; Haroux, 1986).

Fig.III-4 presents the variations in As, Fe and Mn observed at B39. All follow the same scheme with low values in winter-spring and high values in summer-autumn. These variations are concomitant to those of temperature and evolve inversely to dissolved oxygen ones. Oxidation of pyrite is not likely as the influent, the dissolved oxygen and NO_3 are considerably low ([D.O.] = 2.2±0.8 mg/l; [NO_3] = 0.7±0.8 mg/l). The parallel evolutions suggest a reduction of Fe and Mn (hydro)oxydes (Bonte et al., 2013). This process can be

enhanced by micro-organisms that are stimulated by a temperature increase (Jesuβek et al., 2012; Bonte et al., 2013) what create anaerobic conditions.

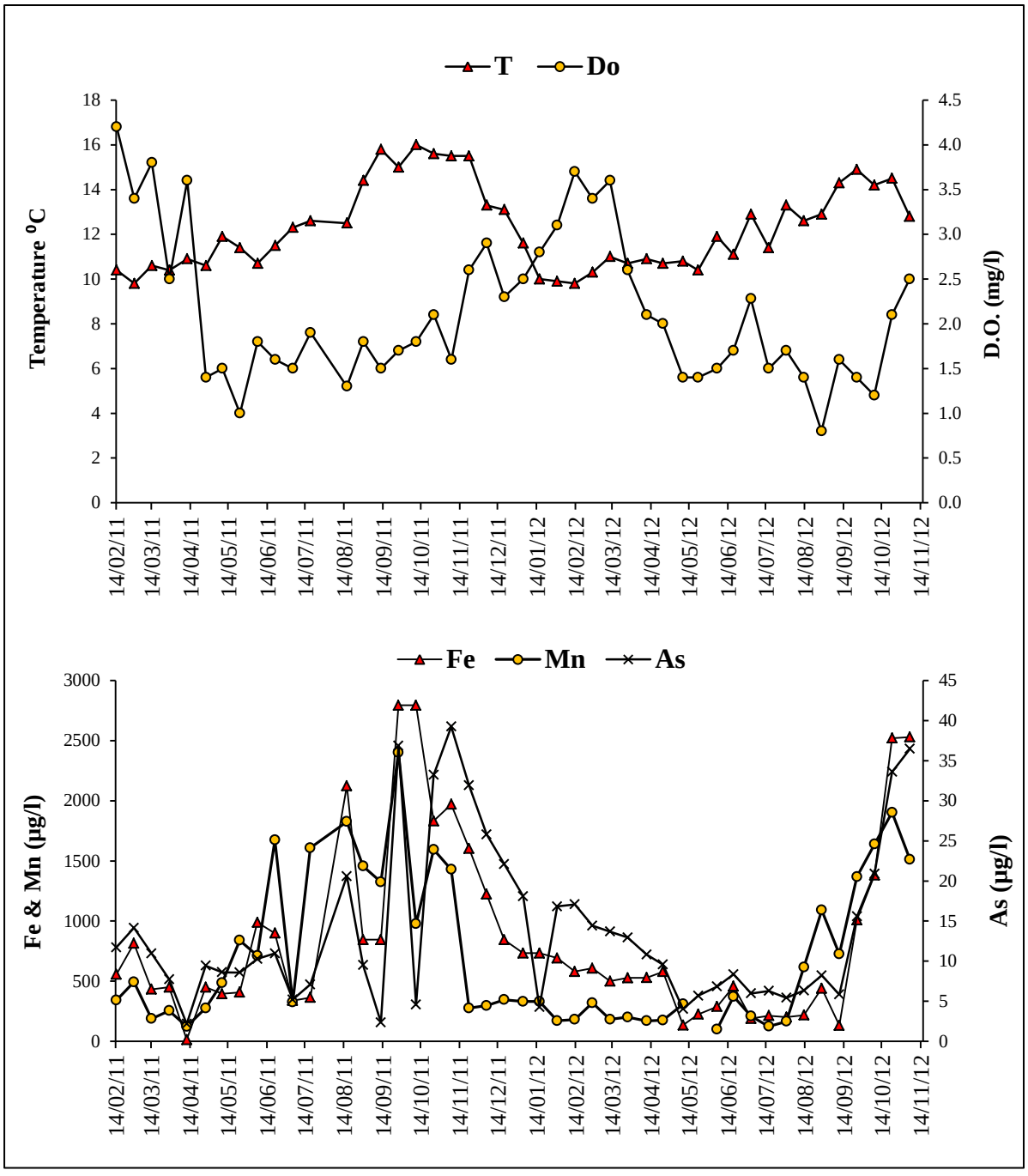

Fig III-4: Variations of Mn, Fe and As (µg/l), Water temperature (°C) and D.O. (mg/l) at B39.

1.2 Other toxic and unwanted elements: Copper, Fluor, Selenium, Cadmium

Copper is a chalcophile metallic element that occurs naturally in rock, soil, water, sediment, and air. It is a natural constituent of soil and will be transported into streams and waterways in runoff either due to natural weathering or anthropogenic soil disturbances (Kashin and Ivanov, 2008). The average crustal abundance of Cu is 60 mg/kg (Plant et al., 2012); typical concentrations in igneous and sedimentary rocks are 4-200 mg/kg and 2-90 mg/kg, respectively (WHO, 1998; Reimann and de Caritat, 1998), in basalts and gabbros are 40-60 mg/kg. Copper is used in the production of electrical wire as well as plumbing, roofing, etc. Cu can also be used as a fungicide - it is one of the main components in Bordeaux mixture (0.05-2% Cu) used in vineyards – or herbicide. In water, only a small proportion of copper is present as free Cu^{2+} ions (WHO, 1998). Copper is both an essential nutrient and a drinking-water contaminant (98/83/CE guidelines of 2000 µg/l). An average of 7.0 µg/l has been proposed for waters worldwide by Oyarzún et al. (2013); concentrations over 0.05 mg/l are not naturally encountered in groundwater (Brigano et al., 2005). Acute exposure to Cu could cause massive haemolysis and renal dysfunction (Barceloux, 1999c) and gastrointestinal problems. Chronic exposure to Cu seriously affects those with Wilson's disease (transport of Cu).

Concentrations observed in the study site are on the range of the values generally measured; they vary from 0.5 (B39) to 61.6 µg/l (B11) and are clearly below the guideline value (2000 µg/l, 98/83/CE). Potot et al. (2012) recorded similar results in alluvial groundwater from Var valley, France (up to 13.24 µg/l), and Bhattacharya et al. (2006) from Rio Dulce alluvial aquifers, Argentina with a mean value of 6.0 µg/l. Greater concentrations have been proposed by Sidenko and Sherrif (2005) from Thompson groundwater, Canada (mean of 52.2 µg/l). The two large campaigns realised in december-2010 and june-2012 show that boreholes from B1 to B12 exhibit the highest concentrations in Copper (Fig.III-5) that can reach the value of 340.9 µg/l (B1, 04/06/2012). During 2010-2012, this area was the object of numerous drilling and repairing works carried out after the detection of water's leak on the water pipes requesting groundwater. It should be likely that Copper, present in certain metallic parts of water pipes has been mobilized (Brigano et al., 2005).

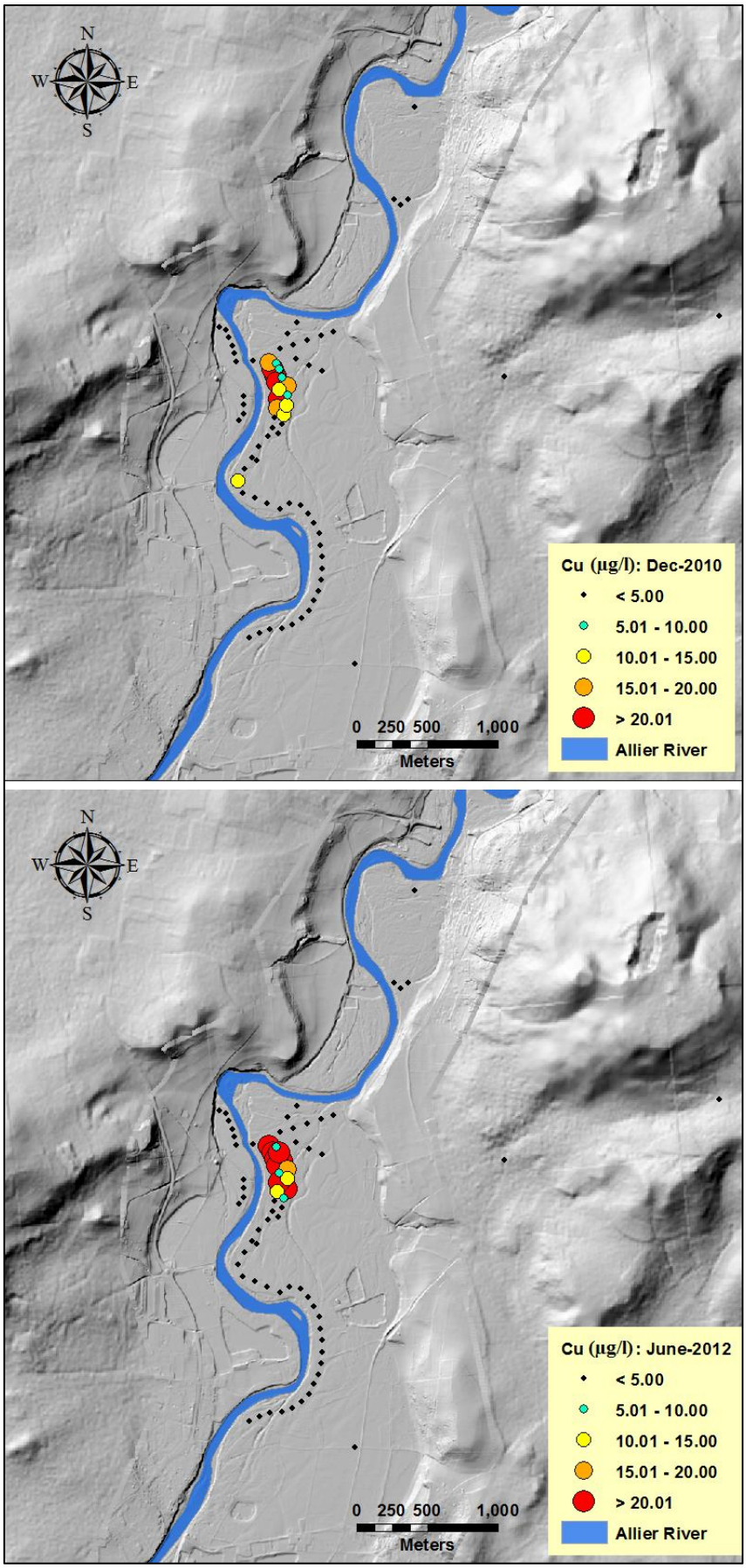

Figure III-5: Spatial distribution of copper concentrations (Cu) during two field campaigns of low flow (Dec-2010) and high flow (June-2012) stage of Allier River.

Fluoride is the 13th most abundant element in the Earth's crust, with an average crustal abundance of 300 mg/kg (Tebbut, 1983). Unlike the other halogens, fluoride is mostly derived from rocks and minerals rather than air, sea water or anthropogenic activities (Plant et al., 2012). The highest concentrations occur in acid igneous rocks such as granite, rhyolite as well as organic-rich sediments (Davison et al., 2004; Edmunds and Smedley, 2005). However anthropogenic sources exist: phosphate-based fertilizers, glass manufacture, pharmaceuticals,…Typically, levels of fluoride in fresh water are less than 1 mg/l (FOREGS, 2005); European guideline 98/83/CE impose a maximum concentration of 1500 μg/l. Excess in fluoride can generate dental and/or skeletal fluorosis.

Selenium is also a chalcophile element. The average crustal abundance of Se is generally very low (0.05-0.09 mg/kg, Taylor and McLennan, 1985). Anthropogenic activities are then the major source of Se with an estimated release of 76000-88000 tons per year compared with the natural release of Se estimated to be 4500 tons per year (Plant et al., 2012). Common anthropogenic sources are the following: fossil-fuel combustion, metal extraction, phosphate-based fertilizers. Typical values of selenium in groundwater and surface water range from 0.00006 to 0.4 mg/l, with some areas having as much as 6 mg/l (WHO, 1986; Fordyce, 2005). Maximum concentration admitted from European regulation is of 10 μg/l.

In the study site, all the sampling points present selenium and fluoride concentrations below the guidelines values (Fig.III-6): Se values vary from <0.005 to 1.4 μg/l and F concentrations from <100 to 586 μg/l, respectively. However some differences have been noticed between two groups: 1) hills' springs, P13 and boreholes fed by a mixed origin (southern aquifer and/or hills + Allier River), 2) boreholes close to the Allier River.

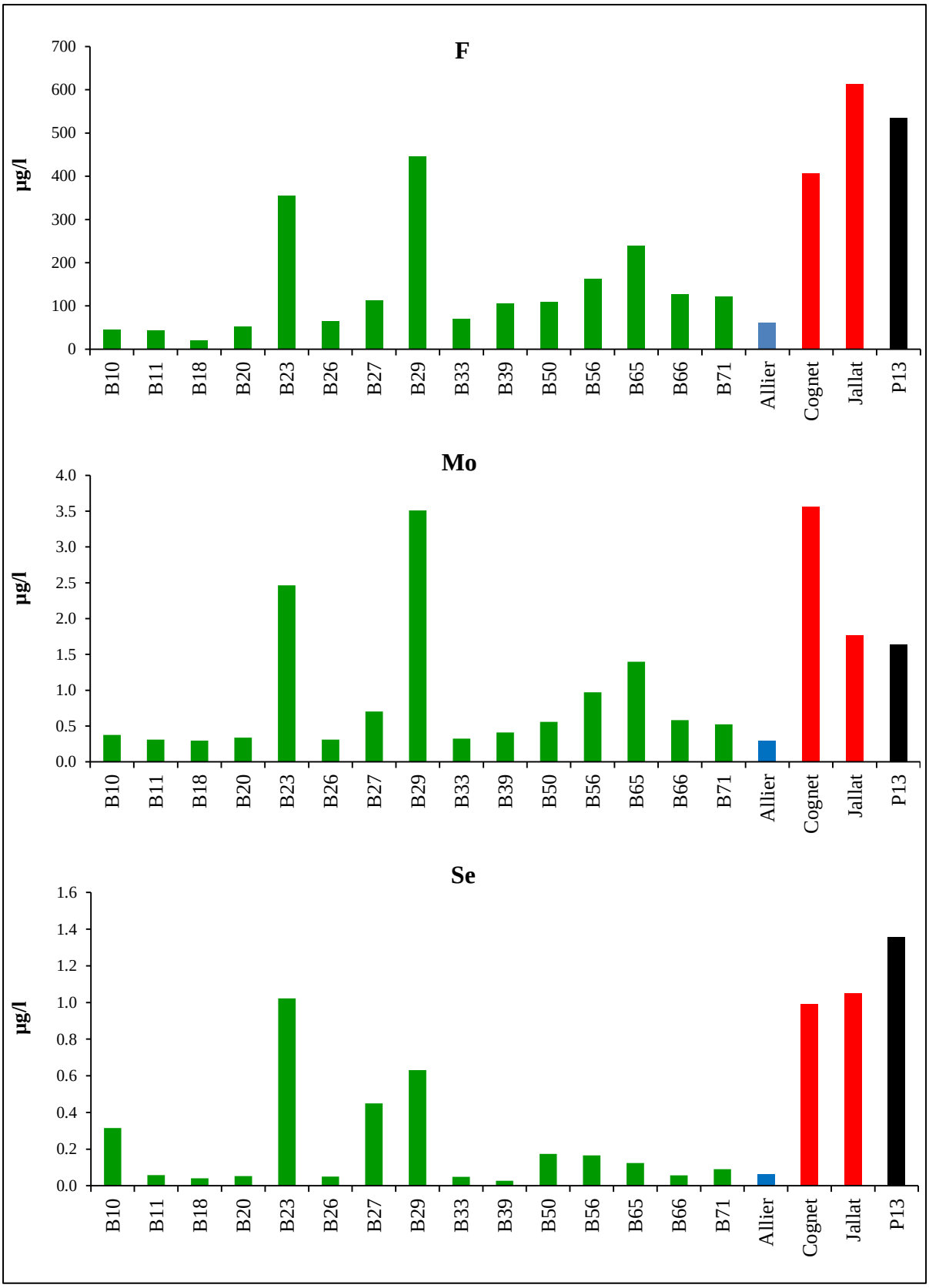

Fig.III-6: Mean concentrations (µg/l) of F, Se and Mo in the sampling points.

Fluoride values vary concomitantly with Se and Mo (Fig.III-6), components that have been recognized to be a part of mineral fertilizers (OFEFP, 1991). Then Jallat, Cognet and P13 are characterized by the highest concentrations in these elements. Boreholes B23, B27 and B29, mainly fed by hills and southern aquifer end-members, and B65, B56, for which the participation of southern aquifer is essential, present also high values in both F, Se and Mo. Temporal evolution (Fig.III-7) additionally shows that all these elements are characterized by higher concentrations in spring-summer than in winter what may confirms their agricultural origin.

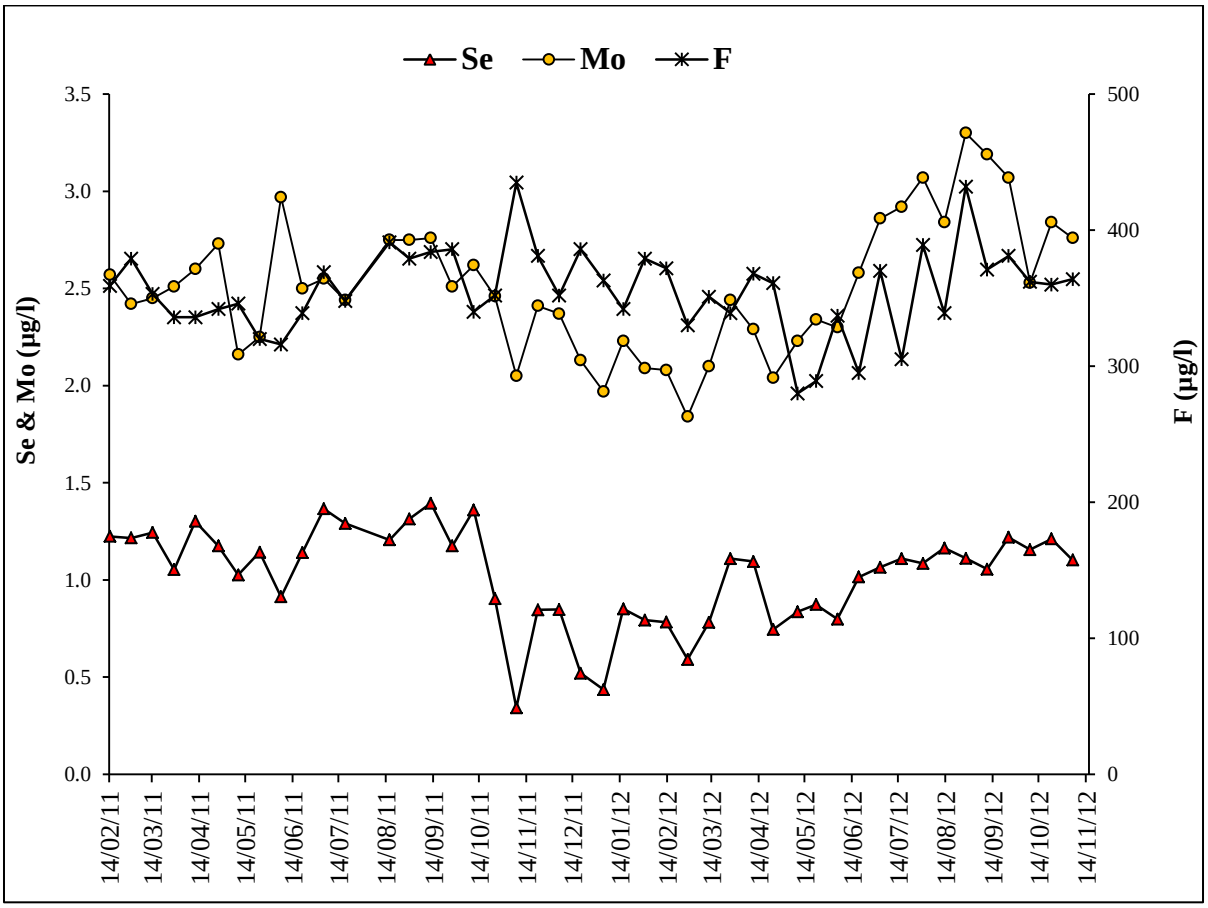

Fig.III-7: Temporal evolution of Se, Mo and F at B23.

Cadmium has properties closely similar to zinc and it is particularly concentrated in Zn-sulphide ore deposits (Reimann and de Caritat, 1998). In continental crust, basalts, granite and gneiss, concentrations in Cd are close to 0.1 mg/kg (Wedepohl, 1991). It is estimated that approximately 8100t of Cd per year enter the biosphere from natural sources (Nriagu, 1980b). Anthropogenic sources of Cd in soils include rock-phosphate fertilizer, ash from fossil-fuel combustion, waste from cement and metallurgic works, municipal refuse and sewage sludge.

Concentrations of Cd may reach 500 mg/kg in phosphorites used for manufacture and fertilizers. About 40% of Cd is deposed from the atmosphere. In surface waters, Cd (Cd^{2+} is the only stable oxidation state) is most soluble under oxidizing conditions at pH less than 8 (Plant et al., 2012); solubility is also affected by changes in Eh (Ferguson, 1990). Under reducing conditions, Cd bound on organic matter and co-precipitated with hydrous oxides of Mn and possibly Fe. Irrigation through surface water or groundwater high in Cd levels can contaminate soils (Plant et al., 2012).

In the study site, the concentrations in Cd of the boreholes are generally low and present a mean value of 0.02±0.32 µg/l. Extremes punctual values have been measured on the 26/4/2011 at B23 (7.13 µg/l) and B29 (4.46 µg/l). These boreholes are the only ones affected by these high concentrations associated with high values of Al, As, Fe, Mn and Pb (Table III-2) what can be related to a punctual pollution of an agricultural origin (fertilizers).

Table III-2: mean and 26/4/2011 concentrations of Al, As, Cd, Mn, Fe and Pb at B23 and B29

Boreholes		Al (µg/l)	As (µg/l)	Cd (µg/l)	Mn (µg/l)	Fe (µg/l)	Pb (µg/l)
B23	**26/04/2011**	69.28	6.44	7.13	4.92	121.20	0.255
	mean	4.10	4.98	0.17	0.27	5.21	0.03
B29	**26/04/2011**	30.77	5.65	4.46	0.32	62.32	0.145
	mean	3.79	4.22	0.11	0.20	4.56	0.04

1.3 Summary

The results show that the distribution of trace elements in alluvial aquifer of Allier River exhibits spatial and temporal variation. The analyses of selected trace elements in groundwater indicate that anthropogenic sources (mostly agricultural activities), beside natural one, possibly influence the quality of groundwater. Some toxic traces, such as arsenic, manganese and iron, have been detected in concentrations above the drinking water limits in borehole B39 (no longer pumped for its high content in Mn). It is also observed that boreholes close to the hills present higher concentrations in most of the traces indicating the influence of the water coming from hills, represented by both Cognet and Jallat springs.

2. Pharmaceutical active compounds (PhACs)

Most of the results presented in this paragraph have been submitted to Environmental International in 2014 (accepted with moderate revisions): *Evaluation of pharmaceuticals in Surface Water: reliability of PECs compared to MECs (Appendix F).*

The presence of pharmaceuticals in the aqueous environment is generally related to anthropogenic processes (Vystavna et al., 2012): industrial discharges, animal manure, wastewater treatment discharge, waste and runoff of unused drugs discharged in domestic waste landfill or in sewage water. Results of previous studies argue that wastewaters are the main sources of pharmaceuticals in the aquatic environment (Ternes, 1998; Hirsh et al., 1999; Heberer, 2002; Clara et al., 2004; Bendz et al., 2005; Lee et al., 2005; Lindqvist et al., 2005; Joss et al., 2006; Comeau et al., 2008); the most contaminated are hospital wastewaters (Steger-Hartmann et al., 1997) as they content high concentrations of medicines. When administered to a human, a part of medicine drugs is excreted unchanged or metabolized in urine and feces and reaches the environment via sewage. A particular attention must be paid to the contamination of surface waters as they are partly used for drinking water supplies, or are in connection with alluvial systems that are used for these purposes, because they directly collect partially untreated wastewaters from Sewage Treatment Plants (STPs) and/or the leakage of septic tanks (Ternes et al., 1999). The concentrations of pharmaceuticals in surface water depend on various factors: consumption of medicines in the water catchment area of a water body, absorption and elimination rates of the pharmaceuticals from the organism, elimination rate in the STPs, the volume of surface water, and elimination rate in the environment (Ter Laak et al., 2010). In addition, the proportion of sewage treated before discharge in the environment and the disposal modes of unused drugs can be added (Ortiz de Garcia et al., 2013).

The presence of pharmaceutical products in the aquatic environment is known since the 70s. However, the interest of the scientific community on the pharmaceutical has really grown during the last two decades due to their continuous increased use (consumption in France has been multiplied by 200 since the 80s (Dulio et al., 2009)) and to the evolution of analytical techniques that enough improved to allow quantifying the presence of these substances in waters, even at really low concentrations. Then numerous publications deal with the Measured Environmental Concentrations (MECs) of pharmaceuticals that have been detected

with levels which can go from ng/l to µg/l in surface waters of Austria (Clara et al., 2004), Canada (Comeau et al., 2008), Finland (Lindqvist et al., 2005), France (Togola and Budzinski, 2008; Vystavna et al., 2012), Germany (Ternes, 1998; Nödler et al., 2011), Greece (Arditsoglou and Voutsa, 2008), Italy (Zuccato et al., 2005), India (Larsson et al., 2007), Japan (Nakada et al., 2008), Korea (Choi et al., 2008), Norway (Grund et al., 2008), Romania (Moldovan, 2006), Spain (Joss et al., 2006), Sweden (Bendz et al., 2005), Switzerland (Tauxe-Wuersch et al., 2005), Ukraine (et al., Vystavna 2012), USA (MacLeod et al., 2007), Western Balkans (Terzic et al., 2008), ... in groundwater (Barnes et al., 2008; Vuillet et Cren-Olivé, 2011; Müller et al., 2011; Fram et al., 2011; Reh et al., 2013; Lopez-Serna et al., 2013, …), as well as in drinking and tap waters (Heberer, 2002; Kuster et al., 2008; Schwab et al., 2005; Vuillet et Cren-Olivé, 2011; Valcarcel et al., 2011; …).

Moreover, due to the current analytical processes that are not able to measure all the pharmaceutical molecules, to the number and the variability of molecules that may enter the environment, to the high costs and the consumption of time to sample and analyse this molecules, and to the requirements of Commission Directive 93/67/EEC, Commission Regulation 1488/94/EC and Commission Directive 98/8/EC, models to calculate Predicted Environmental Concentrations (PECs) have been developed (Henshel et al., 1997; Stuer-Lauridsen et al., 2000; Castiglioni et al., 2004). If PECs provide important information for the prioritization of pharmaceuticals products for environmental strategies, approximations introduced in the calculations lead to uncertainties (Coetsier et al., 2009). Then a comparison between MECs and PECs, taking into account the methods of calculations and peculiarly the parameters included in the calculation, is necessary to assess the validity of predicted concentrations. Most of the studies present a comparison between MECs and PECs calculated by using national consumption data (Heberer and Feldmann, 2005; Johnson et al., 2007; Besse et al., 2008; Coetsier et al., 2009; Ort et al., 2010; Ter Laak et al., 2010; Vystavna et al., 2012; Ortiz de Garcia et al., 2013), only few of them use local consumption (Oosterhuis et al., 2013) despite the fact that local patterns can highly modify the estimations.

During our study, fourteen campaigns, every 4 weeks from October 2011 to October 2012, have been achieved and concerned (Fig.III-8) Allier River, two pumping boreholes (B33, B29) and one piezometer (P13). This paragraph presents the results obtained in Allier River, in groundwater and a comparison between Measured concentrations (MECs) and Predicted Concentrations (PECs) according to the consumption data, gathered from the CPAM (social health care system of Puy-de-Dôme).

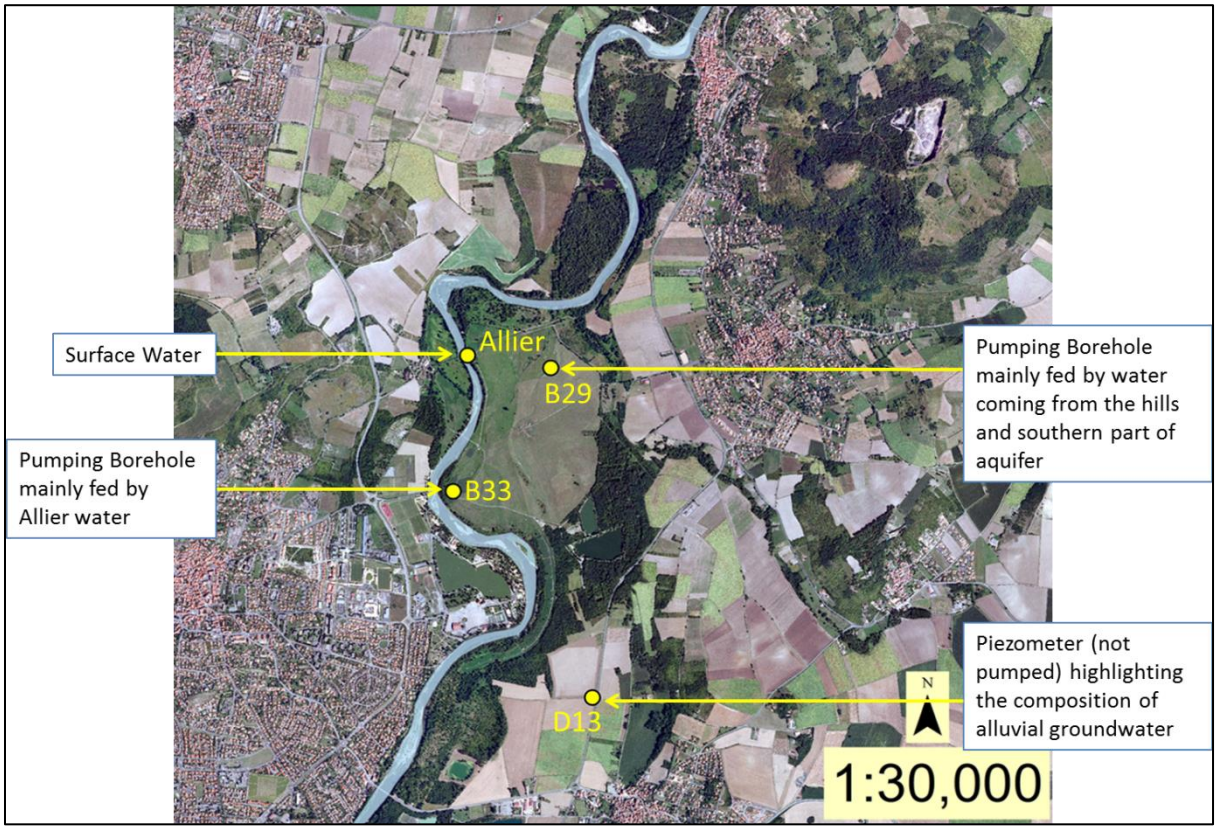

Fig.III-8: location and characteristics of the sampling points selected for pharmaceuticals, pesticides and biological investigations.

2.1. Measured concentrations (MECs)

2.1.1 Detected molecules

Variations of the concentrations of 47 PhACs have been evaluated during one hydrological cycle, from October 2011 to October 2012. Statistical calculations are presented in Table III-3a & b, and the analytical results are shown in Appendix D. Vystavna et al. (2012) show that two river basins with similar hydrologic characteristics and water usage (wastewaters, discharge, irrigation …) can however present different pollution status according to the different socio-economic characteristics in terms of population density, economic activities, incomes, lifestyles, etc. Then data collected during the present study have been compared in priority with concentrations measured in French watersheds similar to the Allier basin, when information is available. Nineteen among the 47 PhACs analysed have been positively detected either in surface or in groundwater.

Table III-3a: Statistical (frequency, minimum, maximum and mean values) of measured PhACs in Allier River, P33, P29 and P13.

Detected molecules		Therapeutic classes	LQ	Allier River				B33				B29				P13			
				surface water				pumped borehole close to the river				pumped borehole close to hill				non-pumped borehole			
				Frequency	Min	Max	Mean	Frequency	Min	Max	Mean	Frequency	Min	Max	Mean	Frequency	Min	Max	Mean
				%	ng/l	ng/l	ng/l	%	ng/l	ng/l	ng/l	%	ng/l	ng/l	ng/l	%	ng/l	ng/l	ng/l
Atenolol	ATE	β-blocker	0.001	12	1.3	13.0	4.92	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Acetaminophen	ACE	Antipyretic, analgesic	0.01	21	25.0	200.0	87.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Fenofibric acid	F.A.	Metabolite fenofibrate	0.001	71	1.2	19.0	7.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bezafibrate	BEZ	Hypolipidemic agent	0.001	64	1.3	5.5	3.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Caffeine	CAF	Stimulant	0.01	71	11.0	81.0	41.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Carbamazepine	CARB	Anticonvulsant / mood staibilizing	0.001	79	1.2	5.8	3.3	57.1	1.0	3.9	2.1	85.7	1.3	5.6	3.2	n.d.	n.d.	n.d.	n.d.
Doxycycline	DOX	Antibiotic/antiseptic	0.001	21	1.1	1.8	1.4	n.d.	n.d.	n.d.	n.d.	14.3	1.1	1.4	1.3	14.0	1.3	11.0	2.2
Epoxycarbamazepine	EPO	Metabolite carbamazepine	0.005	7	7.6	7.6	46	7.1	7.0	7.0	7.0	57.1	5.6	14.0	7.7	n.d.	n.d.	n.d.	n.d.
Furosemide	FUR	Loop diuretic	0.001	64	1.6	17.0	4.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Gemfibrozil	GEM	Hypolipidemic agent	0.001	64	1.3	4.6	2.6	n.d.	n.d.	n.d.	n.d.	7.1	28.0	28.0	28.0	n.d.	n.d.	n.d.	n.d.
Hydrochlorothiazide	HYD	Thiazide diuretic	0.005	57	11.0	42.0	22.4	57.1	5.9	28.0	12.8	7.1	37.0	37.0	37.0	n.d.	n.d.	n.d.	n.d.
Iopromide	IOP	Contrast medium	0.005	79	6.4	99.0	29.4	n.d.	n.d.	n.d.	n.d.	7.1	180.0	180.0	180.0	n.d.	n.d.	n.d.	n.d.
Losartan	LOS	Hypotensive agent	0.005	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7.1	7.7	7.7	7.7	n.d.	n.d.	n.d.	n.d.
Metoprolol	MET	β-blocker	0.001	14	1.1	1.3	1.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Naproxen	NAP	NSAID	0.001	64	1.2	20.0	6.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pravastatin	PRA	Hypolipidemic agent	0.001	64	1.8	18.0	5.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Propanolol	PROP	β-blocker/anti-hypertensive	0.001	36	1.0	2.9	1.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Roxithromycine	ROX	Antibiotic/antiseptic	0.005	7	7.6	7.6	7.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sulfamethoxazole	SUL	Antibiotic/antiseptic	0.001	71	1.0	5.3	2.3	50.0	1.2	3.5	2.1	71.4	1.1	5.1	2.6	n.d.	n.d.	n.d.	n.d.

Table III-3b: Statistical (frequency, minimum, maximum and mean values) of measured PhACs in Allier River, P33, P29 and P13.

Non detected molecules	Therapeutic classes	LQ	Allier River				B33				B29				P13			
			surface water				pumped borehole close to the river				pumped borehole close to hill				non-pumped borehole			
			Frequency	Min	Max	Mean	Frequency	Min	Max	Mean	Frequency	Min	Max	Mean	Frequency	Min	Max	Mean
			%	ng/l	ng/l	ng/l	%	ng/l	ng/l	ng/l	%	ng/l	ng/l	ng/l	%	ng/l	ng/l	ng/l
Altrenogest	Veterinary drug / progestogen	0.005	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Amlodipine	Hypotensive agent	0.01	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bromazepam	Anxiolytic	0.005	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chloramphenicol	Antimicrobial/antiseptic	0.001	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Clindamycin	Antibiotic/antiseptic	0.005	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Clofibric acid	Metabolite Clofibrate	0.001	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Dicyclanil	Veterinary / insecticide	0.1	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Estriol	Hormone	0.001	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Fenofibrate	Hypolipidemic agent	0.01	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Fluvoxamine	Anxiolytic	0.005	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ifosfamide	Anticancer agent	0.001	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Indomethacine	NSAID	0.005	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Levamisol	Veterinary drug / dewormer	0.005	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Lincomycin	Antibiotic/antiseptic	0.01	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Methotrexate	Anticancer agent	0.01	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Oxytetracycline	Antibiotic/antiseptic	0.1	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Penicillin G	Antibiotic	0.005	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Progesterone	Hormone	0.001	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ramipril	Hypotensive agent	0.005	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ranitidine	Antiacid	0.005	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sulfamerazine	Antibacterial agent/antiseptic	0.005	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sulfamethazine	Antibacterial agent/antiseptic	0.001	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sulfamethazole	Antibiotic/antiseptic	0.005	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Testosterone	Hormone	0.005	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tetracycline	Antibiotic	0.1	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trimetazidine	Anti-ischemic metabolic agent	0.1	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Trimethoprim	Antibiotic	0.001	n.d.	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

2.1.2 MECs in Allier River

Three hundred and seventy-eight STPs, but only 18 serving more than 2000 inhabitants, have been recognized in the Allier Watershed above the sampling site (45°45'16.20'', 3°13'9.43'', z=320 m). The nearest STP is Cournon's one, 4.2 km upstream to the station, which is dedicated to the treatment of wasterwaters of 36 000 inhabitants living in the Auzon watershed. The treatment processes consist of an activated sludge with prolonged aeration and nitrification / denitrification added to phosphate removal. The STP's effluent discharges in the Auzon River 300 m upper the connection between Auzon River and Allier River. Fig.III-9 shows that high concentrations are measured for non-persistent molecules (e.g. ACE, CAF). That means that the source of pollution is close to the sampling site. It is then assumed that Cournon's STP contributes for a great part to the PhACs concentrations measured at our Allier River sampling site.

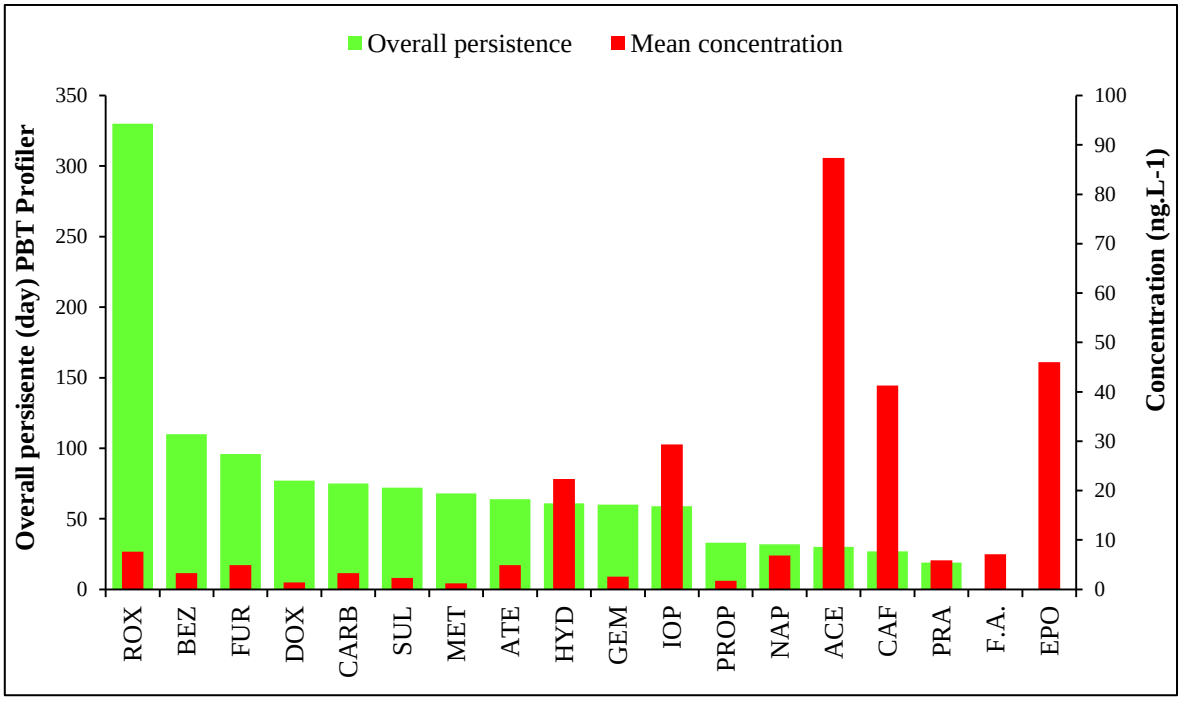

Fig.III-9: mean concentration of PhACs measured at the Allier River sampling site and Overall persistence of molecules (from PBT profiler).

The highest mean concentrations measured in the Allier River correspond to the following molecules: ACE>EPO>CAF>IOP>HYD. ACE and HYD high concentrations are due to high consumption levels of these molecules (Table III-4). CAF is mainly due to the consumption of coffee, tea and soft drinks instead of its pharmaceuticals compound (Camacho-Munoz et al., 2010) and IOP is only consumed in hospitals; data on consumption is thus not available for these two PhACs.

Table III-4: Number of inhabitants and consumption levels of some PhACs in Puy-de-Dôme (year 2011) and in Auzon Catchment (Oct-2011 to Sept-2012). Data have been supplied by the Social Health Insurance of Puy-de-Dôme. The third column highlights the percentage of Auzon population in Puy-de-Dôme and the corresponding percentage for each PhACs. The high percentage of Trimetazidine 26.6% is due to the reimbursement's stop of this molecule in March 2012.

	Number of package sold annually		
	Puy de Dome 2011	**Auzom catchment (Oct-2011 – Sept-2012)**	**Rapport (PdD/A)**
Population (inhabitants)	632311	47930	13.19238
ACETAMINOPHEN	2886894	232084	12.4
AMLODIPINE	69062	5232	13.2
ATENOLOL	40998	2600	15.8
CARBAMAZEPINE	28643	1966	14.6
DOXYCYCLINE	18557	1377	13.5
FLUVOXAMINE	2213	154	14.4
FUROSEMIDE	157633	11060	14.3
HYDROCHLOROTHIAZIDE	197009	14934	13.2
PRAVASTATIN	82800	4887	16.9
PROGESTRONE	33199	2412	13.8
RAMIPRIL	72505	4527	16.0
TRIMETAZIDINE	54555	2050	26.6

The detection frequency is higher for the following molecules: IOP-CARB>CAF-F.A.-SUL>NAP-PRA-FUR-BEZ-GEM>HYD (Fig.III-10). Twenty-eight molecules have not been detected in the Allier River due to low consumption or to the low persistence in the environment (FLU, PROG) or because the quantification limit imposed by the methodology is too high compare to the concentrations of these molecules in the Allier River.

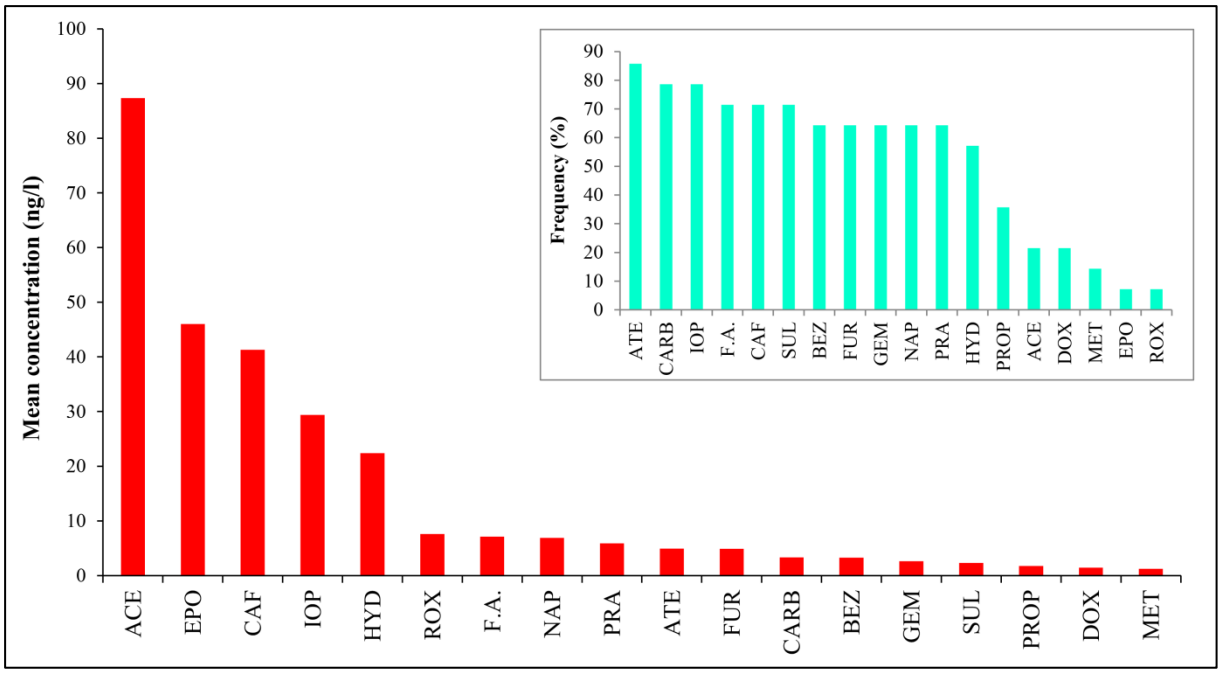

Fig.III-10: Mean concentrations in Allier River (ng/l) and Frequency of detection (%)

2.1.2.1. Medium contrast

Iopromide is a molecule used as a contrast medium in radiographic studies. The organic iodized compounds represent the most present class of contrast agents in the urban effluents (Jançon et al., 2008). Used in great quantities in hospitals and private hospitals, they are the main contributors in the load in halogenated organic by-products in waste waters (Gartiser et al., 1996). This important use, coupled with an extremely reduced metabolism (95% are eliminated without transformation) as well as a poor elimination in the WWTP, of the order of 10%, ends in a high and persistent environmental accumulation (Steger-Hartmann et al., 2000; Jançon et al., 2008). Concentrations up to 0.1 $\mu g.L^{-1}$ have been measured in the Rhine River (ter Laak et al., 2010). The occurrence of IOP in the Allier River is high as it has been recognized in 79% of the samples, mean concentrations are of 29.4 $ng.L^{-1}$, close to the one observed by Bruchet et al. (2005) in the Seine River with values varying between 6.8 and 10.6 $ng.L^{-1}$.

2.1.2.2. Antipyretic, analgesic

Among the nine compounds detected in the Allier River, ***acetaminophen***, one of the most prominent pain killer, presents the highest concentrations between 25 and 200 $ng.L^{-1}$, consistent with the data of Rabiet et al. (2006, max=211 $ng.L^{-1}$), but has been positively detected only three times. Togola and Budzinski (2008) and Vuillet and Cren-Olivé (2011)

found lower values, comprised from 10.6 to 72.3 $ng.L^{-1}$, for the Hérault River, and from 0.4 to 71 $ng.L^{-1}$ for the Rhône-Alpes region, respectively. Concentrations in this molecule are highly variable: 78 to 610 $ng.L^{-1}$ in Serbia (Grujic et al., 2009), 30 $ng.L^{-1}$ (Pedrouzo et al., 2007) to 2420 $ng.L^{-1}$ (Ginebredda et al., 2010) in Spain, 4.1 to 73 $ng.L^{-1}$ in South Korea (Kim et al., 2007), not detected in U.K. (Roberts et al., 2006), 2.1 $ng.L^{-1}$ (Conley et al., 2008) to 10 $\mu g.L^{-1}$ in U.S. (Kolpin et al., 2002). These variations could be explained by the degradation and dilution factors that decrease the concentrations of this non-conservative molecule downstream the STPs (Vystavna et al., 2013). The low ratio of detection (21%) for ACE is also due to its labile behaviour.

2.1.2.3. Stimulant

Caffeine is the most widespread PhAC in the environment (Nikolaou et al., 2007) with the highest frequency reported in similar studies (Spongberg et al., 2011) and is often considered as a good anthropogenic waste marker. This molecule has a labile behaviour in the environment (Benotti and Brownawell, 2007); concentrations can then be lowered rapidly in the environment. In the Allier River, concentrations in caffeine vary from 11 $ng.L^{-1}$ to 81 $ng.L^{-1}$ with a mean value of 41.3 $ng.L^{-1}$. These values are consistent with the ones found in the Hérault River in France (13-107.2 $ng.L^{-1}$ in Togola and Budzinski, 2008) and in the Jalle River (40-75 $ng.L^{-1}$, Vystavna et al. 2012). They are lower than those measured in Costa Rica (max=1.12 $mg.L^{-1}$ in Sponberg et al., 2011) where a natural origin from plants could be invoked, South Korea (105 $ng.L^{-1}$, Kim et al., 2007), Spain (415.7 $ng.L^{-1}$, Fernandez et al., 2010), U.S. (med = 0.1 $\mu g.L^{-1}$, Koplin et al., 2002).

2.1.2.4. Anticonvulsant, mood stabilizing

Along with caffeine, ***carbamazepine*** has been proposed as an anthropogenic waste marker as it is one of the most frequently detected drugs in aquatic environment and it is poorly degraded in STPs (Ternes, 1998; Heberer and Feldman, 2005). Literature provides then large information on concentrations of this molecule in surface waters. Carbamazepine in the Allier River presents concentrations between 1.2 to 5.8 $ng.L^{-1}$, with a mean value of 3.3 $ng.L^{-1}$. These values are in accordance with the values of Seine River (1.1 to 2.6 $ng.L^{-1}$, Bruchet et al., 2005) generally lower than the concentrations available in France (13.9-56.3 $ng.L^{-1}$ in Rabiet et al., 2006; 0-56.3 $ng.L^{-1}$ in Togola and Budzinski, 2008; 105-675 $ng.L^{-1}$ in Coetsier et al., 2009; mean of 13.9 $ng.L^{-1}$ in Vuillet and Cren-Olivé, 2011; 17-27 $ng.L^{-1}$ in Vystavna et al., 2012) or in other countries like Canada (0.24-28 $ng.L^{-1}$, Lissemore et al., 2006), Germany

(max = 1075 ng.L^{-1} in Herberer, 2002), Italy (max = 175.3 ng.L^{-1} in Zuccato et al., 2005), Serbia (6-130 ng.L^{-1} in Grujic et al., 2009), South Korea (mean = 25 ng.L^{-1} in Kim et al., 2007), South Wales (1-356 ng.L^{-1} in Kaspryzk-Hodern et al., 2008), Spain (11-90 ng.L^{-1} in Gros et al., 2006; 9-110 ng.L^{-1} in Pedrouzo et al., 2007; nd-104 ng.L^{-1} in Fernandez et al., 2010; 80-3090 ng.L^{-1} in Ginebreda et al., 2010; 1.2-266.7 ng.L^{-1} in Osorio et al., 2012), Switzerland (30-250 ng.L^{-1} in Ollers et al., 2001), Ukraine (2-272 ng.L^{-1}, Vystavna et al., 2012). Small values comparable to the ones of our study have been reported by Togola (2006) for the Gironde and Adour River estuaries and by Spongberg et al. (2011) in Costa Rica (1-3 ng.L^{-1}). As this carbamazepine is noted to be highly resistant to biodegradation and thus highly recalcitrant under standard biological wastewater treatment conditions (Clara et al., 2005; Kosjek et al., 2009; Donner et al., 2013), the consumption factor may be invoked to explain the differences observed between the different studies. ***Epoxycarbamazepine***, one of the metabolite of carbamazepine, has been positively detected only one time at a concentration largely exceeding the CAR's one.

2.1.2.5. Antibiotics

In our study, ***doxycycline*** has been detected only three times and with low concentrations (mean=1.4 ng.L^{-1}). Most of the studies carried out on PhACs show an absence of DOX (Hirsch et al., 1999; Kolpin et al., 2002; Focazio et al., 2008, Vulliet and Cren-Olivé, 2011; Wei et al., 2011). Concentration of 74 ng.L^{-1} with an occurrence of 77% has been reported by Spongberg et al. (2011) in Costa Rica river waters. Tetracycline antibiotics have been shown to dissipate rapidly in the aqueous environment due notably to photocatalytic degradation (Makowski et al., 2009). The relatively high occurrence and concentration found by Spongberg et al. (2011) likely indicates high usage in Costa Rica compared to previously reported studies. Low concentration and occurrence in the Allier River is related to both factors of low consumption and photodegradation. ***Sulfamethoxazole*** has been recognized in 71% of the samples with concentrations varying from 1 to 5.3 ng.L^{-1}. These values correspond to the ones measured by Vuillet and Cren-Olivé, 2011 in the Rhône-Alpes region (1.9 ng.L^{-1}). SUL is frequently detected in surface waters with concentration generally higher than those measured in the Allier River: up to 0.2 µg.L^{-1} in the Seine River (Bruchet et al., 2005), up to 0.15 µg.L^{-1} in U.S. (Koplin et al., 2002), up to 0.5 µg.L^{-1} in Germany (Sacher et al., 2001; Hirsch et al., 1999), up to 12 µg.L^{-1} in Spain (Ginebredda et al., 2010). These big amplitudes are in relation with the WWTP's processing, SUL is better eliminated through reverse osmosis (Watkinson et al., 2007) than activated sludge (Göbel et al., 2007).

Roxithromycine has been measured one time with a concentration of 7.6 ng.L^{-1}. This low occurrence corresponds to the ones reported in the studies of Vuillet and Cren-Olivé (2011) with 14% and Koplin et al. (2002) with 5% of the samples that present a positive detection of ROX. The value measured is in the range of the ones of Rhône-Alpes (Vuillet and Cren-Olivé, 2011: mean of 4.9 ng.L^{-1}) but is lower than those collected in Seine River (Bruchet et al., 2005: up to 236 ng.L-1), U.S. surface waters (Koplin et al., 2002: up to 0.2 µg.L^{-1}) and Germany (Hirsch et al., 1999: 0.56 µg.L^{-1}). The input and persistence of antibiotics, such as DOX into the environment is of major concern due to possible development of bacteria resistance to these compounds (Kachatourian, 1998).

2.1.2.6. β-blockers

Information on atenolol, metoprolol and propanolol, current β-blockers, is incomplete since only a few studies take these molecules into account. ***Atenolol*** has been detected in twelve samples among fourteen in the Allier River, with concentrations varying from 1.3 to 13 ng.L^{-1} and a mean value of 4.9 ng.L^{-1}, values in agreement with the mean of 4.7 ng.L^{-1} reported by Vulliet and Cren-Olivé (2011) in Rhône-Alpes watersheds. Other data gathered from the literature review are systematically higher: 0-465 ng.L^{-1} in Spain (Gros et al., 2007; Ginebreda et al., 2010; Fernandez et al., 2010, Osorio et al., 2012), median value of 17.2 for the Po River (Zuccato et al., 2005). ***Metoprolol*** has been detected in 14% of samples with a mean concentration of 1.2 ng.L^{-1}. These values correspond to the ones collected by Vuillet and Cren-Olivé (2011) in Rhône-Alpes (0.8 ng.L^{-1}) and Fernandez et al. (2011) in Henares, Jarama and Tajo basins (1.8 to 2.6 ng.L^{-1}). Idem for ***propranolol***, this molecule shows a mean concentration of 1.7 ng.L^{-1} and has been measured in 36% of the samples, values corresponding to the ones of Vuillet and Cren-Olivé (2011, 1.2 ng.L^{-1}) but lower than the measurements of Roberts et al. (2006) that report concentrations up to 107 ng.L^{-1}.

2.1.2.7. Hypolipidemic agents

The mostly found compound reported in the literature is the chlofibric acid as this molecule is administered to doses rather high (in the range of 1 g.j^{-1}, Jançon et al., 2008). However, this molecule has not been recognized in our study. Three lipid regulators and one metabolite have been detected in the Allier River: bezafibrate, gemfibrozil and fenofibric acid with an occurrence of 64, 64 and 71% and a mean concentration of 3.3 ng.L^{-1}, 2.6 ng.L^{-1} and 7.1 ng.L^{-1}, respectively. ***Bezafibrate*** has been positively detected in a lot of studies in France (mean of 3.4 ng.L^{-1} in Rhône-Alpes, Vuillet and Cren-Olivé, 2011), in Italy (57.2 ng.L^{-1} in

Lambro basin, 1.9 ng.L^{-1} in Po River, Zuccato et al., 2005) and in Spain (concentration up to 217 ng.L^{-1} in the Llobregat River, Osorio et al., 2012; up to 37 ng.L^{-1} in the Ebro River, Gros et al., 2007; from 0.3 to 46 ng.L^{-1} for the Henares, Jarama and Tajo basins, Fernandez et al., 2001). Concentrations in ***gemfibrozil*** of the Allier River are in accordance to the ones measured by Togola and Budzinski (2008) in the Hérault River and largely lower than the ones reported by Wang et al. (2010) in China (86.6 ng.L^{-1}) and Koplin et al. (2002) for the U.S. surface waters (median concentration=0.79 µg.L^{-1}). ***Pravastatin*** is primarily used for the treatment of dyslipidemia and the prevention of cardiovascular disease. Values measured in the Allier River are in agreement with the data reported for the Rhône-Alpes neighbouring region (1.6 ng.L^{-1}, Vulliet and Cren-Olivé, 2011). At last, a little information is available on ***fenofibric acid*** as this compound has been only reported, to our knowledge, in the study of Vuillet and Cren-Olivé (2011) with concentrations lower (0.6 ng.L^{-1}) than those measured in the Allier River (mean = 7.1 ng.L^{-1}).

2.1.2.8. Diuretics

Furosemide and hydrochlorothiazide are prescribed for long-term treatments that explain their high occurrence in Allier River; concentrations have to be relied to the consumption factor. ***Furosemide*** is a loop diuretic used in the treatment of congestive heart failure and oedema, determined as stable in the environment during 90 days (Kirit et al., 1980). Values found for the Allier River are in agreement with the measurements (median = 3.5 ng.L^{-1}, max = 67.2 ng.L^{-1}) achieved in the Po River by Zuccato et al. (2005). They are lower than concentrations of 254.7 ng.L^{-1} reported by same author for Lambro River. ***Hydrochlorothiazide*** is a diuretic drug frequently used for the treatment of hypertension, congestive heart failure, symptomatic oedema, diabetes insipidus, renal tubular acidosis. Concentrations evaluated for the Allier River are lower than those been reported for Spain and Italy: Llobregat River presents concentration from 0 to 2435.5 ng.L^{-1} (Osorio et al., 2012), Henares, Jarama and Tajo Rivers from 4.2 to 960.3 ng.L^{-1} (Fernandez et al., 2010), mean for Lambro River is of 255.8 ng.L^{-1}, median value for Po River is of 4.6 ng.L^{-1} (Zuccato et al., 2005).

2.1.2.9. Anti-inflammatory drugs

Most of the studies deal with diclofenac, ibuprofen, acetylsalicylique acid, PhACs that are not measured in our study. Two NSAID have been measured in the Allier River: ***indomethacine*** never observed and ***naproxen*** with 9 measurements upon 14. Concentration is of 6.9 $ng.L^{-1}$ for the mean value and can reach 20 $ng.L^{-1}$ what is consistent with the values observed in the literature: 0 to 9.1 $ng.L^{-1}$ in the Hérault River (Togola and Budzinski, 2008), 3.5 $ng.L^{-1}$ for Rhône-Alpes basins (Vuillet and Cren-Olivé, 2011), 5.1 $ng.L^{-1}$ for the Yellow River (Wang et al., 2010) and 10.9 $ng.L^{-1}$ for the Pearl River (Zhao et al., 2010).

2.1.2.10. Time-evolution

The observed variations within a sampling location can be due to variation of the consumption rate over time (Nödler et al., 2011), decreasing (bio)degradation in waste water treatment and the environment at low temperature (Daneshvar et al., 2010; Gardarsottir et al., 2010; Suarez et al., 2010), variations of the river's flow rate (ter Laak et al., 2010) and/or dilution of surface water by rain water (Baker and Kasprzyk-Hordern, 2013).

Fig.III-11 shows the temporal evolution of the PhACs, flow rate of the Allier River, rainfall height and temperature records from October 2011 to October 2012. Two peaks of concentrations can be seen in February 2012 and September 2012. Positive peak of February 2012 can be explained by low flow rate of the Allier River, small rainfall amount and low temperature. However, the peak registered in September 2012 seems not be related to the temperature but most probably to the high rainfall, the increase of the volume of wastewaters to be treated generates a decrease of the efficiency of the treatment (Ternes, 1998). Variation of consumption with time will be explored in Chapter III, 2.2.2.1.

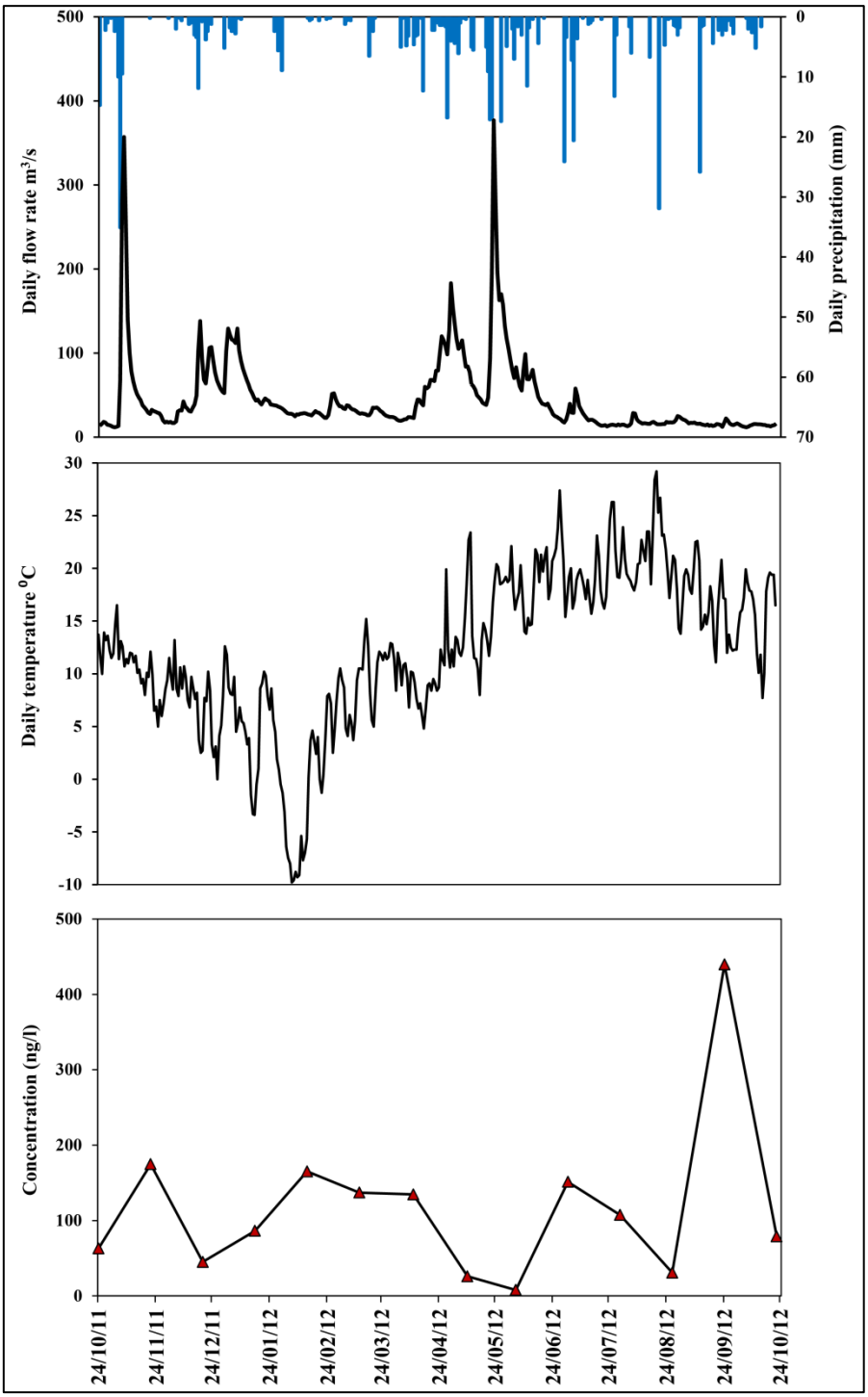

Fig.III-11: Temporal variations of Allier flow rate, rainfall, temperature and PhACs concentrations.

2.1.3. MECs in groundwater

Regarding pharmaceuticals, groundwaters were generally less contaminated than surface waters (Vuilliet and Cren-Olivé, 2011) since the number of molecules detected, the frequencies of their detection and their average levels are generally less elevated in groundwaters. Fig.III-12 presents the concentrations of Allier River, B33, B29 and P13.

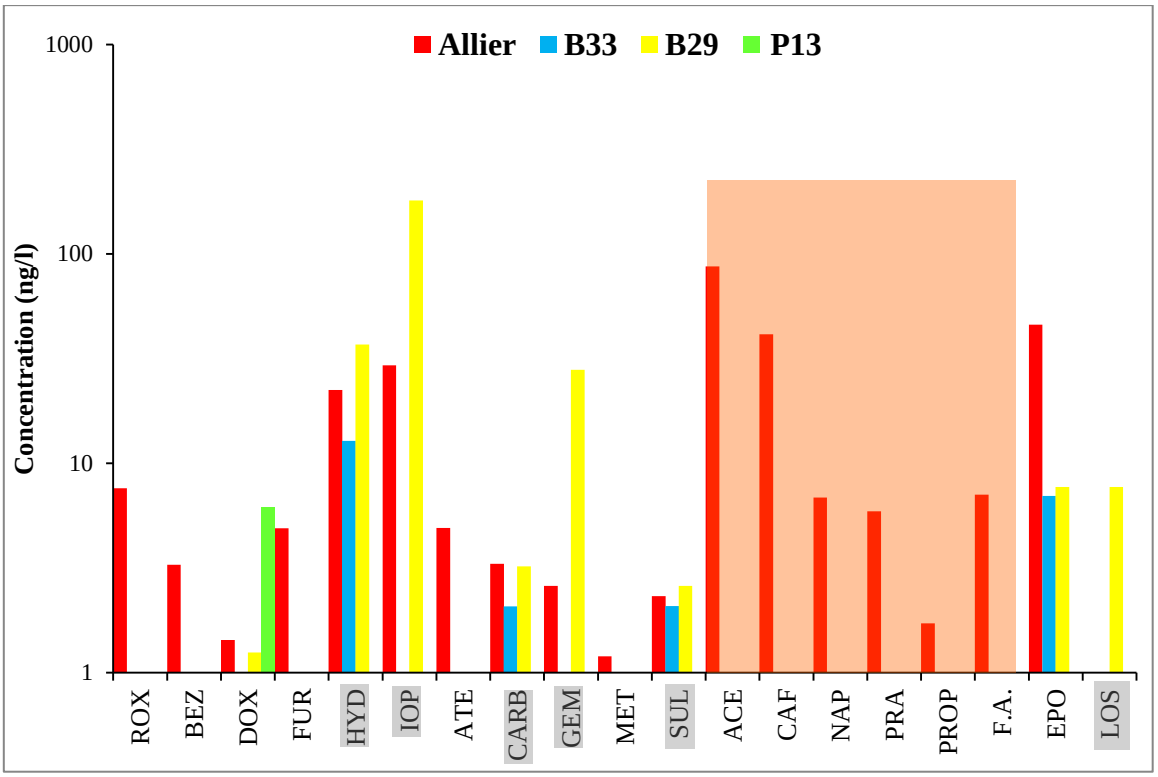

Fig.III-12: Log (concentrations) in Allier River, B33, B29 and P13. Red square gathers the less persistent molecules logically detected only in the Allier River. In grey, PhACs with concentrations higher in B29 than in Allier River.

The less persistent molecules are found only in the Allier River. In the Allier alluvial aquifer, 8 molecules upon the 47 analysed have been positively detected, in the following order of frequency: CARB>SUL>HYD>EPO>DOX (other molecules have been recognized only one time) and with a decreasing mean in the following order: IOP>HYD>GEM>SUL>LOS-EPO.

According to their concentration coupled with their occurrence, 3 PhACs are of importance in Allier alluvial groundwater: CARB, SUL and HYD. ***Carbamazepine*** has been already identified as the most relevant pharmaceutical compound for groundwater infiltration (Loos et al., 2010, Dulio et al., 2009) in accordance with its persistence within the environment as carbamazepine is little subject to degradation and adsorption, either in wastewater treatment or during transition to groundwater (Clara et al., 2004; Preux et al., 2001). Ternes (1998) report elimination rate of 10% in STPs. Vuillet and Cren-Olivé (2011) have measured CARB in 70% of the samples collected in Rhône-Alpes groundwaters with a mean concentration of 10.4 $ng.L^{-1}$. In Spain, Lopez-Serra et al. (2013) have reported concentration up to 115 $ng.L^{-1}$ in an unconfined alluvial system. Concentrations measured in the Allier alluvial aquifer are far lower than these values but CARB is present in 85% of B29 samples and 57% of B33

samples attesting of the importance of this molecule in groundwater. ***Sulfamethoxazole*** has also been detected in groundwater as attesting by the studies of Vuillet and Cren-Olivé (2011) in Rhône-Alpes (mean of 3 $ng.L^{-1}$) and Barnes et al. (2008) in U.S. (mean of 1.11 μg/l). In our study, concentrations of 2.6 $ng.L^{-1}$ and 9.1 $ng.L^{-1}$ have been measured for B29 and B33 respectively. Concentrations in SUL are low and in the same range of order than the Allier River's ones. Concentration of ***hydrochlorothiazide*** in groundwater has, to our knowledge, never been reported in the literature. This pharmaceutical compound is present in 57% of the samples acquired at B33 and presents a mean concentration of 12.8 $ng.L^{-1}$ two times lower than the one measured in the Allier River. Only one positive detection has been achieved in B29.

2.1.3.1. Tracing groundwater origin

The three groundwater sampling points B33, B29 and P13 show nevertheless different behaviour concerning the PhACs. Fig.III-12 highlights these differences. B33 presents concentrations in CARB, SUL, EPO and HYD lower than those of the Allier River in accordance with the fact that this borehole is mainly fed by water coming from the Allier River and that the concentrations of PhACs logically decrease during their transfer through alluvial layers. Concentrations measured at B29 are generally higher than the ones of Allier River. Moreover losartan has been only detected in B29. On the other hand, the only detected PhAc in P13 is DOX, detected 2 times. This quite-absence of pharmaceuticals detected in P13 is due to its particular location, within agricultural fields, and to the origin of the water mainly coming from a southern origin and neither connected to the Allier River nor the neighbouring hills. On the contrary, B29 is both fed by the Allier River, the southern aquifer and the neighbouring hills with a main contribution of the latter two. Obviously, thanks to the results obtained in B33 and P13, the majority of PhACs is coming from the neighbouring hills occupied by small towns and with a poor waste water treatment organisation (Fig.III-13).

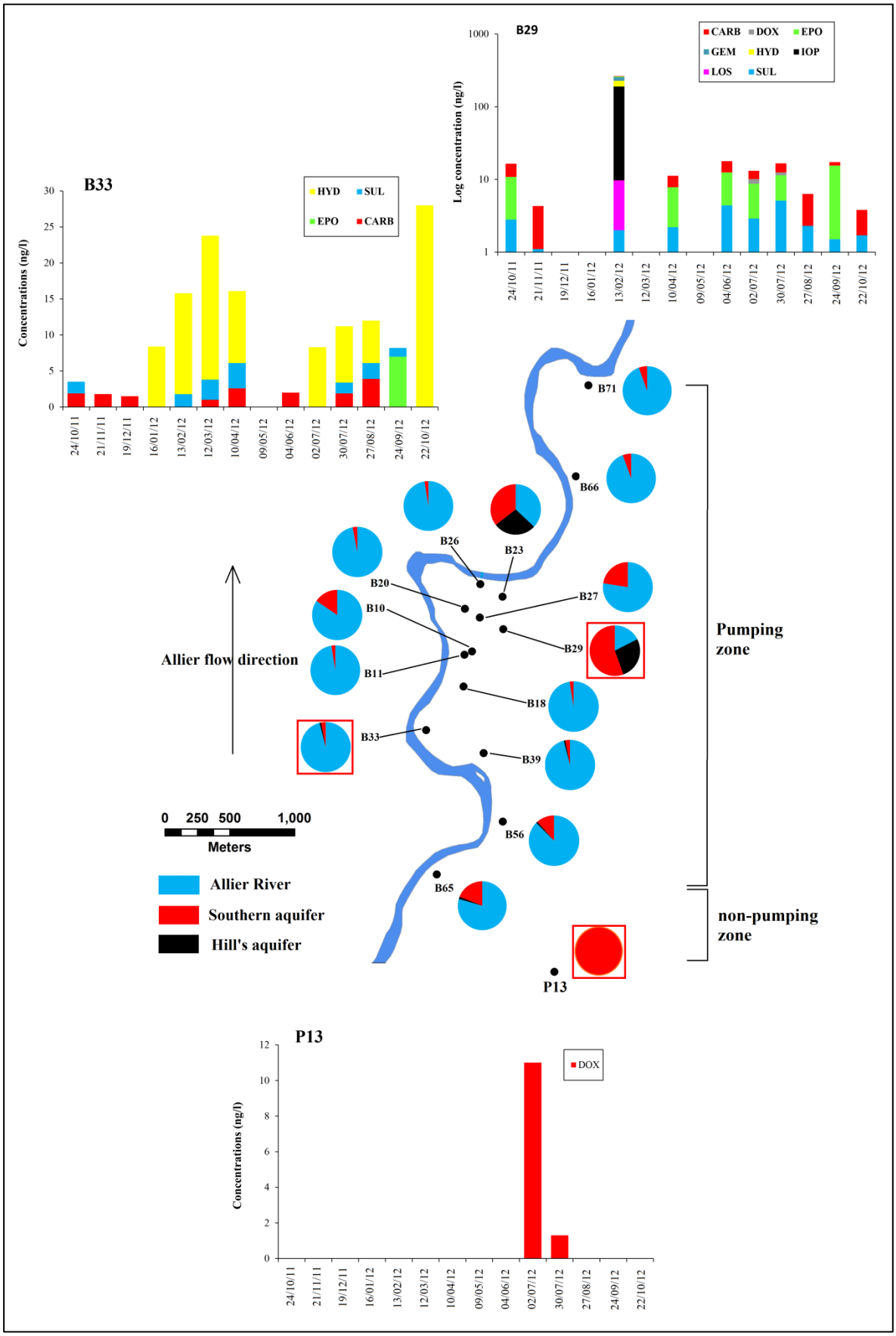

Fig.III-13: PhACs concentration in B33, B29 and P13 and origin of groundwater.

2.2. Predicted concentrations (PECs)

2.2.1. Selection of PhACs

Sixteen among the 47 PhACs analysed have been selected (Table III-5) for they belong to the priority list of the AFSSAPS (French Agency of Sanitary Safety of Food and Health Products, 2008): acetominophen (ACE), amlodipine (AML), atenolol (ATE), caffeine (CAF), carbamazepine (CAR), doxycycline (DOX), epoxycarbamazepine (EPO), fluvoxamine (FLU), furosemide (FUR), hydrochlorothiazide (HYD), ifosfamide (IFO), losartan (LOS), pravastatin (PRA), progesterone (PROG), ramipril (RAM), trimetazidine (TRI). PECs of Caffein and Ifosfamide cannot be determined because no or poor information is available on the consumption on these two molecules: caffeine is mainly due to the consumption of coffee, tea and soft drinks instead of its pharmaceuticals compound (Camacho-Munoz et al., 2010) and ifosfamide is only consumed in hospitals.

Table III.5: Pharmacokinetics parameters of the target PhACs

Name	Therapeutic class	Available without medical prescription	Administration route	Absorption rate a_j (min-max)	Excretion rate e_j (min-max)	Elimination rate in STP F_{step} (min-max)
Acetaminophen (ACE)	pain killer - antipyretic	yes	Oral	1[1,2,3] 0,95[5]	0,59-0,77[1] 0,06[5] 0,85[4]	0,97[5] >0,9[8] 0,99[10] 0,96[13]
			Parenteral	1		
			Rectal	1[1] 0,95[5]		
Amlodipine (AML)	Calcium chanel blocker	no	Oral	1[1,3] 0,64-0,9[2]	0,1[1,2,3,4]	-
Atenolol (ATE)	β blocker	no	Oral	0,50[1,2,3]	1[1,3,4]	0,61[6] 0-0,76[4] 0,58[11] 0,08[10]
			Parenteral	1		
Carbamazepine (CAR)	anti-epileptic	yes*	Oral	1[1] 0,9[5] 0,85-0,9[12]	0,01-0,02[1] 0,03[2] 0,12[5] 0,01-0,03[12]	0[6] 0-0,53[4] 0,03-0,1[7] 0,29[5] 0-0,2[8] -1,21[11] 0,37[12] 0,09[10]
10,11-epoxycarbamazepine (EPO)	Pharmacologically active metabolite of carbamazepine	-	-	-	0,8[5]	0,0185[5]
Doxycycline (DOX)	tetracycline	no	Oral	1[1,2,3]	0,4-0,72[1] 0,72[4]	0,06[4]
			Parenteral	1		
Fluvoxamine (FLU)	selective serotonin reuptake inhibitor	no	Oral	1[1,3] 0,53[5]	0,02[2,3] 0,04[5]	0,63[5]
Furosemide (FUR)	loop diuretic	yes*	Oral	0,65[1] 0,6[2,3]	1[1,4]	0-0,62[4]
			Parenteral	1		
Hydrochlorothiazide (HYD)	thiazid diuretic	no	Oral	0,6-0,8[1] 0,5-0,6[3] 0,65-0,75[2]	0,95[1]	0,23-0,31[7]
Ifosfamide (IFO)	alkilating agent	no (hospital use only)	Parenteral	1	0,12-0,53[2,3] 0,5[9] 0,61[5]	0,03[5]
Losartan (LOS)	angitensin II receptor antagonist	no	Oral	1[1,2,3]	>0,04[1,3] 0,04-0,6[2]	0,88-0,89[7]
Pravastatine (PRA)	HMG CoA reductase inhibitor	no	Oral	0,34[1,3]	0,5[4]	-
Progesterone (PROG)	progestins	no**	Oral	0,99[5]	0,1[5]	0,245[5]
			Dermal	0,1[1]		
Ramipril (RAM)	ACE inhibitor	no	Oral	0,56[1] 0,5-0,6[2,3]	0,02[2,4]	-
Trimetazidine (TRI)	anti-anginal	yes*[n]	Oral	-	-	-

*First dispensation requires medical prescription and only prescribed amount is subsidised. **Except for one pharmaceutical form. [n] Reimbursement stopped since March 2012. [1] www.theriaque.fr, [2] www.drugs.com, [3] www.drugbank.ca, [4] Besse et al. (2008), [5] Ortiz de Garcia et al. (2013), [6] Soulier et al. (2011), [7] Oosterhuis et al. (2013), [8] Joss et al. (2006), [9] Besse et al. (2012), [10] Miège et al. (2009), [11] Vieno et al. (2007), [12] Heberer and Feldmann (2005), [13] Yamamoto et al. (2007).

2.2.2. Calculations of PECs

2.2.2.1. Consumption data

The CPAM (social health care system of Puy-de-Dôme) provided monthly data on subsidised pharmaceuticals molecules in Auzon water catchment. This dataset concerns 91% of the total inhabitants of the Auzon basin (43 833 covered by the national social insurance over a total of 47 930 inhabitants). The dataset comprises the number of packages subsidised by the CPAM which have been bought from October 2011 to October 2012 (Table III-4). Medicines dispensed in hospitals (ifosfamide) and over-the-counter drugs are not included in these dataset.

2.2.2.2. Determination of pharmacokinetic parameters

When consumed, PhACs (Pharmaceuticals Active Compounds) can be absorbed by the digestive tract: a fraction will be eliminated directly by feces while the other will pass into the body. The absorption rate depends on the route of administration. The fraction which is not absorbed is eliminated unchanged. The fraction absorbed can then pass through several metabolisation processes that can be summarized into two steps: phase I and phase II reactions. Phase I reactions correspond to oxidations (hydroxylation, N or S-oxidation, etc) and give metabolites that are different from the parent compounds. These metabolites can show a pharmacological activity. Phase II reactions correspond to conjugations with functional groups which enhance elimination from the body and lower the pharmacological activity of the parent compounds. The main groups are glucuronide and sulfonide whose conjugated metabolites are susceptible to be cleaved in the sewage water and regenerate parent compounds (Heberer and Feldmann, 2005), even if sulfonide ones appears to be more stable (Johnson et al., 2007; Kumar et al., 2012). Glucuronide and sulfonide conjugates should then be considered together with the excreted unchanged parent compound in order to calculate excretion rate.

Pharmacokinetic parameters (absorption, excretion unchanged and glucuro- or sulfo-conjugated, Table III-5) have been determined through a general review that includes www.theriaque.org (official French summaries of products characteristics), www.drugs.com, www.drugbank.ca and literature review (Heberer and Feldmann, 2005; Besse and Garric, 2008; Carballa et al., 2008; Besse et al., 2012; Ortiz de Garcia et al., 2013; Oosterhuis et al., 2013). Injected products were logically set to an absorption rate of 1. When no data is available, the most conservative parameters are taken: absorption and excretion rates are set

equal to 1. For some molecules, excretion rates include glucuro-conjugates but do not consider sulfo-conjugates, eventually leading to an underestimation of excretion.

2.2.2.3. Determination of Fstp (elimination rate in STPs) and environmental parameters

The elimination rates of each PhAC for various type of STPs (Table III-5) were reviewed in the literature (Heberer and Feldmann., 2005; Joss et al., 2006; Vieno et al., 2007; Carballa et al., 2008; Miege et al., 2009; Besse and Garric, 2008; Besse et al., 2012; Soulier et al., 2011; Ortiz de Garcia et al., 2013; Oosterhuis et al., 2013). When no data was available, the most conservative value was taken: the elimination rate was set equal to 0 (i.e. the molecule is not eliminated at all by STP).

The daily flow rates of the Allier and Auzon Rivers have been extracted from www.hydro.eaufrance database (French Ministry of Ecology and Sustainable Development).

2.2.2.4. Model used to calculate PECs

The model used in this publication is adapted from the models proposed by Heberer and Feldmann (2005) and EMEA (2006).

It was assumed that the entire amount of each product subsidised was consumed and that the consumption profile of the 91% of Auzon basin inhabitants covered by national health insurance can be applied to the entire population. Amounts of each PhAC monthly excreted within the Auzon catchment are calculated by equation 1:

$$m_{Auzon,x} = \sum b_j \times u_j \times m_j \times [(1 - a_j) + a_j \times e] \text{ (Equation 1)}$$

where, m_{Auzon} is the total amount of the PhAC excreted during the month x in the Auzon catchment, b_j is the number of packages of formulation j subsidised during the month x in the Auzon catchment, u_j is the number of units per package of formulation j, m_j is the amount of PhAC per unit of formulation j, a_j is the absorption rate for formulation j which depends on the mode of administration, and e is the portion of the PhAC excreted unchanged or as glucuro- and/or sulfo- conjugates after its absorption. For metabolites, $(1 - a_j)$ member has been suppressed from equation 1, since the part of the PhAC that is not absorbed is not metabolized, and m_j member has been divided by the molecular mass of the parent molecule and multiplied by the molecular mass of the metabolite.

The pharmacokinetic parameters may differ from one reference to another (Table III-5). When more than one value is available for at least one pharmacokinetic, a range of predicted amounts excreted annually in the catchment area can be derived from minimum and maximum values by using the equations 2 and 3:

$$m_{Auzon,x,min} = \sum b_j \times u_j \times m_j \times [(1 - a_{j,max}) + a_{j,max} \times e_{min}] \text{ (Equation 2)}$$

$$m_{Auzon,x,max} = \sum b_j \times u_j \times m_j \times [(1 - a_{j,min}) + a_{j,min} \times e_{max}] \text{ (Equation 3)}$$

where, $m_{Auzon,x,min}$ and $m_{Auzon,x,max}$ are respectively the minimum and the maximum amounts of the PhAC excreted during the month x in the Auzon catchment by people covered by the national health insurance, $a_{j,min}$ and $a_{j,max}$ are respectively the minimum and the maximum absorption rate for the formulation j, and e_{min} and e_{max} are respectively the minimum and the maximum excretion rate of PhAC after its absorption.

STP of Cournon treats wastewater of 36000 inhabitants of the Auzon catchment, the amount of PhAC incoming into Cournon's STP is calculated by equations 4 and 5:

$$m_{inf,x,min} = m_{Auzon,x,min} \times \frac{pop.STP}{pop.Auzon} \text{ (Equation 4)}$$

$$m_{inf,x,max} = m_{Auzon,x,max} \times \frac{pop.STP}{pop.Auzon} \text{ (Equation 5)}$$

where $pop.Auzon$ is the number of inhabitants of Auzon catchment covered by national health insurance and $pop.STP$ is the number of habitants linked to the STP of Cournon. Amount of PhAC exiting the STP of Cournon is given by equations 6 and 7:

$$m_{eff,x,min} = m_{inf,x,min} \times (1 - Fstp_{max}) \text{ (Equation 6)}$$

$$m_{eff,x,max} = m_{inf,x,max} \times (1 - Fstp_{min}) \text{ (Equation 7)}$$

where, $Fstp_{min}$ and $Fstp_{max}$ are respectively the minimum and the maximum elimination rates (Table 1) for the same type of STPs as the one installed in Cournon city.

The minimal and maximal PECs for each PhAC incoming into the Allier River is finally calculated by using equations 8 and 9:

$$PEC_{min} = \frac{m_{eff,x,min}}{flow_{AUZON+ALLIER}} \text{ (Equation 8)}$$

$$PEC_{max} = \frac{m_{eff,x,max}}{flow_{AUZON+ALLIER}} \text{ (Equation 9)}$$

where, $flow_{AUZON+ALLIER}$ is the daily flow rates (m^3/s) of Allier and Auzon Rivers measured the day of the corresponding sample.

Environmental degradation and sorption are currently not included in the prediction. Moreover incoming concentrations from the upper Allier Basin is not taken into account. Upstream amounts of labile molecules, such as Acetaminophen, able to reach downstream part are extremely low (Buerge et al., 2003; Kasprzyk-Hordern et al., 2009; Vystavna et al., 2013). However, for conservative molecules, concentrations coming from the upper basin could enhance concentrations at the sampling site.

2.3. Comparison between PECs and MECs

Annual averages of PEC and MECs have been used to calculate PEC/MEC ratios (Fig.III-14, Table III-6) to see if PECs and MECs are in the same order of magnitude. An absence of values within the MECs dataset means an absence of PhACs within the Allier River or a concentration below the quantification limit. To evaluate the impact of these low values annual averages of MECs are calculated: 1) by considering that an absence of measurement corresponds to a concentration equal to 0 $ng.L^{-1}$, 2) by considering that an absence of values corresponds to an absence of measurements (Ter Laak et al., 2010), 3) by attributing to the absent value, a concentration equal to LQ/2 (Choubert et al., 2011), 4) by attributing to the absent value, a concentration equal to LQ (Coetsier et al., 2009).

Table III-6: **PECs, MECs (in ng.L^{-1}) and PEC/MEC ratios**

PhACs	LQ (ng.L^{-1})	nb	Min (ng.L^{-1})	Max (ng.L^{-1})	Mean (ng.L^{-1})	Med (ng.L^{-1})	MEC $_{without0}$	MEC $_{with0}$	MEC $_{LQ/2}$	MEC $_{LQ}$	PEC_{min}	PEC_{max}	PEC	PEC/MEC $_{with0}$	PEC/MEC $_{without0}$	PEC/MEC $_{LQ/2}$	PEC/MEC $_{LQ}$
ACE	10	3	25.0	200.0	87.3	37.0	87,3	18,7	22,6	26,6	1,1	156,8	78,9	4,2	0,9	3,49	2,97
AML	10	0	-	-	-	-	0,0	0,0	5,0	10,0	0,1	0,3	0,2	-	-	0,03	0,02
ATE	1	12	1.3	13.0	4.9	4.2	4,9	4,2	4,3	4,4	1,7	6,8	4,3	1,0	0,9	1,00	0,98
CAF	10	10	11.0	81.0	41.3	37.5											
CAR	1	11	1.2	5.8	3.3	3.3	3,3	2,6	2,7	2,7	0,1	5,4	2,7	1,1	0,8	1,01	1,01
DOX	1	3	1.1	1.8	1.4	1.4	1,4	0,3	0,7	1,1	1,3	2,3	1,8	5,9	1,3	2,59	1,66
EPO	5	1	46.0	46.0	46.0	46.0	46,0	3,3	5,6	7,9	11,8	16,9	14,4	4,4	0,3	2,56	1,81
FLU	5	0	-	-	-	-	0,0	0,0	2,5	5,0	0,0	0,1	0,0	-	-	0,01	0,00
FUR	1	9	1.6	17.0	4.9	2.9	4,9	3,2	3,3	3,5	7,5	15,6	11, 6	3,7	2,4	3,47	3,30
HYD	5	8	11.0	42.0	22.4	18.0	22,3	12,8	13,9	14,9	7,0	8,0	7,5	0,6	0,3	0,54	0,50
IFO	1	0	-	-	-	-											
LOS	5	0	-	-	-	-	0,0	0,0	0,5	1,0	0,3	0,5	0,4	-	-	0,78	0,39
PRA	1	9	1.8	18.0	5.9	3.9	5,9	3,8	4,0	4,2	4,5	4,5	4,5	1,2	0,8	1,14	1,09
PROG	1	0	-	-	-	-	0,0	0,0	0,5	1,0	0,9	0,9	0,9	-	-	1,71	0,86
RAM	5	0	-	-	-	-	0,0	0,0	2,5	5,0	0,6	0,7	0,7	-	-	0,27	0,13
TRI	100	0	-	-	-	-	0,0	0,0	32,1	64,3	1,6	1,6	1,6	-	-	0,05	0,02

Fig.III-14: Temporal evolution of MECs (Measured Environmental Concentrations) and PECs (Predicted Environmental Concentrations). PECmax and PECmin are the maximum and minimum 3 value of PECs when data and pharmacokinetic parameters are available, LQ is Limit of Quantification.

PEC/MEC ratios were used to assess the reliability of PEC calculation over a long period (14 months). This assessment was made on the basis described by Coetsier et al. in 2009:

-if PEC/MEC was in [0.2; 4]: PEC was acceptable.

-if PEC/MEC was less than 0.2: PEC was significantly underestimated.

-if PEC/MEC was more than 4: PEC was significantly overestimated.

-if PEC/MEC was higher than 8: PEC was strongly overestimated.

All the selected PhACs have been sorted by using this classification (Table III-7). Most of them appear to be acceptable thanks the methodology of Coetsier et al. (2009).

Table III-7: Classification of PhACs according to PEC/MEC ratios

$PEC/MEC_{with0}<0.2$	$0.2<PEC/MEC_{with0}<4$	$4<PEC/MEC_{with0}<8$
	ATE, CAR, FUR, HYD PRA	ACE, DOX, EPO
$PEC/MECwithout0<0.2$	$0.2<PEC/MEC_{without0}<4$	$4<PEC/MEC_{without0}<8$
	ACE, ATE, CAR, DOX, EPO, FUR, HYD, PRA	
$PEC/MEC_{LQ/2}<0.2$	$0.2<PEC/MEC_{LQ/2}<4$	$4<PEC/MEC_{LQ/2}<8$
AML, FLU, TRI	ACE, ATE, CAR, DOX EPO, FUR, HYD, LOS PRA, PROG, RAM	
$PEC/MEC_{LQ}<0.2$	$0.2<PEC/MEC_{LQ}<4$	$4<PEC/MEC_{LQ}<8$
AML, FLU, RAM TRI	ACE, ATE, CAR, DOX EPO, FUR, HYD, LOS PRA, PROG	

2.3.1. Pravastatin

PEC/MEC ratios are comprised between 0.77 and 1.19 and show a good correspondence between PECs and MECs at an annual scale. Fig.III-14 presents the evolution of MEC, PEC and LQ (Limit of Quantification) of pravastatine for the October 2011-October 2012 period. The two curves are characterized by similar shapes, MECs presenting however bigger amplitudes. This marginal difference could be explained by calculations method that includes mass of PhAC rejected through the whole month and then attenuates daily variations of PECs whereas MECs consist of punctual measurements. As information on the PRA's (bio) degradability is not available, inputs of PRA from the upper Allier basin, before the connection between the Allier and the Auzon Rivers, can be implied and explain the slightly higher MECs.

2.3.2. Acetaminophen

PEC/MEC ratios indicate an acceptable correspondence between PECs and MECs with values comprised between 0.90 and 4.22 with a general overestimation. Fig.III-14 shows the evolution of MEC, PEC_{min}, PEC_{max} and LQ of ACE. Differences quoted between PEC_{min} and PEC_{max} can be explained by excretion parameter (Table III-6) that varies from 0.06 to 0.85. MECs of ACE vary between PEC_{min} and PEC_{max} and present an evolution that differs significantly from the calculated concentrations. Only three positive measurements have been achieved for this molecule at the Allier sampling site. This could be explained by the behaviour of acetaminophen within the environment as this molecule is recognized as a non-persistent one (Lam et al., 2003; Loffler et al., 2005; Yamamoto et al., 2009) or most probably by an uncompleted consumption of sold medication.

2.3.3. Hydrochlorothiazide

PEC/MEC ratios dataset, varying from 0.33 to 0.59, is consistent whatever the method of calculations selected and shows a clear underestimation of PECs compare to MECs. Fig.III-14 highlights MEC, PEC_{min}, PEC_{max} and LQ of hydrochlorothiazide evolutions. Same peaks are observed on the three concentration curves, PECs presenting attenuated evolution. This underestimation could be explained by a wrong evaluation of the pharmacokinetic parameters. As no information about the persistence of hydrochlorothiazide in the environment is available, to our knowledge, supply by the upper part of the Allier basin could also be suspected and generate MECs above PECs.

2.3.4. Doxycycline

PEC/MEC ratios of doxycycline vary from 1.26 to 5.9 and highlight the significant overestimation of PECs compare to MECs. Fig.III-14 presents the same trends, doxycycline has been measured only three times during the whole period of sampling and peaks do not correspond to PECs ones. This molecule is considerably affected by biodegradation (Kümmerer and Cunningham, 2006) and photoreaction (Kummerer, 2009) that could partly explain the difference observed.

2.3.5. Carbamazepine and epoxycarbamazepine

PEC/MEC ratios for carbamazepine show a good correspondence between PECs and MECs as the values vary between 0.83 and 1.05. Generally, PEC_{min} are slightly underestimated and PECmax are slightly overestimated (Table III-6, Fig.III-14). MECs evolve between PECmin

and PEC_{max} curves and present the same shape. The model of calculation is then clearly adapted to evaluate PEC of carbamazepine, marginal difference could be corrected with a best fitting of excretion and elimination parameters. This molecule is well-known to be persistent in the environment; an input from the upper Allier basin should be taken into account. Nevertheless, as the consumption of carbamazepine is really low, it is probable that the concentration before the junction between Allier and Auzon Rivers is highly diluted by the Allier River.

Epoxycarbamazepine that is a metabolite of carbamazepine does not follow the same scheme. Only one positive measurement has been achieved during the sampling period and even does not match the PEC calculated for the same time (Table III-6, Fig.III-14). Evaluation of Epoxycarbamazepin through PEC calculations seems to be difficult.

2.3.6. Atenolol

This molecule presents the same behavior than the one of carbamazepine: good correspondence of PECs and MECs are shown both by PEC/MEC ratios that vary from 0.87 to 1.02 (Table III-6) and by Fig.III-14 that presents the evolution of MEC of atenolol between PEC_{min} and PEC_{max}, concentrations curves evolving similarly. Moreover, literature on the persistence of this PhAC reports a half-life up to 166 days (Liu and Williams, 2007; Yamamoto et al., 2009), concentrations of atenolol measured at the investigated site should include incomes from the upper part of the Allier Basin, before the connection with Auzon River. The same conclusion can be achieved for this pharmaceutical with a possible best fitting by modifying excretion and elimination parameters thanks to observations.

2.3.7. Furosemide

PEC/MEC ratios give values comprised between 2.36 and 3.67 (Table III-6). These values are close to the limit value of 4 imposed by Coetsier et al. (2009). MECs curve (Fig.III-14) presents the same shape as PEC_{min} and PEC_{max} curves but is clearly below the two latters. This could imply either an uncompleted use of medicine prescribed either a degradation of FUR within the environment. According to the literature review achieved during this study, no data is available on elimination rate of this molecule in surface water, PBT profiler gives a DT50 equal to 60 days. This seems in accordance with an uncompleted used of this molecule after being sold. This conclusion should be verified and completed with further experimentation on this molecule.

2.3.8. Other molecules

AML, FLU, LOS, PROG, TRI have not been detected in the Allier River during the sampling campaign. PECs have been compared, for these five molecules, to LQ or LQ/2. For AML, FLU and TRI, PEC/MEC ratios are lower than 0.2 indicating that PECs are underestimated compare to the evaluate MECs. AML and FLU present low consumption patterns in the Auzon basin (Table III-6) and concentrations in the Allier River are certainly lower than LQ or even LQ/2. Concentrations of RAM seem to be closer to LQ/2 (Table III-6) as $PEC/MEC_{LQ/2}$ is comprised between 0.2 and 4. Quantification limit of TRI is high (100 $ng.L^{-1}$, Table III-3), explaining the absence of detection of this molecule during the sampling campaign. Concentrations of this molecule should be lower than LQ. At last, estimation of MECs of LOS and PROG by LQ or LQ/2 seems to be in good agreement with PECs.

3. Agricultural pesticides and chemical fertilizers

Modern agriculture depends on the addition of fertilizers and pesticides to improve production methods. Ubiquitous in today's farming culture, pesticides are used to protect the crops against weeds (herbicides), fungal parasites (fungicides), insects (insecticides) and slugs and snails (molluscicides). Fertilizers can be either in an organic or a chemical form, and supply cropland with nutrients such as nitrogen, potassium and phosphorous which are vital for plant growth. Synthetic fertilizers, in particular, increase yield and productivity of agricultural products by supplying excess nutrients to agricultural soils (Cazalas et al., 2004). Not surprisingly, the current agricultural practice is considered to be the main source of surface and groundwater pesticides contamination in both Europe (E.E.A., 2000; Tappe et al., 2002; IFEN, 2002) and North America (Thurman et al., 1994; Kolpin et al., 1998, 2004). Moreover, run-off (leaching) from agricultural fields has been shown to impact both aquatic and terrestrial ecosystems and degrade the quality of groundwater destined for human consumption (Horrigan et al., 2002; Gregory et al., 2002; Aelion and Conte, 2004). Such anthropogenic sources of drinking water contamination constitute a major problem in both developing and industrialized countries around the world (Tilman et al., 2002; Camargo and Alonso, 2006; Nas and Berktay, 2006; Vryzas et al., 2012; Reilly et al., 2012; Hermosin et al., 2013). Beside agriculture, there are several other sources of pesticides in the environment. For example, they are used as a means of maintaining pavements, parks, sports facilities, production and industrial and urban applications (Denham and White, 1998). Globally, about 2.5 million tons of pesticides are sprayed onto cultivated land per year (Bergstrom and Stenstrom, 1998; Centner, 1998). In the late 1990s, about 500 10^6 kg of pesticides were sprayed annually in Europe (Candela, 2003). This corresponds to an average pesticide dose of 4.4 kg/ha (Candela, 2003). In France, about 19 million hectares of crops are sprayed annually with pesticides, i.e. 35% of the total surface area of France.

Pesticides as well as nitrogen and phosphorous detections in surface and groundwater have created a concern about quality status of drinking water supplies (Spalding and Exner, 1993; Welch et al., 2011). Intrinsic factors such as high precipitation, shallow water tables, sandy soil, and high pesticides and/or fertilizers usage may contribute to the high contamination potential (Novak et al., 1998). The observed contamination is the result of the large quantities used, the mobility and molecules in the environment, and the increasingly sensitive analytical techniques used to detect and measure them. Concerning pesticides, the presence of degradation products in significant quantities is of importance as metabolites may be as toxic as parent compounds (Reddy et al., 1997). Pathways of fertilizers are better known than

pesticides'ones. As soon as they are applied to soils, they are subjected to numerous chemical, physical and biological processes (Puckett and Hughes, 2005). Nitrogen fertilizers contain nitrogen in one of three forms: ammonium (NH_4^+), nitrate (NO_3^-) or urea ($CO(NH_2)_2$). The activity of soil microbes usually means that, whatever form of fertilizer is used, the end product in the soil is always nitrate (Chowdary et al., 2005; Almasri, 2007). This microbial process, known as nitrification, is very important because it happens in most soils, particularly when the soil is moist and reasonably warm, as well as is sufficiently rapid to convert most ammonium or ammonium-yielding fertilizers to nitrate within two or three weeks (Cazalas et al., 2004). Anthropogenic sources of nitrogen include: 1) punctual source including industrial sewage, refuse dumps, etc., discharged directly into the surface water, 2) diffuse sources including runoff and leaching from rural and urban land, and 3) precipitation (Kumar and Anderson, 1993). Nitrate can react in four different ways in the soil: uptake by crop, immobilizer soil organic matter, destroyed by microbes or leached in groundwater. Leaching, which is explained by Blackmer (1988), is the mechanism of nitrogen loss that poses the greatest threat to groundwater supplies. Consequently, nitrate concentration in groundwater can be very high and constitutes a major pollution for drinking water (Horrigan et al., 2002; Fewtrell, 2004). Water from rain or irrigation carry nitrate when it percolates through the soil. In fact, besides being extremely soluble, nitrate does not adhere to the surfaces of the particles in most soils. At these latitudes, the clay particles carry on overall negative charge. Thus, negatively charged ions such as nitrate are repelled and more vulnerable to being washed out in groundwater whereas positively charged ions such as ammonium are strongly attracted to clay particles and more vulnerable to erosion. However, this erosion of ammonium in surface water is not frequent because ammonium is very easily and rapidly transformed into nitrate by the process of nitrification in the soil (Addiscott, 1991; Blackmer, 1988). The control of nitrate leaching to aquatic systems continues to be an important legislative requirement in Europe, with instruments such as the Nitrates Directive (91/676/EEC 1991) and Water Framework Directive (2000/60/EC 2000) requiring limits on nitrate concentrations in surface water and groundwater.

Due to this concern, a monitoring survey has been established to evaluate the occurrence of pesticides and fertilizers in both surface and groundwater from the Allier alluvial aquifer since this area is under agricultural and animal production practices. Determination of pesticides and fertilizers in the shallow alluvial aquifer of the Allier River is important because of the heavy reliance of shallow groundwater as a drinking water source. Four

sampling points have been selected: Allier River as the main recharge source of the alluvial aquifer, B33 close to Allier River, B29 close to the hills in the eastern side of the alluvial system (extensively used for agricultural activities), and piezometer P13 directly surrounded by agricultural lands. Fifty-six water samples (14 for each point) have been collected on 4-weeks basis from October 2011 to October 2012. Our objective is to assess the occurrence and the concentrations of pesticides (and their metabolites) as well as fertilizers (NO_3^-, K^+, PO_4^{-2}, and NH_4^+) in the Allier alluvial hydrosystem.

3.1. Pesticides in surface and groundwater

3.1.1. Pesticide detections in Allier River

The presence of pesticides in surface water is affected by pesticide usage volume and transport characteristics within surface water systems, and weather pattern (Stover and Hamill, 1994). Pesticides can be transported in water in dissolved form or with suspended sediment arising from soil erosion (Leonard, 1990). The Allier basin is distinguished by extensive application of various agricultural activities that they may significantly contribute to excessive pesticide compounds into Allier water. Among the 383 pesticides analysed, 22 different pesticide compounds (16 herbicides, 5 fungicides, and 1 insecticide) are detected in water samples from Allier River (Table III-8). The analytical results of pesticides in surface and groundwater are presented in Appendix D.

The results show that the compound concentration ranges between 0.006 and 0.15µg/l with the following order: AMPA> Tributyl phosphate >Metolachlor> Alachlor> Glyphosate> Pymetrosine.

The maximum concentration measured is for ***AMPA***, a metabolite of glyphosate herbicide. AMPA has a greater environmental persistence (half-life in soil: 76-240 days; Battaglin et al., 2005) than glyphosate (half-life in soil: 2-197 days; Battaglin et al., 2005). Hence, AMPA has been detected more frequently (3 times) than glyphosate (only one time) in this study. Maximum concentrations of AMPA (0.150µg/l) and Tributyl Phosphate (0.138 µg/l) exceed the regulatory level of 0.1µg/l (EU Directive 98/83/EC). According to French regulations, in untreated water used to produce drinking water, the quality limits are 2µg/l per individual substance and 5µg/l for all pesticides together (IFEN, 2001). The AMPA has been frequently detected in the last few years in French streams (IFEN, 2002; Botta et al., 2009), Argentina (Aparicio et al., 2013), and USA (Koplin et al., 2004). Botta et al. (2009) detected very high concentrations of AMPA (75- 90µg/l) in the Orge river (France), connected to storm sewer.

Concentrations up to 3.9µg/l of AMPA have been detected in USA streams by Koplin et al. (2006).

The most ubiquitous compounds in all the samples from the Allier River are: diflufenican (herbicide, Detection Frequency of 50% of the analysed samples, maximum concentration: 0.012 µg/l), AMPA (metabolite of herbicide, Detection Frequency of 21%, maximum concentration: 0.15 µg/l), diuron (herbicide, Detection Frequency of 21%, maximum concentration: 0.017 µg/l), and carbendazim (fungicide, maximum concentration: 21%, maximum concentration: 0.008 µg/l).

The continuous detection of ***diflufenican*** in Allier River may be either due to extensively use as a systematic herbicide commonly used in culture of wheat in France (0.125 kg/h; Gianessi et al., 2003), or due to high persistence in water with a half-life of 180 days. This herbicide is also frequently detected in surface water with concentration generally higher than those recorded in the Allier River: up to 1.16µg/l in Guadalquivir River, Spain (Hermosin et al., 2013), and up to 0.1µg/l Vemmenhog catchment, Sweden (Kreuger, 1998).

Diuron is both mobile and relatively persistent, and is therefore prone to off-site movement in surface runoff, and migration to groundwater (Andrieux et al., 1997). As a consequence, this herbicide, banned in France in December 2008 in application of the EC directive 2007/417/EC, is detected three times in the Allier River, with low concentrations that range between 0.008 and 0.017 µg/l, and a mean value of 0.011 µg/l. This herbicide has been detected frequently in french surface water (IFEN, 2002). Higher concentrations of diuron have been recorded in Neste River, France with a maximum value of 0.35 µg/l by Morin et al. (2009); in Vemmenhog catchment, Sweden with a maximum value of 0.2 µg/l by Kreuger (1998); in Guadalquivir river basin, Spain with concentrations between 0.01 and 20.9 µg/l and mean value of 2.36 µg/l by Hermosin et al. (2013).

Carbendazim is a widely used broad-spectrum benzimidazole fungicide playing an important role in plant disease control as the systemic (European Commission, 2007). Typically, carbendazim is applied to control a broad spectrum of diseases on arable crops (e.g. cereals, oilseed rape), fruits and vegetables, usable is also in post-harvest food storage and as a seed pre-planting treatment (European Commission, 2007). Its half-life is 8-32 days in soils and 2-25 months in water, depending on the temperature and pH (Solel et al., 1979). In this study,

carbendazim has been detected only 3 times with very low concentrations (mean value of 0.007 µg/l).

The rest of compounds are detected mostly once or twice at trace levels during the study period. This could be due to: low quantity applied, short half-life within the environment or low water solubility. All the water samples, except for the 19/12/11 and 16/1/13, are characterized by a simultaneous occurrence of pesticides and their metabolites. Atrazine is detected in one sample at very low level (0.009 µg/l), despite the fact that it was banned in 2003. Probably its presence in surface water is due to the high inertia of this contaminant (Giuliano, 1995). These results are generally in good agreement with those given by French Minister of Agriculture Report (IFEN, 2002).

Fava et al. (2010) stated that pesticide contamination in surface water is seasonally dependent and generally short-lasting. As displayed in Fig.III-15, significant seasonal variations of pesticide concentrations are observed with a marked peak at the beginning of spring and during summer in relation with the application periods. No pesticides molecules have been detected in December and January.

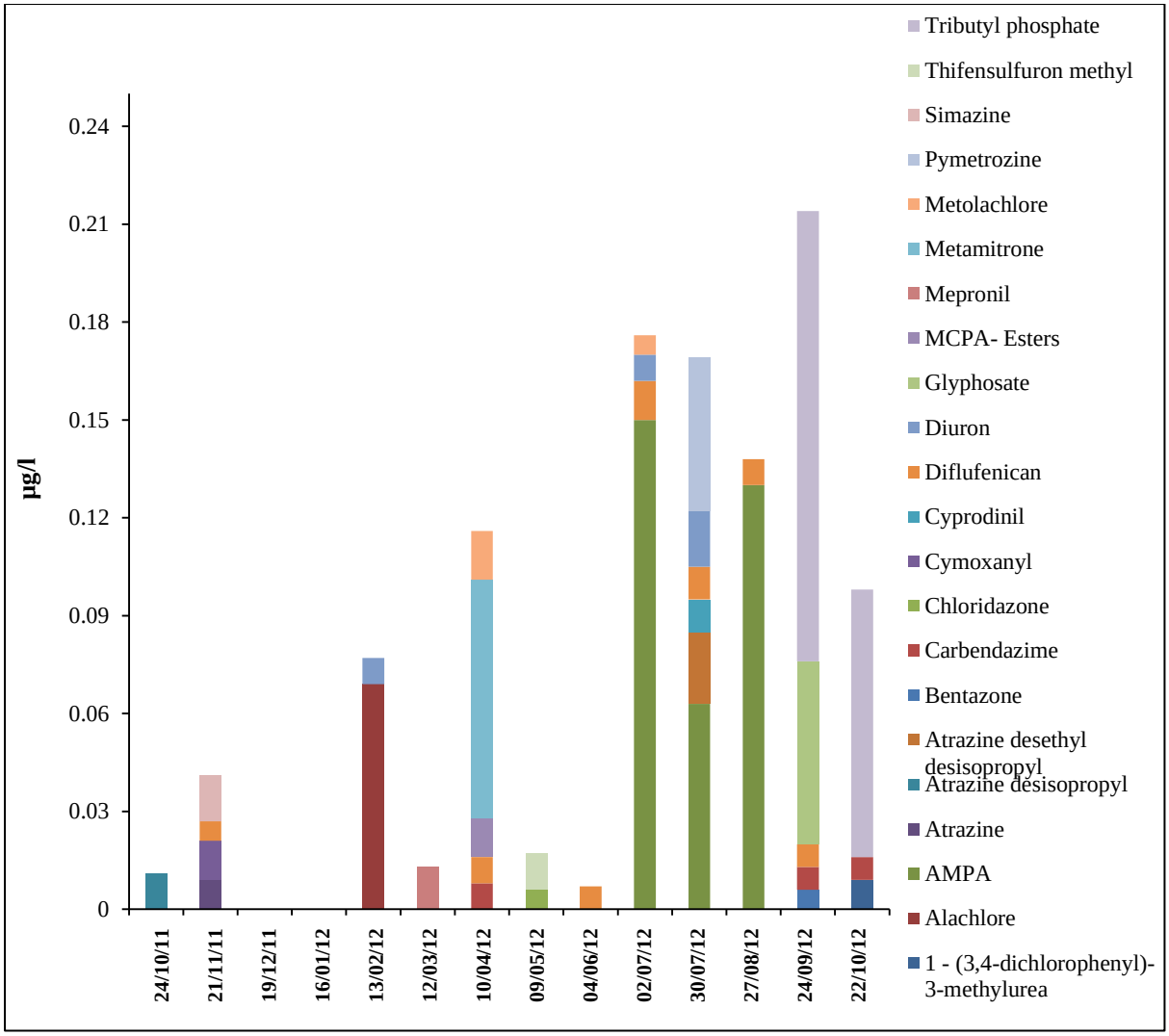

Fig.III-15: Temporal variation of detected pesticides from Allier River

Table III-8: Statistical analyses (detection frequency, minimum, maximum, and mean values) of detected pesticides in Allier River, B33, B29 and P13

Pesticide compounds		AB	Use	LQ	Allier River				B33				B29				P13			
					Surface water				pumping boreholes close to the river				pumping boreholes close to the hills				non-pumping piezometer			
					DF%	Min	Max	mean	DF%	Min	Max	mean	DF%	Min	Max	mean	DF%	Min	Max	mean
					%	µg/l	µg/l	µg/l	%	µg/l	µg/l	µg/l	%	µg/l	µg/l	µg/l	%	µg/l	µg/l	µg/l
1	1 - (3,4-dichlorophenyl)-3-methylurea	DCPMU	Herbicide		7	0.009	0.009	0.009	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
2	Atrazine	ATZ	Herbicide		n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	71	0.009	0.016	0.012	n.d	n.d	n.d	n.d
3	Alachlor	ALC	Herbicide		7	0.069	0.069	0.069	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
4	AMPA	AMPA	Herbicide		21	0.063	0.150	0.114	7	0.140	0.140	0.140	n.d	n.d	n.d	n.d	7	0.077	0.077	0.077
5	Atrazine desethyl	ADE	Herbicide		7	0.009	0.009	0.009	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	28	0.027	0.032	0.030
6	Atrazine desethyl desisopropyl	ADI	Herbicide		7	0.022	0.022	0.022	7	0.071	0.071	0.071	n.d	n.d	n.d	n.d	14	0.026	0.041	0.034
7	Atrazine desisopropyl	ADID	Herbicide		7	0.011	0.011	0.011	7	0.006	0.006	0.006	28	0.006	0.013	0.008	14	0.007	0.061	0.034
8	Azamethiphos	AZA	Insecticide		n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	7	0.016	0.016	0.016
9	Bentazone	BTZ	Herbicide		7	0.006	0.006	0.006	7	0.006	0.006	0.006	7	0.006	0.006	0.006	7	0.006	0.006	0.006
10	Carbendazim	CBZ	Fungicide		21	0.007	0.008	0.007	7	0.007	0.007	0.007	7	0.009	0.009	0.009	n.d	n.d	n.d	n.d
11	Chloridazon	CLZ	Herbicide		7	0.006	0.006	0.006	n.d	n.d	n.d	n.d	7	0.006	0.006	0.006	n.d	n.d	n.d	n.d
12	Cymoxanil	CYM	Fungicide		7	0.012	0.012	0.012	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
13	Cyproconazole	CYP	Fungicide		n.d	n.d	n.d	n.d	7	0.005	0.005	0.005	7	0.007	0.007	0.007	n.d	n.d	n.d	n.d
14	Cyprodinil	CYPL	Fungicide		7	0.010	0.010	0.010	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
15	Dichlorvos	DDVP	Insecticide		n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	7	0.016	0.016	0.016	n.d	n.d	n.d	n.d
16	Diflufenican	DFF	Herbicide		50	0.006	0.012	0.008	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	7	0.008	0.008	0.008
17	Diuron	DCMU	Herbicide		21	0.008	0.017	0.011	7	0.006	0.006	0.006	n.d	n.d	n.d	n.d	7	0.008	0.008	0.008
18	Foramsulfuron	DMTD	Herbicide		n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	7	0.01	0.01	0.01	n.d	n.d	n.d	n.d
19	Glyphosate	GLP	Herbicide		7	0.056	0.056	0.056	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
20	Hexaconazole	HEX	Fungicide		n.d	n.d	n.d	n.d	7	0.005	0.005	0.005	n.d	n.d	n.d	n.d	7	0.016	0.016	0.016
21	MCPA- Ester	MCPA	Herbicide		7	0.012	0.012	0.012	7	0.013	0.013	0.013	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
22	Mepronil	MEP	Fungicide		7	0.013	0.013	0.013	n.d	n.d	n.d	n.d	7	0.009	0.009	0.009	n.d	n.d	n.d	n.d
23	Metamitron	MET	Herbicide		7	0.073	0.073	0.073	n.d	n.d	n.d	n.d	14	0.028	0.096	0.062	n.d	n.d	n.d	n.d
24	Metolachlor	MTLC	Herbicide		14	0.06	0.015	0.011	n.d	n.d	n.d	n.d	14	0.013	0.038	0.026	n.d	n.d	n.d	n.d
25	Piperonyl butoxide	PBO	Insecticide		n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	14	0.011	0.019	0.016
26	Pymetrozine	PYM	Insecticide		7	0.047	0.047	0.047	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
27	Quizalofop	QE	Herbicide		n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	7	0.013	0.013	0.013
28	Sebuthylazine	SEB	Herbicide		n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	7	0.006	0.006	0.006
29	Simazine	SIM	Herbicide		7	0.014	0.014	0.014	n.d	n.d	n.d	n.d	28	0.012	0.02	0.014	7	0.011	0.011	0.011
30	Sulfosulfuron	SFS	Herbicide		n.d	n.d	n.d	n.d	7	0.006	0.006	0.006	14	0.016	0.026	0.021	7	0.017	0.017	0.017
31	Thifensulfuron methyl	TFM	Herbicide		7	0.011	0.011	0.011	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
32	Thiodicarb	TDC	Acaricide		n.d	n.d	n.d	n.d	7	0.006	0.006	0.006	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
33	Tributyl phosphate	TBP	Fungicide		14	0.082	0.138	0.110	n.d	n.d	n.d	n.d	21	0.060	0.086	0.069	14	0.092	0.098	0.095
34	Triflumuron	TRF	Insecticide		n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	7	0.007	0.007	0.007	n.d	n.d	n.d	n.d

3.1.2. Pesticide detections in groundwater

3.1.2.1. Borehole B29

Table III.8 reports the results obtained on B29 samples: 15 different pesticide compounds (9 herbicides, 4 fungicides and 2 insecticides) have been detected. Atrazine (ATZ) is by far the most detected contaminant and appears in 10 out of 14 water samples. Simazine (SIM) comes next and is positively measured in 5 water samples. Concentrations are quite low: 0.009 to 0.016 µg/l (ATZ) and 0.012 to 0.02 µg/l (SIM). Atrazine desisopropyl, the metabolite of atrazine, was detected in 4 samples with maximum concentration of 0.013 µg/l, and Tributhyl phosphate was detected in only 3 samples of this borehole but in higher concentrations up to 0.086 µg/l.

Atrazine [2-chloro-4-(ethylamino)-6-isopropylamino-1,3,5-triazine] is a widely used herbicide for its benefits in controlling weeds and increasing the yield of agricultural products, especially for corn. ATZ and its degradation products (desethylatrazine or DEA; deisopropyl atrazine or DIA) are common contaminants of groundwater in agricultural regions of the United States (Kolpin et al., 1996), France (IFEN, 2001), Italy (Fava et al., 2010), Germany (Guzzella et al., 1996), China (Geng et al., 2013) and Gaza strip (Shomar et al., 2005). Simazine (2-chloro-4,6-bis(ethylamino)-1,3,5-triazine) is a synthetic herbicide used for pre-emergence control of broad-leaf weeds and annual grasses in agricultural and non-crop fields (Sprynskyy et al., 2008; Carlson et al., 2006). It is the second most commonly detected pesticide in surface and groundwater in the USA, Australia and Europe (Ignatowicz-Owsieniuk and Skoczko, 2002), causing much concern due to its carcinogenic potential (Chen et al., 2004). SIM and its metabolites have been extensively monitored worldwide (Gunasekara, 2004), in USA (concentration of 3.8µg/l in groundwater of California; Spurlock et al., 2000), in Denmark (concentrations <0.1 µg/L; Spliid and Koppen, 1998). Concentrations measured in this study on ATZ and SIM are in good agreement with those given by French Minister of Agriculture Report which stated that ATZ (and metabolites) and SIM are among the most detected pesticides in groundwater throughout France (IFEN, 2002). These two pesticides have been banned by French Minister of Agriculture since 2003. This continued detection suggests a stock of this compound in the soil and/or unsaturated zone (high persistence) that could be partly mobilized during infiltration. Detection of atrazine in B29 for 10 months is greater than the reported ATZ half-life of 101-147 days (Zacharias et al., 1991) but is consistent with reports of Klint et al. (1993) who do not found any atrazine's degradation in groundwater after 593 days of incubation in a laboratory batch experiment.

Vonberg et al. (2014) detected ATZ continuously for 20 years in the Quaternary aquifer of Rhine, Germany, with concentrations close to the threshold of 0.1µg/l, despite the fact that ATZ was banned in Germany in 1991. Higher ATZ concentrations are observed from Ebro River alluvial aquifer, Spain with a maximum level of 0.33 µg/l reported by Herrero-Hernández et al. (2013).

All the detected pesticides content were below EU regulation of drinking water limits 0.1 µg/l. However, ***metamitron*** has been detected with a concentration close to the limit (0.096 µg/l) on the 2/7/12. None of the water samples exhibits total concentrations higher than the EU limit of 0.5 µg/l set for drinking water. At least one pesticide compound was observed in each water sample from B29, except for the 04/06/2012 campaign. The number of pesticides detected reaches six for the campaign of the 22/10/2012.

Groundwater pesticides contamination is less or at all seasonal-dependent (Fava et al., 2010). However, groundwater from B29 displays more pesticide detection during summer and autumn compare to winter and spring (Fig.III-16). ATZ concentrations, for example, are lower in winter/autumn than those of summer. This was already observed by Baran et al. (2007) in Brévilles agricultural catchment (France). Intensive agricultural activities in the hills and in the southern part of the aquifer are believed to be the main source of pesticide contamination rather than from Allier River. The pumping process makes the waters, and its contaminants, circulating to B29.

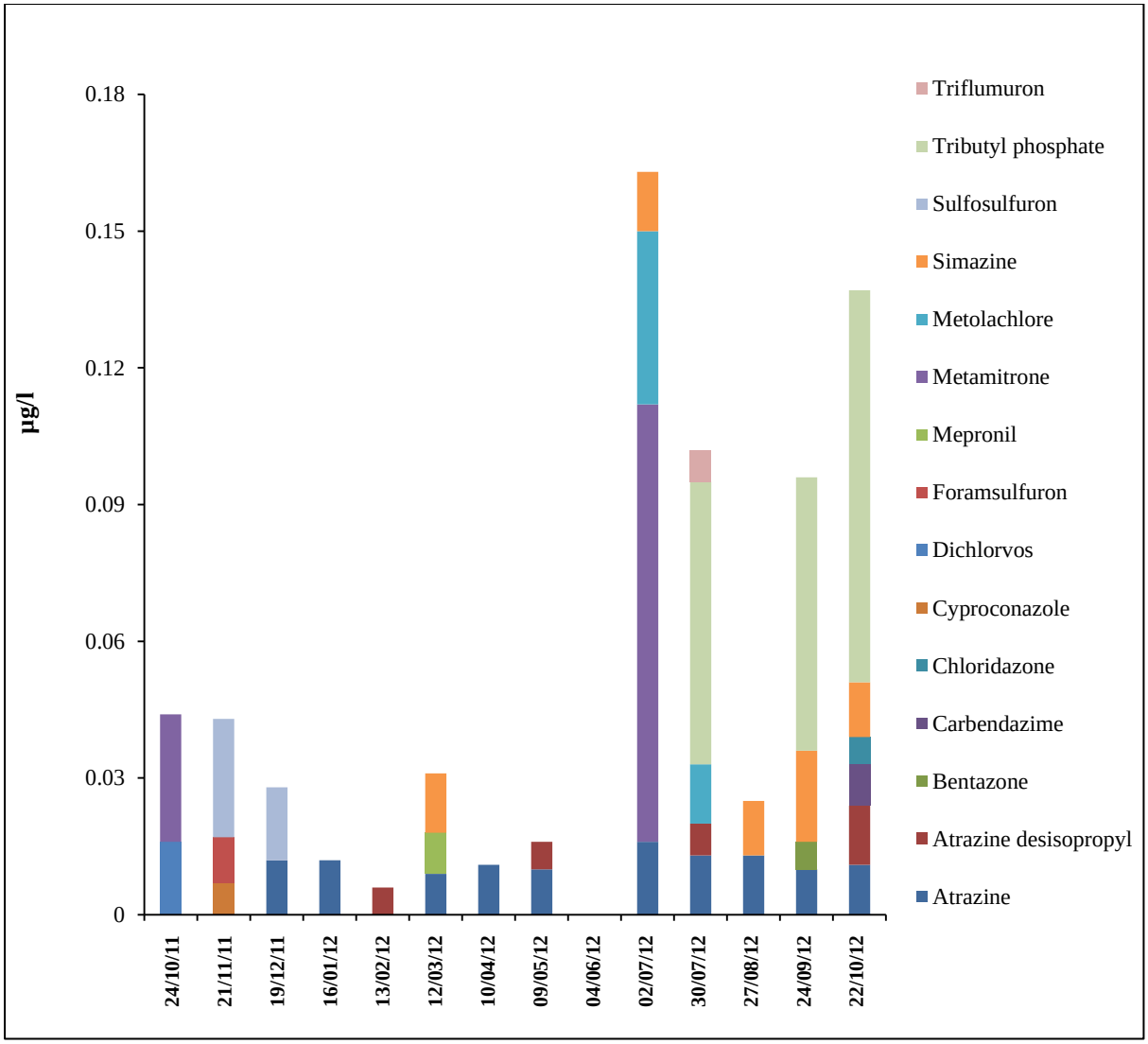

Fig.III-16: Temporal variation of detected pesticides from borehole B29

3.1.2.2. Borehole B33

Concerning borehole B33, 11 different pesticide compounds (7 herbicides, 3 fungicides, and 1 acaricide) are detected in this borehole as shown in Table III-8. Each of these compounds is detected only one time during the study period. Only 50% of the water samples collected at this borehole during the study period contains pesticides (no pesticides or below the quantification limits of analytical methods). The detected pesticides are all in trace level much lower than EU drinking water limit of 0.1 µg/l, ***AMPA*** excepted (0.14 µg/l on the 13/2/12). Seasonal variation in pesticide is not clear in B33 (Fig.III-17), as a peak of AMPA is observed on the 13/2/12. Allier River is considered to be the main source of contaminants with a possible retention or delay within the bank of the Allier River or within the alluvial system itself through adsorption or microbiological processes.

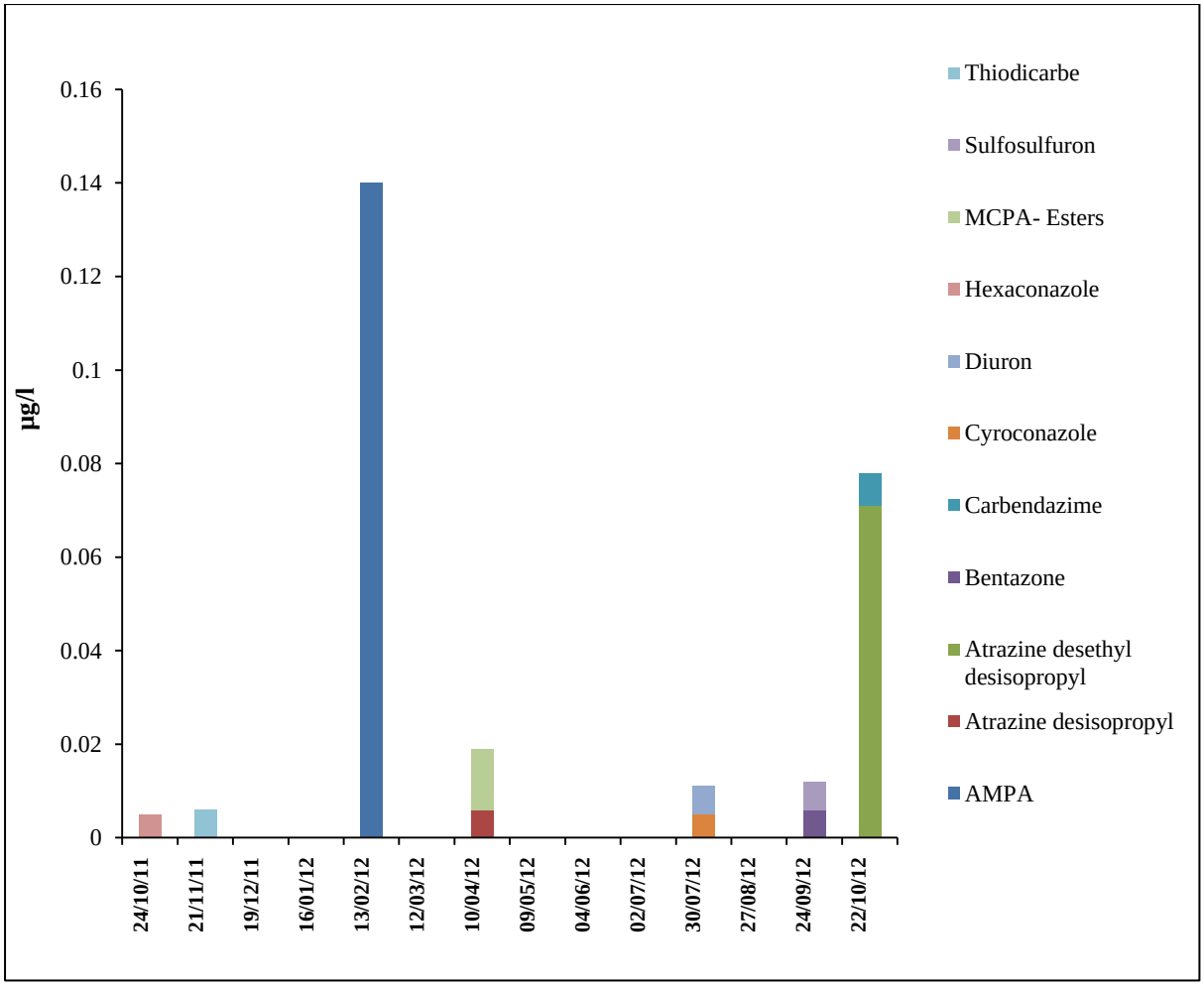

Fig.III-17: Temporal variation of detected pesticides from borehole B33

3.1.2.3. Piezometer P13

In total, 15 various pesticide compounds (11 herbicides, 2 fungicides, and 2 insecticides) have been detected in P13. The highest concentration (0.032 µg/l on the 24/9/12) has been recorded for ***atrazine desethyl***, the main metabolite of atrazine (Table III-8). ***Tributyl phosphate*** is observed in only two samples but present the highest concentration compare to other compounds with values reaching 0.098µg/l. Ten water samples present at least one pesticide, seven have been measured on the 22/10/2012. Seasonal variations follow the same behaviour than the Allier River and B29 with high concentrations in summer/autumn and low concentrations in winter/spring (Fig.III-18).

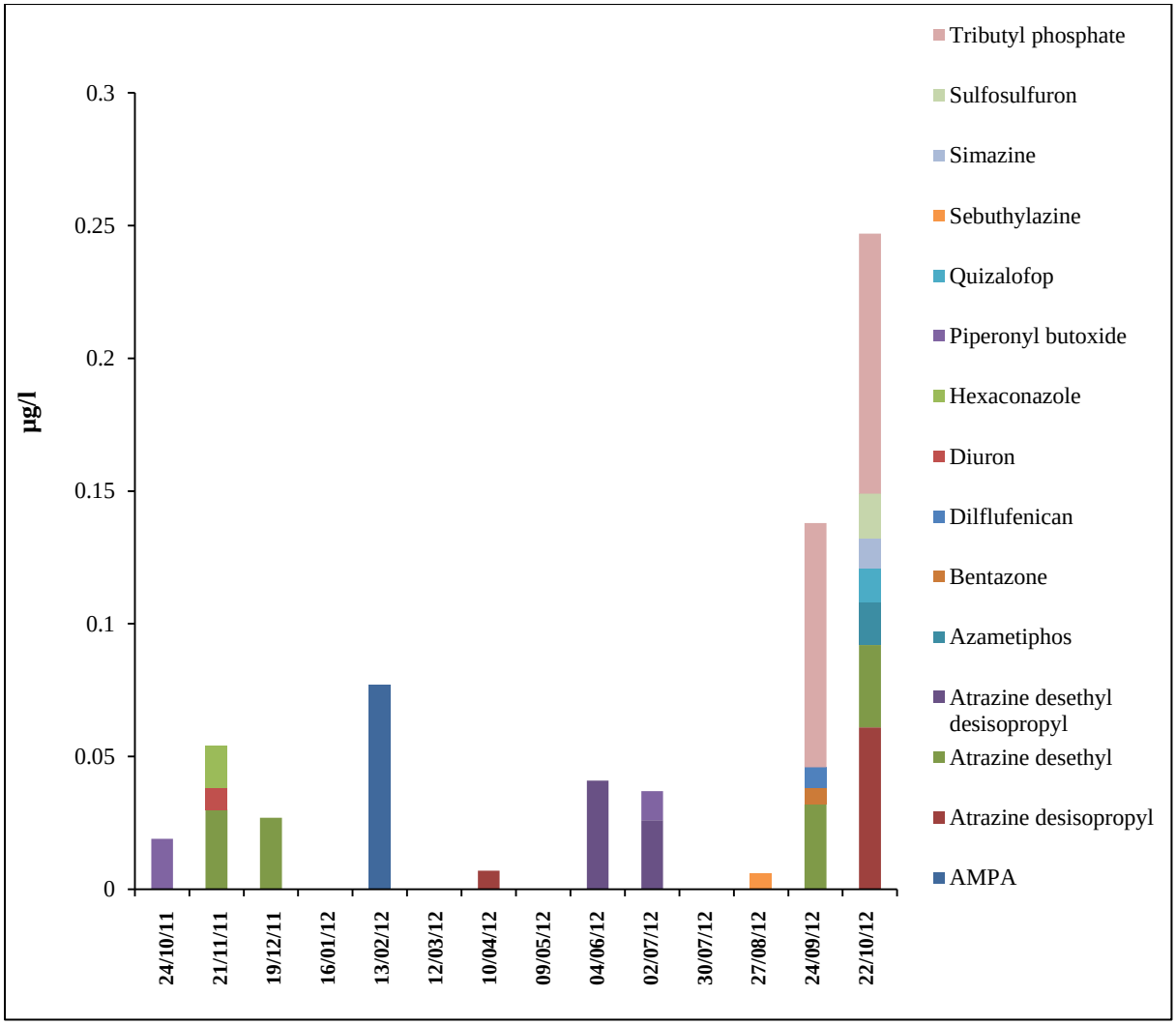

Fig.III-18: Seasonal variation of detected pesticides from piezometer P13

3.2. Agricultural fertilizers in surface and groundwater

Many studies indicate that agricultural practices result in nitrate (NO_3^-) contamination of groundwater, with concentrations in shallow aquifers commonly exceeding the drinking-water maximum admissible concentration of 50 mg/L (EC, 1980; USEPA, 1986). Dissolved nitrate concentrations in the Allier River are low and vary between 1.9 and 6.9 mg/l with a mean value of 4.2 mg/l (Table III-9). In groundwater, the nitrate concentrations are much higher than those of the Allier, excluding borehole B33 which is located very close to the Allier and presents a mean concentration of 4.3 mg/l. B29 is characterised by nitrate concentration that range between 17.9 and 24.8 mg/l with a mean value of 20.3 mg/l. The maximum concentrations of nitrate are recorded in piezometer P13 and vary from 29.4 to 37.9 mg/l with a mean value of 33.2 mg/l. The origin of nitrate in B29 and P13 is probably related to the application of organic fertilizers in agricultural fields around these sampling

points, as shown by pesticides measurements. Usually, the ammonia (NH_3) within the nitrogen fertilizer is transformed in soil into nitrate by nitrification process (Ii et al., 1997). Ammonium (NH_4^+), also a source of nitrate, has not been detected above quantification limits (<0.05mg/l) in any groundwater samples, indicating that it may be totally converted into nitrate since the alluvial aquifer is shallow and aerobic. NH_4^+ ion is detected in the same range of values in the Allier River with a concentration up to 0.25 mg/l. The agricultural origin is revoked and the main source of ammonium in the Allier River could be the effluent of the waste water treatment plant of Cournon, which is located close above sampling site.

In addition to NO_3^-, other reviews address groundwater susceptibility to contamination by other agricultural contaminants with potential health or ecological implications such as phosphorus (Simms et al. 1998; Sharpley et al. 2000). Phosphorous (P) is one of the most important macro-nutrient for living systems and it is an essential element for plant growth and for a couple of physiological functions that are concerned with energy transformations. The principle sources of P in groundwater systems include overlying soil, dissolution of minerals that contain phosphate in aquifer sediments, agricultural fertilizer, animal waste, and leaking septic systems or infiltration of wastewater (Fuhrer et al., 1999). Globally, the main user of phosphorous is agriculture, accounting for about 90% of the total world demand (Gupta et al., 2014). Once applied in fields, water-soluble P fertilizers ($H_2PO_4^-$or HPO_4^{-2}) are either directly available for the crop or become quickly unavailable due to being adsorbed onto soil particles. Phosphorous leaching to groundwater is relatively rare because P is tightly held by these soil particles. The strong bond of P with clay minerals and metal hydroxides as well as its involvement in the biological cycle are responsible for low concentrations of phosphate in groundwater (Holman et al., 2008). Although P is not a harmful constituent in drinking water, its presence in groundwater can be of considerable concern and environmental significance.

The results of this study indicate the presence of phosphate (PO_4^{-2}) in both surface and groundwater, but at low concentrations (Table III-9). The concentrations of phosphate in the Allier River vary between <0.05 (detection limit) and 0.12 mg/l with a mean value of 0.08 mg/l. In groundwater, the maximum concentrations of PO_4^{-2} are recorded for B33 with values ranging between 0.05 and 0.19 mg/l. B29 presents values between <0.05 and 0.10 mg/l. Piezometer P13 content of PO_4^{-2} reaches to a maximum value of 0.18 mg/l with a mean

value of 0.11mg/l. There are three possible sources for the PO_4^{-2} found in surface and groundwater from the Allier alluvial aquifer: anthropogenic sources such as fertilizers, natural origins in the soil or aquifer sediments, or a combination of both. Andrade and Stigter (2011) observed similar results from the shallow alluvial aquifer of the Mondego River, Portugal, with a mean value of 0.18 mg/l. Welch et al. (2010) recorded higher phosphate concentrations (0.12-1.12 mg/l) in the Mississippi River alluvial aquifer in relation both to agricultural activities and natural sources.

Some other inorganic constituents of groundwater that are present in agricultural additives include potassium (K^+) which is detected in low amounts in both surface and groundwater. Allier River and B33 show similar contents of K^+ with a mean value of 3.1 mg/l. B29 and P13 also display similar behaviour in K^+ but in higher contents with mean value of 11.9 and 10.9 mg/l, respectively. Other than agricultural inputs, potassium is common in many soluble rocks constituting the study site that could supply this ion to groundwater.

Table III-9. Analytical results of fertilizer contents for selected sampling points.

Date	B29				B33				P13				Allier River			
	NO_3	K	PO_4	NH_4	NO_3	K	PO_4	NH_4	NO_3	K	PO_4	NH_4	NO_3	K	PO_4	NH_4
24/10/2011	24.8	12.1	0.07	<0.05	3.2	4.3	0.13	<0.05	34.3	11.4	0.14	<0.05	2.8	4.1	0.06	<0.05
21/11/2011	20.6	13.1	0.09	<0.05	4.4	3.2	0.12	<0.05	35.9	10.7	0.09	<0.05	4.7	2.7	0.10	0.07
19/12/2011	20.2	12.1	0. 07	<0.05	4.4	4.0	0.12	<0.05	29.4	12.0	0.09	<0.05	5.2	3.6	0.11	<0.05
16/01/2012	21.2	11.9	0.10	<0.05	4.9	2.6	0.11	<0.05	34.7	9.8	0.14	<0. 05	5.7	2.4	0.09	0.10
13/02/2012	21.7	12.3	<0.05	<0.05	5.6	3.3	0.08	<0.05	34.4	12.1	0.12	<0.05	6.9	3.6	0.07	0.25
12/03/2012	19.4	11.0	<0.05	<0.05	6.5	2.6	0.07	<0.05	35.4	10.8	0.07	<0.05	5.2	3.1	<0.05	0.07
10/04/2012	20.8	12.4	<0.05	<0.05	6.0	2.4	0.05	<0.05	37.9	10.3	0.07	<0.05	3.3	3.4	0.05	<0.05
09/05/2012	18.9	11.1	<0.05	<0.05	4.3	2.1	0.12	<0.05	32.5	11.3	<0.05	<0.05	3.7	1.7	0.05	<0.05
04/06/2012	21.0	11.4	<0.05	<0.05	5.0	2.5	0.19	<0.05	32.4	9.7	0.18	<0.05	4.7	2.1	0.10	0.06
02/07/2012	21.0	11.1	0.07	<0.05	2.9	3.1	0.15	<0.05	31.4	11.3	0.14	<0.05	4.6	3.2	0.07	0.06
30/07/2012	19.7	11.1	<0.05	<0.05	2.8	2.9	0.14	<0.05	31.9	9.3	0.15	<0.05	3.7	3.2	0.12	0.06
27/08/2012	19.1	12.3	<0.05	<0.05	2.6	3.5	0.14	<0.05	32.3	11.7	0.06	<0.05	3.3	3.0	0.12	<0.05
24/09/2012	17.9	11.8	<0.05	<0.05	3.4	3.5	0.15	<0.05	32.5	11.4	<0.05	<0.05	3.5	3.5	<0.05	0.18
22/10/2012	18.4	13.1	<0.05	<0.05	3.8	3.6	0.12	<0.05	30.3	10.6	0.06	<0.05	1.9	3.4	0.07	<0.05

3.3. Summary

Upon the 383 pesticides selected on the basis of their potential to contaminate ground and surface waters and their ability for analysis, only 34 have been measured at detectable levels. Atrazine (and its metabolite atrazine desisopropyl) as well as dilflufenican are the most frequently detected compounds. Allier River seems to be more contaminated than groundwater (more pesticides detected, higher detection frequency and higher concentrations). Seasonality has been noticed with higher concentrations in summer. It has to be quoted moreover that two of these compounds (AMPA and tributyl phosphate) occurred sometimes at concentrations higher than 0.1 µg/L (EU limit for drinking water). The results obtained on fertilizers distribution confirm that the boreholes in the eastern side of the Allier River, represented by B29, and the southern aquifer, represented by P13, are contaminated by nitrate and potassium. Allier River and B33 demonstrate high concentrations of phosphate; the main source is believed to be the waste water treatment plant of Cournon rather than agricultural practices.

CHAPTER IV
CONCLUSION

In conclusion, the main results concerning the functioning of the system will be reminded. This synthesis will come along with recommendation for the management of this type of water resource, with a focus on the Allier alluvial aquifer. Perspectives in terms of theoretical research will be also supplied for this hydrosystem or similar aquifers.

1. Synthesis of the results

Considering the fundamental role played by alluvial aquifer in the socio-economic context of a many regions of the world for their uses (drinking, industrial and agricultural purposes) and their ecological role in relation with their connection to surface water, the functioning of these systems has to be well understood. However, due to the interconnection of these systems to many water masses such as precipitation, rivers, pounds, alluvial aquifers, a simple model is not suitable. The complexity of the model increases with the exploitation of this shallow groundwater through large scale pumping what modify the general circulation of groundwater and then their quality. Simultaneous observation and interpretation of spatial and temporal variations in groundwater chemistry and isotope can support the assessment of groundwater recharge sources and contamination by human activities and allow establishing a solid conceptual model that includes water-rock interactions, influence of pumping, recharge and vulnerability.

1.1. Functioning of the alluvial aquifer

On a hydrodynamical point of view, groundwater circulates generally from south to north, with a natural alimentation from the hills in the non-pumped part of the aquifer. Pumping increase the participation of the Allier River to the supply of boreholes, especially those located close to the River. Some parts of the River banks are sealed and prevent leakage of surface waters in these areas. With the help of piezometric maps illustrating water circulation during day and night, four end-members have been identified for the supply of the study site: Allier River, neighbouring hills, southern part of the alluvial hydrosystem and rainfall.

The general chemical type of groundwater evolve from Ca-Na-Mg/HCO3 for boreholes close to Allier River to Ca-Mg/HCO3 for boreholes of the eastern part of the site in relation with a possible mixing with incomes of water from the hills or the southern aquifer. This is confirm by saturation index calculations which highlight the dissolution of crystalline alluviums for boreholes close to Allier River and the volcano-sedimentary formations for boreholes close to the hills. The isotopic signatures of most of boreholes fall on, or close to the GMWL (Global Meteoric Water Line) and behave similarly to Allier River, demonstrating a strong interaction with the Allier River. Boreholes close to the hills present more enriched values, close to the one of hills'springs and southern aquifer and drop into MMWL (Mezel Meteotic Water Line) indicating that these points could be partly recharged by other sources than Allier River. Morevover, boreholes located in the eastern part of the site present a better chemical stability than boreholes close to the Allier River.

These observations lead to the calculations of the participation rate of each end-member to the chemistry of boreholes by using the concentrations of ions [Cl^-], [K^+], [SO_4^{2-}]. The contribution of Allier River recharge is significant in the majority of boreholes, contributing up to 100% in boreholes adjacent to it. The influence of Allier River declines with distance from the river where boreholes seem more affected by waters coming from the hills of the southern part of the aquifer.

1.2. Vulnerability to contamination

Contamination has been explored through trace elements, pharmaceuticals and pesticides.
The analysis of selected trace elements in groundwater indicates that anthropogenic sources (mostly agricultural activities), beside natural ones, possibly influence the quality of groundwater. All the boreholes present concentrations below the drinking water limits except B39 characterized by high concentrations in As, Mn and Fe. This borehole has been stopped for 20 years because of its high content in Mn. Concentrations in boreholes close to the hills are in most of the case and for most of traces higher than the rest of the area, indicating the participation of water coming from the hills.

Investigations on phytosanitaries on four points (Allier River, P13, B29 and B33) show that the Allier River presents the highest concentrations and the highest diversity in molecules. 34 phytosanitary molecules have been positively detected in both surface and groundwater, upon which Atrazine and diflufenican, among the most used herbicides, are the most detected.

Groundwater samples are quite homogeneous in terms of quantity of molecules detected and concentrations reached, showing the influence of agricultural activities not only at a local scale, in the surrounding hills or the southern part of aquifer but also within the whole Allier Basin, B33 being mostly fed by Allier River.

Regarding pharmaceuticals, groundwater is generally less contaminated than surface water, characterized by the presence of low persistent molecules. However, spatial variability could be noticed. B29, close to the hills presents higher concentrations than Allier River and one pharmaceutical molecule (Losartan) that has not been detected elsewhere, attesting for the contribution of water coming from the hills. The quite-absence of pharmaceuticals in P13 seems to be due to its particular location, within agricultural fields, and to the origin or groundwater mainly coming from a southern origin and neither connected to Allier River nor the neighboring hills.

Beside this study, sixteen PhACs have been selected for they belong to the priority list of the AFFSAPS and they are a part of the dataset acquired on the Allier River during one year measurement, from October-2011 to October-2012. Nine among the sixteen targeted molecules have been positively detected in the surface waters of the Allier River. Atenolol, carbamazepine and caffeine are the most frequently measured PhACs in relation both with consumption and persistence in the STPs and the environment. Acetominophen and caffeine, despite their (bio)degradation facility in the STPs and environment, present the highest concentrations of the database due to the fact that these compounds are among the most used in France. Comparison between MECs and PECs has been achieved by using an adaptation of the models proposed by Heberer and Feldmann (2005) and EMEA (2006). On annual basis, most of the PEC calculations are acceptable for they are comparable to the corresponding MECs. Concentrations within the environment could then be evaluated by using PECs. However, on a smaller timestep, PECs lead to some uncertainties. The seasonal evolution of PECS and MECS shows that PECs of ATE, HYD, PRA, FUR and CARB are in agreement with MECs but pharmacokinetics parameters included in the equation have to be adapted in order to obtain coherent values. However PECs of DOX, EPO and ACE do not correspond to MECs and cannot then be used as a reliable estimation of concentrations.

Fig.IV-1 proposes a conceptual scheme of functioning. Thus, we highlight that even if rock-water interaction is an important process in the chemical acquisition of groundwater

chemistry, anthropogenic activities may threat its quality. Then, contributions of end-members highlight the main issues for protecting groundwater from anthropogenic contamination. Southern and eastern parts of the aquifer suffer from the entrance of groundwater of a lower quality showing the importance of a better definition of the protection's area for drinking water supply. Close to the Allier River, attention should be paid to punctual pollution that may occur in such surface water but also to recurring contamination (due to discharge of waste water treatment plant for example). All this information has to be included in management strategies of groundwater in order to protect sustainability of this valuable resource.

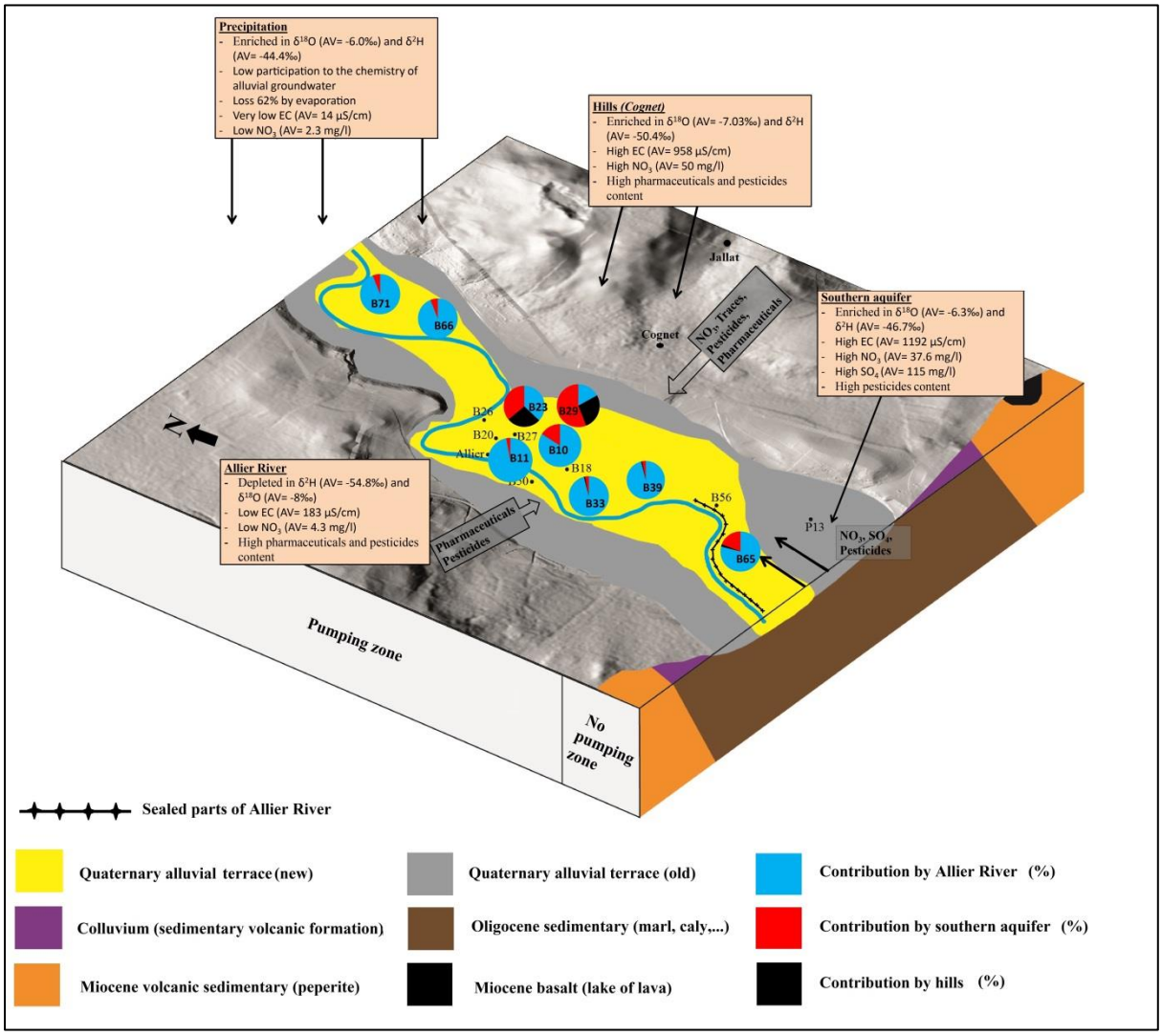

Fig.IV-1. Conceptual scheme determining the functioning of the Allier alluvial aquifer

2. Perspectives

2.1. Management of alluvial aquifers

Groundwater exploitation of alluvial aquifers, for drinking, industrial or agricultural supplies, is generally very advantageous as a result of diverse favorable conditions: high permeability, shallow depth of the aquifer, the possibility of settling batteries of well supplying high extracted debits. Then 45% of the extracted groundwater in France comes from the alluvial hydrosystems. As an example, groundwater form the alluvial aquifer system participate for 70% (9 million m^3) of the total drinking water supply of Clermont-Ferrand for 100 000 inhabitants and thus locally constitutes a fundamental resource. The implementation of a global model of management of this resource appears then essential to assure the sustainability of the exploitation. The understanding of the hydrogeological functioning is a basic requirement and the results obtained during this study allow us to propose some recommendations for an integrated management of the resource of the Allier alluvial aquifer. Concerning the study site, the quality of the exploited groundwater is at present good. Nevertheless, our results concerning the percentages of supply as well as the vulnerability of some wells lead to the following recommendations suitable not only for the study site but also for the Allier alluvial aquifer in general.

At first, it would be advisable to protect better hillsides, high source of contamination in both nutriments, toxic traces, pesticides and pharmaceuticals. As the natural flow of groundwater is circulating from the hills to the river, this recommendation is suitable for all the alluvial system. In the study site, this general circulation is altered by supply of Allier River enhanced by the pumping of boreholes during night. Contamination from hillside is then attenuated by a mixing by surface waters. However, if this mixing could decrease the concentrations of toxic traces and nutriments, Allier River presents the highest concentrations of pesticides and pharmaceuticals that may enter the hydrosystem, even if the filtration by the alluvium formation has been showed. Attention should be paid to the possible contamination supplied by wastewater treatment plants that may contaminate surface waters through effluent and then the related alluvial aquifer. If the recommended protections are not suitable, a survey of the water quality, especially for the detected species, has to be settled in order to insure the supply of drinking water matching the regulations. At last, if boreholes are planned, we

suggest drilling them rather close to Allier River than in the hillside in order to avoid a higher contamination.

2.2. Theoretical Research perspectives

Although extensive monitoring of chemical and physical properties is conducted on alluvial systems, due to the high demand for this valuable resource, current information on its bacterial content is limited. However, bacteria provide an immense contribution to drive the biogeochemical processes in the groundwater ecosystem as in any other ecosystem. Therefore, a proper understanding of bacterial diversity is crucial to assess the effectiveness of groundwater management policies (Sirisena et al., 2013). In parallel to the chemical and isotopic study carried out on the Allier alluvial system, an evaluation of the microbial community structure, richness, and diversity has been achieved. Preliminary results open perspectives for improvement of the knowledge of the functioning of alluvial aquifers.

Prokaryotic abundances have been quantified through flow cytometry. In a first step, Fig.IV-2 shows that surface waters contain more bacteria than groundwater.

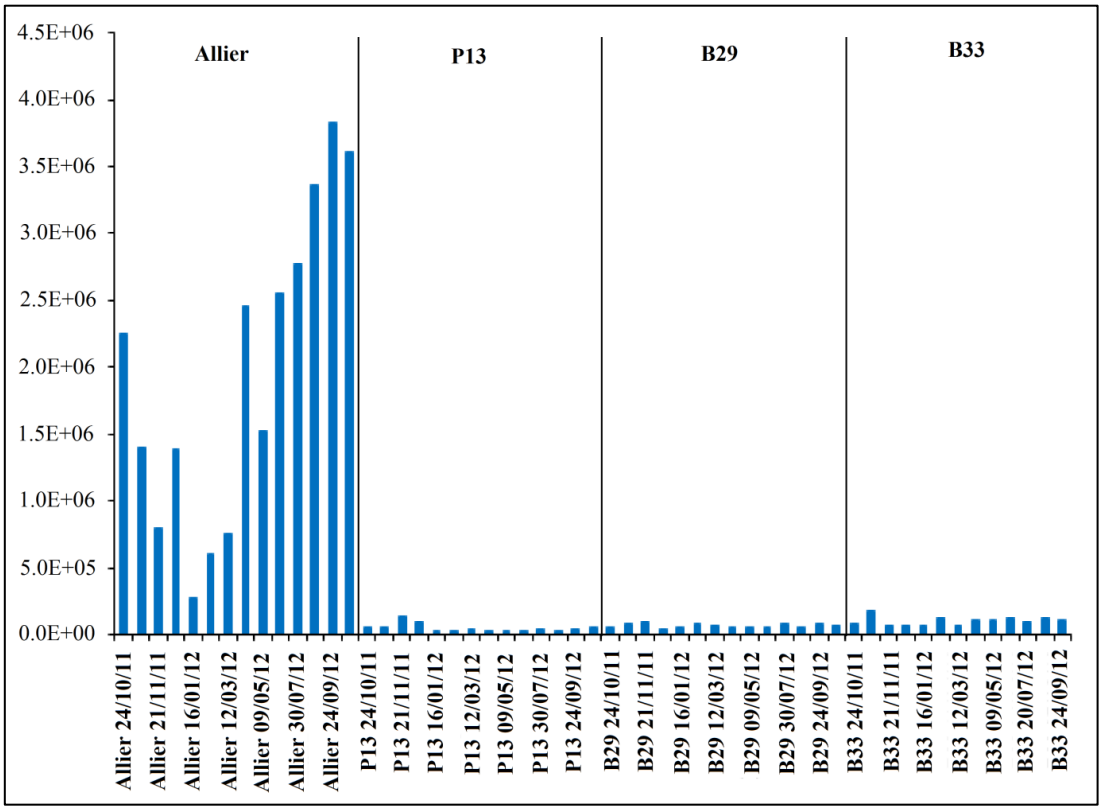

Fig.IV-2: Bacteria in surface and groundwater samples

The decline in bacterial densities with increasing distance from the Allier River could be a result of the filtering effect of the bed sediments (Ellis et al., 1998). However results provided by Denaturing Gradient Gel Electrophoresis analysis, highlight the fact that the richness in bacterial communities is higher in groundwater than in Allier River (Fig.IV-3).

Higher competition in surface water could lead to a decrease of the diversity within the surface water. Moreover, Storey et al. (1999) stated that, in the hyporheic zone, that connect the stream and the alluvial groundwater system, the biofilm growth form of interstitial micro-organisms will create a variety of microniches, allowing coexistence of a great diversity of microbial types, and promoting the activity of some otherwise poor competitors.

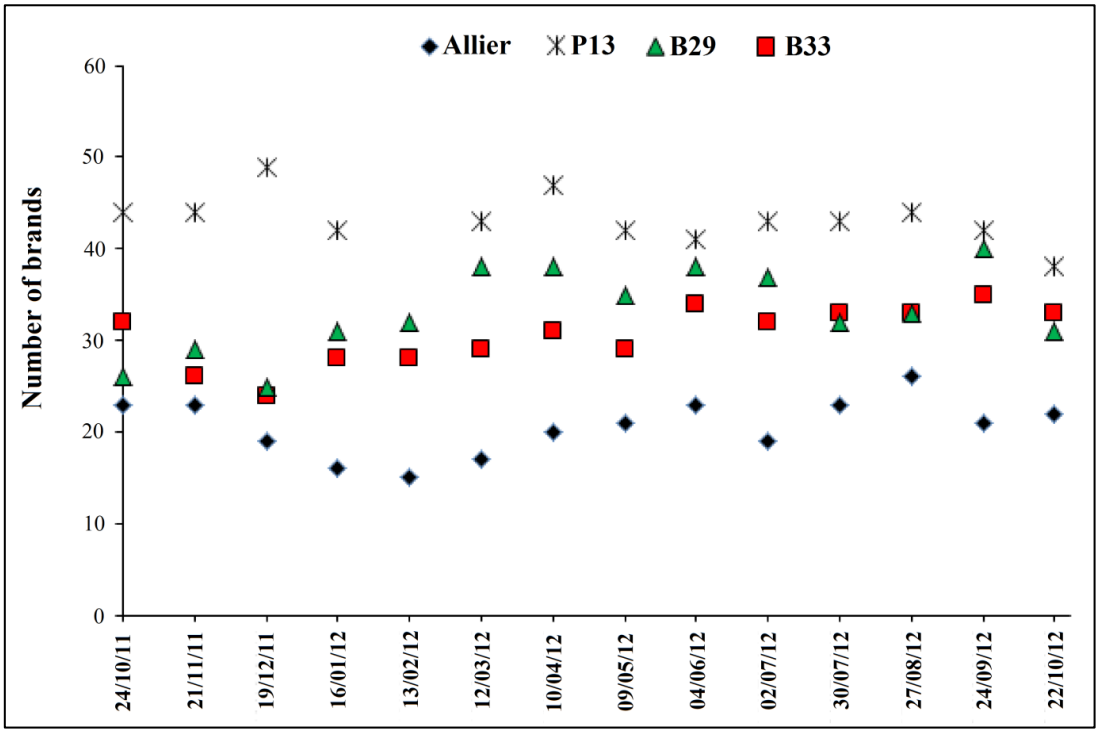

Fig.IV-3: Bacteria richness in surface and groundwater samples

At last, cluster analysis achieved thanks to the results of DGGE indicates that groundwater presents also a higher stability (68.2% of correspondence for B29, 73.5% for B33, 78.8% for P13) within time compare to Allier River (65.8% of correspondence; Fig.IV-4). This stability of aquifer water samples indicates that the microbial community composition was highly variable (Fig.IV-4).

These first results on microbiology seem very interesting and should be combined with chemical results in order to highlight the influence of chemistry, and more peculiarly contamination, on microbiology and vice versa.

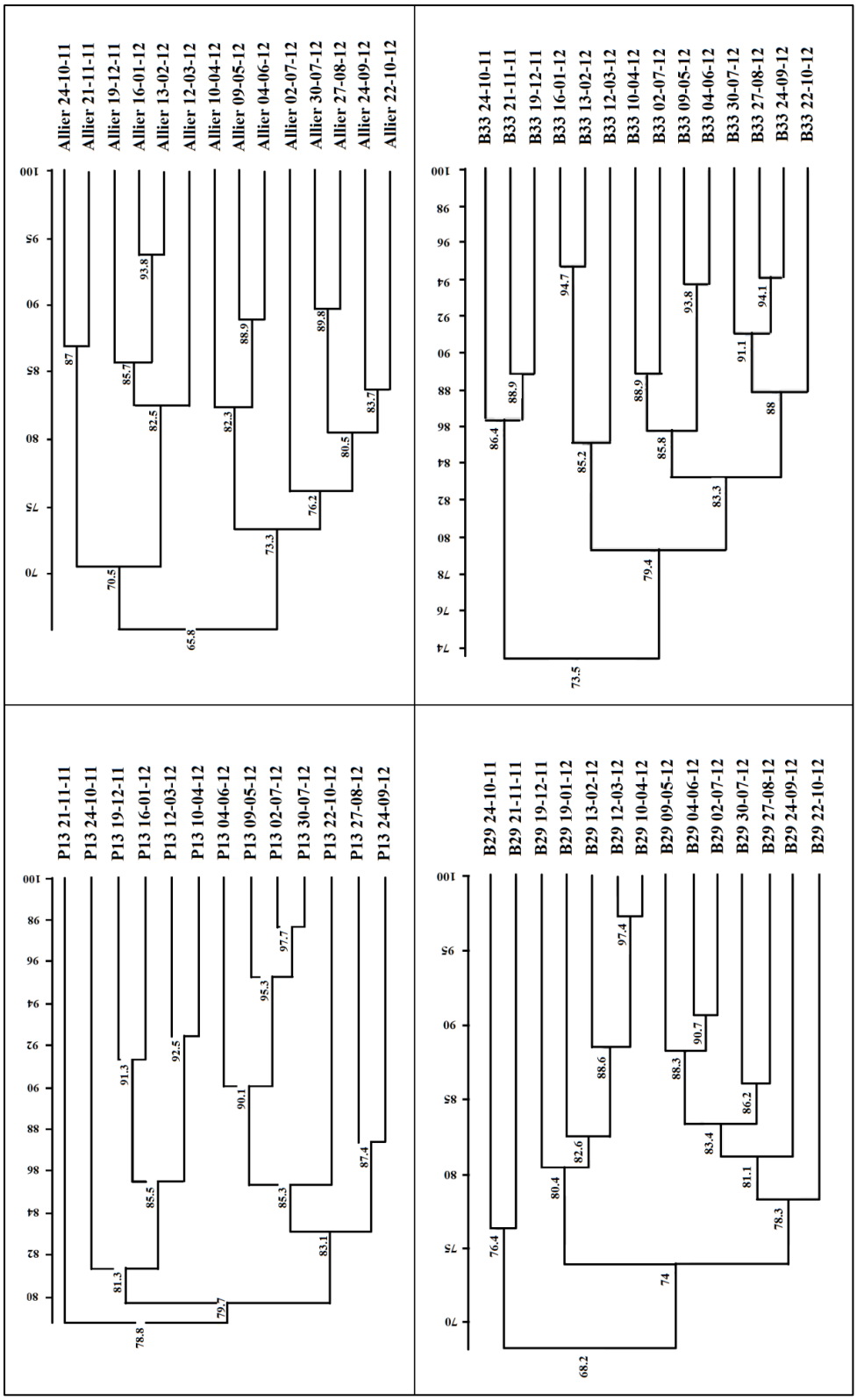

Fig.IV-4: Cluster analysis of DGGE gel for surface and groundwater sample

This work contributed to the improvement of the knowledge of the alluvial aquifers by proposing an interdisciplinary study, adaptable to other similar hydrosystems and offering a precious help for the management of this type of resource. The scientific approach, in a fundamental optics with final applied objective allows in the one hand an international valuation of the results and on the other hand, to supply precise answers to the questioning of the users of alluvial aquifer resources.

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APPENDICES

APPENDIX A

Water level, physico-chemical and hydrochemical parameters (mg/l)

Sample ID	Date	WL	T	Do	pH	EC	SiO_2	CO_2	HCO_3	Cl	NO_3	SO_4	PO_4	Ca	Mg	Na	K
B10	14/02/2011	312.73	11.3	5.1	6.80	443	19.4	27.1	171	24.5	17.3	31.6	<0.05	42.6	15.7	20.1	4.9
B10	28/02/2011	312.77	11.0	5.4	6.89	457	19.7	34.5	184	26.4	18.5	35.8	<0.05	51.3	16.9	18.2	4.5
B10	14/03/2011	312.87	13.0	6.0	6.96	466	22.0	34.7	184	27.3	18.6	38.3	0.07	46.3	16.7	17.0	4.2
B10	28/03/2011	313.09	11.2	7.5	7.01	430	22.4	36.4	171	25.0	15.7	30.6	<0.05	44.4	15.0	15.4	4.2
B10	11/04/2011	313.08	12.5	6.8	6.92	465	21.7	32.4	183	26.3	17.4	36.7	0.05	46.7	17.8	18.2	4.8
B10	26/04/2011	312.66	13.5	5.7	7.07	493	22.5	30.3	195	28.6	19.7	41.2	<0.05	49.8	17.6	18.3	4.8
B10	09/05/2011	312.62	12.9	6.2	7.00	509	22.4	23.2	203	29.5	20.7	44.1	<0.05	56.0	18.0	17.1	4.5
B10	23/05/2011	312.9	12.6	5.2	7.06	466	21.1	36.1	185	28.1	18.6	46.3	<0.05	49.7	15.6	17.0	4.5
B10	06/06/2011	312.85	12.1	5.8	7.03	436	18.7	31.0	165	22.9	13.6	29.5	<0.05	39.3	12.9	16.5	4.3
B10	20/06/2011	312.54	14.1	5.9	7.03	474	17.5	41.5	192	28.2	19.0	39.6	0.14	52.8	16.3	18.2	4.5
B10	04/07/2011	312.96	14.6	5.2	6.99	468	15.7	34.3	187	28.4	19.7	38.6	0.05	47.4	16.1	18.9	4.5
B10	18/07/2011	313.14	12.9	5.5	7.11	474	19.0	28.5	187	27.9	19.0	39.0	0.14	47.5	16.2	18.6	4.5
B10	16/08/2011	313.1	13.5	6.9	7.07	344	20.1	15.1	146	19.4	9.6	21.6	0.09	36.5	11.0	16.1	5.4
B10	29/08/2011	312.11	13.2	7.4	7.03	414	22.0	28.9	168	22.9	14.4	32.2	0.16	45.3	12.9	16.1	4.2
B10	12/09/2011	311.92	13.7	6.4	6.99	417	17.8	27.6	171	22.7	13.4	32.3	<0.05	38.0	14.3	17.9	4.8
B10	26/09/2011	312.52	13.9	6.2	7.02	397	22.1	31.3	165	22.1	12.1	30.0	<0.05	38.6	13.8	18.5	5.2
B10	10/10/2011	311.73	14.4	6.0	6.97	378	21.1	31.3	156	21.0	10.1	26.7	0.09	36.7	12.9	16.7	4.6
B10	24/10/2011	312.49	13.4	6.2	7.05	370	20.0	18.1	156	20.3	8.9	24.5	0.12	34.9	12.2	17.1	5.4
B10	07/11/2011	313.65	13.1	6.1	7.18	374	18.5	21.3	164	20.4	9.6	25.5	<0.05	35.8	12.7	17.9	6.0
B10	21/11/2011	313.32	13.4	6.6	7.27	360	18.4	4.6	153	19.6	8.9	24.3	0.05	36.4	11.6	16.0	4.4
B10	05/12/2011	312.77	11.8	7.0	7.16	286	19.6	28.7	123	17.9	5.0	13.8	0.06	29.4	10.6	15.3	5.8
B10	19/12/2011	313.27	10.6	5.0	7.23	291	18.3	14.8	128	16.9	5.1	15.6	0.08	29.0	9.3	18.5	4.8
B10	03/01/2012	312.96	11.1	6.6	7.12	273	16.3	16.7	118	17.5	4.5	13.0	0.27	26.4	9.5	15.1	4.0
B10	16/01/2012	312.71	11.0	6.2	7.11	285	19.8	18.5	122	17.9	5.1	15.1	0.09	27.6	9.8	14.6	3.8
B10	30/01/2012	312.15	9.0	6.4	7.17	306	19.8	20.4	131	18.6	5.6	17.1	<0.05	29.3	10.5	15.2	4.8
B10	13/02/2012	312.72	9.3	5.3	7.06	298	17.0	20.4	128	18.3	5.3	16.7	0.08	29.4	10.6	17.6	4.5
B10	27/02/2012	312.8	10.6	4.2	7.17	300	19.9	16.2	128	17.1	4.9	15.7	0.09	28.2	9.7	15.8	4.2
B10	12/03/2012	312.98	11.9	3.3	7.14	301	19.7	19.9	127	16.3	4.4	15.5	<0.05	26.7	9.1	15.4	4.8
B10	26/03/2012	312.71	11.9	6.4	7.12	262	20.1	19.7	107	16.2	4.4	11.9	0.14	22.3	8.1	14.2	3.8
B10	10/04/2012	311.61	11.7	6.1	7.07	272	19.1	22.2	112	18.3	5.4	13.9	0.08	24.9	8.9	15.5	5.4
B10	23/04/2012	313.02	11.1	6.2	7.12	247	19.5	21.3	101	16.9	5.4	11.9	0.06	22.0	7.6	11.9	2.9
B10	09/05/2012	313.54	12.3	7.3	7.13	221	18.4	17.4	90	16.0	5.2	10.1	0.09	21.7	7.2	12.0	2.6
B10	21/05/2012	313.27	11.7	6.8	7.05	256	22.6	17.8	105	17.7	5.9	13.5	0.07	23.1	8.3	12.9	2.7
B10	04/06/2012	313.87	11.9	7.1	7.11	245	19.3	17.1	105	16.1	5.1	11.5	<0.05	23.5	7.8	12.6	2.7
B10	18/06/2012	313.5	14.0	7.2	7.08	290	18.0	27.3	122	17.2	6.6	14.4	<0.05	28.2	9.1	13.2	3.1
B10	02/07/2012	313.31	13.3	6.9	7.22	311	18.0	22.2	139	18.5	7.3	15.2	0.05	30.3	9.6	13.6	3.3
B10	16/07/2012	313.17	13.0	6.6	7.20	314	19.3	23.1	133	19.3	9.0	17.1	<0.05	30.7	9.4	13.4	3.5
B10	30/07/2012	313.2	14.6	5.2	7.23	257	18.1	9.7	118	15.7	4.3	10.7	<0.05	25.6	8.0	13.4	2.9
B10	13/08/2012	313.31	14.7	4.1	7.26	274	18.6	10.2	114	16.1	4.5	11.8	0.05	24.8	7.8	13.0	3.4
B10	27/08/2012	313.08	14.5	6.5	7.46	270	18.0	15.1	129	15.8	4.4	11.6	<0.05	28.1	7.9	12.9	3.2
B10	10/09/2012	313.2	14.8	4.1	7.47	275	18.9	16.9	126	15.7	4.3	11.5	<0.05	28.2	8.2	13.0	3.2
B10	24/09/2012	313.14	15.0	6.1	7.72	274	17.7	6.9	122	16.1	4.3	11.7	0.05	26.8	7.7	12.7	3.2
B10	08/10/2012	312.77	14.3	5.2	7.23	311	19.4	19.9	123	17.5	7.0	16.2	0.05	31.3	9.8	14.5	3.5
B10	22/10/2012	312.88	14.2	5.0	7.33	307	20.3	22.5	132	17.0	6.2	15.0	<0.05	27.3	10.0	14.4	3.5
B10	05/11/2012	313.02	12.7	4.8	7.68	291	18.8	12.7	127	16.6	4.9	13.7	<0.05	26.2	9.1	14.9	3.5
B11	14/02/2011	313.21	10.4	5.7	7.08	173	14.2	24.3	66	11.7	6.2	7.4	0.08	13.7	4.5	11.8	2.9
B11	28/02/2011	313.28	8.5	6.2	6.85	175	13.7	17.4	65	12.4	6.9	7.8	0.08	14.2	4.6	10.5	2.7
B11	14/03/2011	313.38	10.6	6.3	7.10	172	14.6	24.1	62	13.6	7.3	8.4	0.09	14.2	4.6	9.5	2.4
B11	28/03/2011	313.58	9.0	6.9	6.98	179	15.6	19.0	65	14.0	6.8	8.4	0.08	15.3	4.5	9.2	2.5
B11	11/04/2011	313.56	9.8	7.3	6.82	173	14.6	10.2	65	12.7	6.1	7.8	0.08	14.0	5.4	9.7	2.7
B11	26/04/2011	313.06	9.8	5.8	7.50	171	14.7	12.0	65	12.7	5.7	7.7	0.08	13.4	4.7	9.6	2.6
B11	09/05/2011	313.07	10.7	5.2	7.01	182	15.1	13.9	68	13.6	5.4	8.1	0.06	14.7	5.0	8.9	2.5
B11	23/05/2011	313.28	10.3	4.1	7.11	190	13.8	18.5	72	14.9	5.6	8.5	0.06	15.5	5.3	10.3	2.4
B11	06/06/2011	313.33	9.8	3.4	7.06	195	13.3	20.4	73	15.4	5.3	8.6	0.06	15.7	5.1	10.7	2.7
B11	20/06/2011	312.97	11.5	4.0	7.02	222	12.4	23.9	87	18.2	4.6	9.7	0.11	20.7	6.1	11.6	2.8
B11	04/07/2011	313.5	13.9	5.4	7.02	214	12.8	24.5	95	15.6	4.1	9.0	0.09	20.3	5.6	11.2	2.9
B11	18/07/2011	313.65	12.5	4.6	7.14	222	14.3	15.7	92	15.8	4.3	8.7	0.10	20.2	5.9	12.4	3.1
B11	16/08/2011	313.47	13.0	2.9	7.17	225	15.5	17.8	88	17.7	4.1	9.7	0.11	20.0	6.0	12.9	4.2
B11	29/08/2011	312.51	12.5	4.3	7.01	227	17.8	25.0	92	17.6	2.5	9.3	<0.05	19.4	5.8	12.0	3.2
B11	12/09/2011	312.3	15.3	3.8	6.99	215	13.7	21.1	89	17.2	2.2	8.3	0.06	17.0	5.8	13.5	3.6
B11	26/09/2011	312.97	16.7	3.7	6.97	224	17.2	22.9	85	20.0	2.9	9.2	0.07	16.9	5.8	15.0	4.2
B11	10/10/2011	312.12	16.1	4.1	6.90	220	17.1	20.6	84	19.0	2.6	8.6	0.10	17.3	5.8	15.4	4.7
B11	24/10/2011	312.95	16.2	3.4	6.91	271	16.7	18.8	79	20.3	3.2	8.4	0.37	15.9	5.2	13.9	3.8
B11	07/11/2011	314.32	14.9	4.3	6.96	222	16.2	15.5	84	20.2	3.0	8.7	0.08	19.5	5.7	14.6	3.9
B11	21/11/2011	313.91	14.9	4.8	7.08	227	16.5	19.7	96	17.6	2.0	8.0	0.09	19.3	6.1	12.2	3.4
B11	05/12/2011	313.26	14.8	4.0	7.14	200	16.3	24.1	78	15.1	3.9	8.3	0.10	14.7	5.1	12.8	3.5
B11	19/12/2011	313.68	13.4	3.5	7.10	189	15.9	11.8	74	13.7	4.3	8.5	0.13	13.9	4.4	12.5	3.4
B11	03/01/2012	313.53	13.8	4.3	7.13	171	11.0	7.2	70	12.4	4.1	7.3	0.08	13.6	4.7	12.3	2.9
B11	16/01/2012	313.2	12.6	4.9	7.19	161	15.0	15.1	66	11.3	4.5	6.8	0.09	13.0	4.3	11.9	3.0
B11	30/01/2012	312.71	11.2	6.1	7.28	158	14.7	10.9	63	10.4	4.8	6.4	0.08	11.4	4.0	10.6	2.9
B11	13/02/2012	313.31	8.5	5.4	7.13	152	11.8	8.6	63	10.5	5.2	6.4	0.07	11.8	4.1	11.5	3.1
B11	27/02/2012	313.31	10.9	5.8	7.21	157	14.8	7.2	59	10.9	5.3	6.5	0.07	11.7	3.9	11.0	2.8
B11	12/03/2012	313.58	11.2	5.4	7.14	205	14.7	13.9	65	11.4	4.8	6.5	0.07	13.0	4.1	11.0	2.9
B11	26/03/2012	313.22	11.2	7.0	7.11	172	14.4	10.2	60	13.0	5.9	7.2	0.12	12.4	4.5	10.6	2.6
B11	10/04/2012	311.9	9.7	7.0	7.13	178	13.2	12.0	62	15.3	6.4	7.9	0.08	13.5	4.8	12.2	3.5
B11	23/04/2012	313.73	10.4	5.5	7.12	200	15.6	16.0	79	15.7	3.5	7.4	0.07	17.3	5.4	11.0	2.6
B11	09/05/2012	314.22	10.2	5.7	7.13	185	14.5	16.2	72	14.2	4.5	8.0	0.08	15.9	5.3	11.3	2.2
B11	21/05/2012	313.95	10.4	5.6	6.95	194	19.0	19.7	73	14.7	3.8	8.1	0.06	16.5	5.3	10.9	2.1
B11	04/06/2012	314.36	10.4	5.1	7.12	176	14.7	11.2	76	12.0	4.3	7.4	0.07	15.7	5.0	10.9	2.2
B11	18/06/2012	314.02	11.8	5.0	7.21	189	13.8	21.1	79	11.6	3.7	7.4	<0.05	17.4	5.2	10.8	2.4
B11	02/07/2012	313.77	12.8	4.8	7.05	218	15.7	12.7	89	14.3	3.0	7.7	0.09	20.5	5.7	11.1	2.5
B11	16/07/2012	313.71	12.2	4.5	7.26	206	16.2	16.4	93	13.5	3.1	7.7	<0.05	18.8	5.4	11.0	2.6
B11	30/07/2012	313.72	13.8	5.0	6.96	223	20.8	11.4	96	14.2	2.4	7.5	<0.05	20.1	6.0	11.9	2.4
B11	13/08/2012	313.81	13.7	4.1	7.16	223	17.6	10.4	101	14.1	2.4	7.6	0.07	21.0	5.9	11.9	2.9
B11	27/08/2012	313.71	13.6	4.4	7.12	216	17.2	22.0	96	13.8	2.5	7.7	<0.05	22.4	6.0	11.7	2.6
B11	10/09/2012	313.68	14.0	4.2	7.35	228	18.2	19.4	99	13.6	2.1	7.4	<0.05	20.9	5.8	11.3	2.6
B11	24/09/2012	313.62	13.3	2.5	7.41	206	17.1	10.7	90	13.0	3.2	7.6	<0.05	18.8	6.0	12.3	3.0
B11	08/10/2012	313.3	13.6	3.5	7.48	200	14.5	12.3	87	13.2	1.7	7.1	0.05	18.5	5.2	11.8	2.6
B11	22/10/2012	313.46	14.3	2.8	7.44	198	15.8	14.6	84	13.0	2.1	7.4	<0.05	17.3	5.2	11.3	2.7
B11	05/11/2012	313.58	13.1	4.0	7.63	196	14.9	12.0	85	12.9	2.0	7.6	<0.05	18.0	5.3	12.9	3.0

Sample ID	Date	WL	T	Do	pH	EC	SiO_2	CO_2	HCO_3	Cl	NO_3	SO_4	PO_4	Ca	Mg	Na	K
B18	14/02/2011	314.12	11.7	4.1	6.92	225	18.3	18.1	101	14.2	1.2	7.1	<0.05	20.5	6.0	13.5	2.9
B18	28/02/2011	314.19	11.3	3.4	6.91	221	17.7	20.4	99	14.2	1.3	7.4	<0.05	23.3	5.8	12.9	2.7
B18	14/03/2011	314.3	12.2	3.8	7.01	219	20.5	28.0	99	14.4	1.5	7.6	0.05	20.3	6.1	10.8	2.5
B18	28/03/2011	314.5	11.5	4.0	7.06	218	21.5	25.9	99	14.0	1.4	7.5	<0.05	20.6	5.7	10.3	2.6
B18	11/04/2011	314.47	12.2	4.5	6.87	218	20.5	12.7	99	13.6	1.4	7.2	0.08	19.8	6.5	12.5	3.1
B18	26/04/2011	314.71	14.1	3.3	7.11	216	21.7	13.7	98	13.8	1.3	7.3	<0.05	22.1	5.7	11.5	2.6
B18	09/05/2011	314.7	13.3	3.0	7.12	212	20.6	16.7	98	13.8	1.1	7.4	0.06	20.6	5.6	10.7	2.5
B18	23/05/2011	314.72	13.4	2.3	7.19	216	19.3	26.2	101	14.1	1.1	7.3	<0.05	21.1	5.5	9.8	2.6
B18	06/06/2011	314.2	12.5	4.0	7.06	222	18.3	23.4	99	14.0	1.6	7.3	0.05	19.7	5.5	11.9	2.7
B18	20/06/2011	314.69	13.0	3.7	7.09	203	15.7	30.3	87	14.1	3.2	8.1	0.08	21.1	5.4	12.0	2.5
B18	04/07/2011	314.65	14.6	4.1	7.15	221	14.6	18.8	101	14.4	1.9	7.9	0.08	21.4	5.7	12.3	2.8
B18	18/07/2011	314.89	13.7	2.7	7.15	218	16.8	19.7	98	14.0	1.5	7.2	<0.05	20.6	5.6	11.8	2.9
B18	16/08/2011	314.91	15.9	3.0	7.27	218	18.0	11.3	101	13.7	1.6	7.5	<0.05	25.8	5.2	11.1	3.5
B18	29/08/2011	314.65	14.2	3.9	7.30	224	18.1	11.6	104	13.5	1.2	7.2	0.07	23.0	5.4	11.5	2.9
B18	12/09/2011	314.48	14.7	2.3	7.28	223	17.8	11.6	104	13.3	1.2	7.0	<0.05	20.6	5.5	12.2	3.0
B18	26/09/2011	314.49	14.4	1.9	7.29	221	21.2	20.6	104	13.9	0.0	7.1	<0.05	20.6	5.7	13.3	3.5
B18	10/10/2011	314.33	15.1	3.0	7.14	219	18.9	16.0	101	13.6	0.0	6.9	<0.05	20.6	5.5	12.2	3.0
B18	24/10/2011	314.41	13.0	4.2	7.19	219	18.4	11.3	101	13.7	0.0	6.9	<0.05	21.0	5.8	12.6	3.3
B18	07/11/2011	315.56	13.1	4.2	7.22	215	17.2	13.7	99	14.0	0.0	7.1	<0.05	19.2	5.8	12.8	3.6
B18	21/11/2011	315.09	14.0	4.6	7.24	218	17.7	15.5	100	14.3	0.0	7.0	<0.05	20.5	5.5	11.6	2.8
B18	05/12/2011	314.17	12.2	4.6	7.12	224	17.6	18.8	101	14.9	0.0	6.5	<0.05	19.9	6.2	12.3	3.5
B18	19/12/2011	314.69	10.5	4.6	7.11	224	18.2	14.4	99	15.5	1.0	6.7	0.06	21.9	6.3	12.7	2.9
B18	03/01/2012	314.48	11.9	5.0	7.14	221	14.3	11.1	99	15.8	0.0	6.6	0.05	21.8	6.4	12.8	2.5
B18	16/01/2012	314.14	11.5	4.7	7.16	220	18.3	13.7	99	15.8	1.3	6.8	<0.05	21.6	6.2	13.0	3.4
B18	30/01/2012	313.64	11.2	5.2	7.28	221	18.9	15.3	98	15.5	1.1	6.6	<0.05	20.1	5.8	11.8	2.9
B18	13/02/2012	314.2	9.6	4.3	7.05	222	12.1	18.5	99	15.9	1.1	7.0	0.05	21.2	6.4	12.7	3.0
B18	27/02/2012	314.21	11.2	4.3	7.14	225	18.9	12.3	100	15.7	1.1	6.9	0.06	20.4	5.9	12.8	3.1
B18	12/03/2012	314.75	11.4	3.7	7.09	244	18.7	24.1	98	15.4	1.0	7.0	<0.05	20.0	5.7	12.7	3.7
B18	26/03/2012	314.13	12.7	4.6	7.07	223	19.5	17.1	96	15.4	1.0	6.9	<0.05	19.7	5.9	12.1	2.9
B18	10/04/2012	313.03	11.6	4.4	7.07	222	17.5	15.3	98	16.7	1.1	7.2	0.06	21.7	6.0	12.5	2.5
B18	23/04/2012	314.7	11.3	5.0	7.14	220	18.7	21.6	95	16.3	1.2	6.8	<0.05	18.9	5.9	11.9	2.6
B18	09/05/2012	315.19	12.6	5.5	7.06	219	18.9	9.0	93	16.5	1.9	7.7	0.06	20.8	6.1	12.0	2.3
B18	21/05/2012	314.89	11.8	4.9	6.92	220	22.0	18.1	95	16.7	1.6	7.9	0.07	21.3	6.4	12.1	2.3
B18	04/06/2012	315.28	12.2	7.5	7.01	220	18.0	21.8	92	16.2	1.9	7.5	<0.05	20.0	6.1	12.0	2.3
B18	18/06/2012	314.92	12.9	5.2	7.18	225	21	18.8	99	15.0	1.6	7.4	<0.05	21.6	6.0	11.6	2.4
B18	02/07/2012	314.73	13.1	6.0	6.95	243	17.5	20.1	111	15.2	1.5	7.3	<0.05	24.4	6.1	11.3	2.5
B18	16/07/2012	314.58	13.5	6.6	7.15	236	18.5	19.2	116	15.2	1.4	7.2	<0.05	24.8	6.2	11.9	2.8
B18	30/07/2012	314.62	13.8	5.2	7.01	241	18.9	16.4	110	14.7	1.1	6.8	<0.05	24.1	6.4	12.3	2.5
B18	13/08/2012	314.74	13.9	4.5	7.12	241	19.1	17.1	114	14.5	1.2	7.0	0.06	23.3	6.1	11.6	2.5
B18	27/08/2012	314.64	13.7	4.3	7.18	241	19.1	23.6	109	14.4	1.1	7.2	0.05	26.5	6.6	12.6	2.8
B18	10/09/2012	314.58	14.2	3.9	7.29	262	19.4	26.8	116	14.0	1.0	6.7	<0.05	23.8	6.3	12.0	2.7
B18	24/09/2012	314.51	14.6	3.9	7.17	237	19.2	14.1	109	14.4	1.3	7.3	<0.05	22.8	6.8	13.2	3.1
B18	08/10/2012	314.22	14.2	4.6	7.52	230	18.1	14.6	107	13.7	1.2	6.7	<0.05	22.9	6.0	12.0	2.6
B18	22/10/2012	314.73	14.1	4.6	7.47	224	19.7	19.8	105	13.6	1.3	7.1	<0.05	21.1	6.1	11.9	2.7
B18	05/11/2012	314.8	12.9	5.5	7.59	225	18.4	13.4	106	13.5	1.2	7.0	0.05	20.8	6.0	12.7	2.8
B20	14/02/2011	313.71	10.9	4.5	7.23	203	18.0	20.8	84	12.6	4.1	8.1	0.06	18.2	5.5	12.9	3.0
B20	28/02/2011	313.20	10.0	4.6	6.93	204	17.9	19.8	87	12.7	4.4	8.5	0.16	21.5	5.5	11.3	2.8
B20	14/03/2011	313.20	12.1	4.1	7.11	200	18.3	27.3	84	13.2	4.9	8.9	0.07	17.9	5.3	10.1	2.6
B20	28/03/2011	313.51	11.0	4.8	6.97	203	19.3	21.3	83	13.2	5.2	8.9	0.05	18.0	5.4	10.0	2.7
B20	11/04/2011	311.35	11.6	6.0	6.95	203	17.4	18.1	82	13.2	5.3	8.9	0.08	17.1	5.9	10.6	2.9
B20	26/04/2011	313.04	13.6	5.0	7.08	199	18.2	15.5	81	13.0	5.1	8.7	0.07	17.1	5.4	10.8	2.9
B20	09/05/2011	312.89	13.2	5.1	7.02	202	18.1		84	13.0	5.0	8.8	0.09	18.2	5.3	9.8	2.6
B20	23/05/2011	312.75	11.9	5.0	7.09	202	17.0	21.5	83	13.9	5.0	8.8	0.05	18.8	5.8	8.9	2.5
B20	06/06/2011	312.87	11.4	5.3	6.99	207	16.0	17.4	83	14.7	4.8	8.9	0.06	17.8	5.1	10.7	2.8
B20	20/06/2011	312.67	12.7	5.3	7.13	214	15.8	25.0	87	15.5	4.6	9.2	0.10	21.6	5.9	12.1	2.9
B20	04/07/2011	313.26	13.8	6.1	7.02	213	12.5	21.3	87	16.5	4.2	9.6	0.17	19.9	5.9	12.3	2.7
B20	18/07/2011	313.27	11.3	5.7	7.10	224	15.7	17.4	92	17.5	3.8	9.1	0.12	19.9	6.1	11.9	3.1
B20	16/08/2011	313.20	13.7	5.4	6.94	231	18.1	20.8	93	18.8	3.6	9.9	0.08	21.3	6.0	12.2	3.9
B20	29/08/2011	312.98	13.4	5.4	7.06	238	19.3	28.9	96	18.3	2.9	9.5	<0.05	21.6	5.7	12.4	3.0
B20	12/09/2011	312.71	12.6	5.7	7.04	241	17.2	18.1	103	17.8	2.2	9.1	<0.05	21.4	6.5	13.1	3.4
B20	26/09/2011	312.68	13.6	4.9	6.99	244	20.0	29.4	104	18.4	2.0	9.2	<0.05	21.5	6.8	14.4	4.1
B20	10/10/2011	312.57	14.0	5.0	6.92	248	17.3	25.7	107	18.1	1.7	8.8	0.07	22.5	6.9	13.0	3.4
B20	24/10/2011	312.49	13.3	5.1	7.05	251	16.6	24.3	107	18.3	1.8	8.6	<0.05	22.3	6.9	12.9	3.8
B20	07/11/2011	312.46	12.7	6.6	6.87	242	16.5	24.6	103	19.4	1.6	9.0	0.05	20.9	7.1	13.8	4.2
B20	21/11/2011	313.21	14.5	5.8	7.01	227	16.8	23.9	92	18.5	2.2	9.0	0.06	19.8	6.3	12.4	3.5
B20	05/12/2011	312.68	11.9	5.1	7.13	231	17.7	23.2	92	17.4	2.3	8.8	0.06	19.7	6.1	12.1	3.4
B20	19/12/2011	311.60	12.4	5.8	7.06	210	16.8	16.9	85	16.4	2.6	8.9	0.72	18.7	5.6	13.5	3.4
B20	03/01/2012	313.42	12.3	5.1	7.11	218	10.6	14.6	90	16.5	2.0	8.9	<0.05	19.3	5.9	13.1	3.2
B20	16/01/2012	313.06	10.6	4.6	7.05	217	16.9	17.4	90	15.6	2.4	9.1	0.06	19.7	5.7	13.2	3.5
B20	30/01/2012	312.48	10.1	4.3	7.15	210	17.2	77.7	90	14.1	2.7	8.4	0.12	18.6	6.2	12.8	4.0
B20	13/02/2012	312.81	9.5	5.0	7.04	194	12.9	18.3	81	13.1	3.1	8.1	0.07	16.8	5.5	13.0	3.4
B20	27/02/2012	312.61	12.0	5.0	7.25	191	17.6	11.6	76	12.7	3.6	7.8	0.07	15.8	4.9	11.9	3.0
B20	12/03/2012	313.00	12.2	5.2	7.09	191	17.0	13.0	76	13.2	4.1	8.1	0.09	15.3	4.6	12.1	4.1
B20	26/03/2012	312.99	12.3	5.8	7.10	195	17.2	10.4	76	13.2	4.3	7.9	<0.05	15.8	5.1	11.9	3.3
B20	10/04/2012	312.76	12.0	5.7	7.02	195	16.7	15.5	76	15.0	5.2	8.6	0.08	15.6	5.1	12.0	3.0
B20	23/04/2012	313.22	10.8	5.5	7.15	196	16.8	16.9	76	15.1	5.2	8.5	0.06	16.1	5.1	11.5	2.8
B20	09/05/2012	313.86	12.1	6.0	7.08	198	16.4	16.7	77	15.5	4.9	9.2	0.05	18.7	5.4	11.6	2.4
B20	21/05/2012	313.57	11.4	5.7	6.97	192	19.3	13.4	78	15.1	4.9	9.2	0.07	16.6	5.5	11.6	2.3
B20	04/06/2012	314.13	11.8	5.7	7.07	194	15.6	12.3	79	13.7	4.3	8.5	0.08	18.2	5.4	11.4	2.4
B20	18/06/2012	313.69	12.4	5.2	7.26	191	15.4	20.2	78	11.7	4.0	7.8	<0.05	17.5	5.1	10.8	2.4
B20	02/07/2012	313.29	12.9	5.4	7.06	190	14.6	9.7	84	11.6	4.0	7.6	0.05	17.3	4.9	10.5	2.5
B20	16/07/2012	311.80	11.5	5.5	7.32	188	15.5	11.8	89	11.3	3.7	7.4	<0.05	18.1	5.1	11.8	2.7
B20	30/07/2012	313.18	13.2	5.0	7.08	196	16.3	13.4	88	12.0	3.3	7.2	<0.05	17.5	5.4	11.5	2.5
B20	13/08/2012	311.16	13.3	4.9	7.04	203	16.4	4.9	92	12.4	3.1	7.5	0.08	18.1	5.3	11.4	2.8
B20	27/08/2012	313.36	13.2	5.1	7.01	209	16.3	24.8	95	13.5	2.4	7.7	0.06	19.9	5.8	11.9	2.8
B20	10/09/2012	313.32	14.0	4.9	7.05	213	16.5	27.6	89	13.7	2.1	7.4	<0.05	17.5	5.0	11.7	2.8
B20	24/09/2012	311.39	14.0	4.2	7.20	207	16.5	16.9	88	14.4	2.2	7.6	<0.05	18.5	5.4	11.5	2.7
B20	08/10/2012	310.71	13.6	4.2	7.30	206	15.7	17.1	87	14.3	1.4	7.1	0.06	19.6	5.5	12.1	2.8
B20	22/10/2012	313.01	13.9	6.0	6.94	203	17.4	26.4	84	15.3	1.4	7.4	0.07	17.2	5.8	12.2	3.0
B20	05/11/2012	313.17	12.4	6.4	7.29	206	16.5	12.3	84	15.7	1.5	7.4	0.07	17.3	5.6	12.9	3.1

Sample ID	Date	WL	T	Do	pH	EC	SiO_2	CO_2	HCO_3	Cl	NO_3	SO_4	PO_4	Ca	Mg	Na	K
B23	14/02/2011	311.85	11.2	4.2	6.84	995	23.2	32.5	517	37.6	19.5	76.4	0.11	106.0	48.0	31.4	11.4
B23	28/02/2011	311.91	10.4	4.3	7.21	971	23.8	44.9	494	39.8	19.9	76.8	0.10	118.8	47.9	29.2	11.7
B23	14/03/2011	311.88	12.5	4.5	7.25	971	26.0	47.0	500	38.5	20.2	77.3	0.11	116.5	46.9	25.4	10.0
B23	28/03/2011	312.16	11.0	5.8	7.23	942	25.5	36.1	469	37.1	19.4	74.8	0.10	107.3	44.6	25.0	10.7
B23	11/04/2011	311.93	12.2	4.8	7.00	973	22.0	36.1	495	37.2	19.7	73.7	0.08	115.6	51.2	26.6	11.0
B23	26/04/2011	311.74	12.4	4.3	7.38	968	27.0	35.2	525	38.0	20.1	75.4	0.07	107.4	47.2	27.5	11.6
B23	09/05/2011	310.93	12.7	4.6	7.32	969	28.3	27.1	498	37.6	20.2	76.6	0.09	110.9	48.1	24.9	10.4
B23	23/05/2011	311.34	13.9	4.4	7.33	875	21.6	40.5	454	35.4	19.0	68.8	0.07	98.1	42.4	21.7	9.3
B23	06/06/2011	311.41	12.0	4.4	7.36	782	37.5	26.6	390	30.7	16.4	60.4	<0.05	80.1	33.2	23.7	9.4
B23	20/06/2011	311.38	13.0	5.3	7.37	850	20.2	40.5	432	33.2	19.2	66.9	0.11	95.8	37.7	28.3	9.3
B23	04/07/2011	311.79	14.8	6.5	7.33	959	17.8	43.3	495	38.9	26.2	91.4	<0.05	114.4	47.5	27.4	10.1
B23	18/07/2011	311.8	12.6	6.5	7.39	959	20.7	27.1	490	40.3	22.1	76.2	0.07	108.8	45.3	27.6	10.3
B23	16/08/2011	311.7	14.8	6.2	7.32	1001	24.5	26.2	516	41.7	25.0	79.3	0.11	123.1	45.8	27.2	13.6
B23	29/08/2011	311.77	13.9	5.6	7.35	998	24.8	60.1	511	40.5	24.5	75.7	<0.05	109.3	44.5	25.1	10.6
B23	12/09/2011	311.53	14.3	5.5	7.27	995	23.7	43.5	498	39.0	25.7	85.4	<0.05	104.0	47.1	30.1	12.3
B23	26/09/2011	311.35	14.2	5.6	7.32	826	26.2	42.5	421	32.5	21.2	72.0	0.07	89.7	39.2	27.2	11.1
B23	10/10/2011	311.41	14.0	4.9	7.33	794	22.7	24.9	392	31.3	19.5	62.7	0.13	86.1	36.2	25.2	10.5
B23	24/10/2011	311.18	13.0	4.1	7.34	668	19.9	28.6	321	27.9	15.1	48.9	0.13	69.1	28.5	21.1	9.2
B23	07/11/2011		12.7	6.0	7.43	384	18.3	14.2	189	18.5	7.5	22.7	0.09	36.2	15.6	15.0	6.7
B23	21/11/2011	311.76	13.4	5.6	7.38	707	20.2	22.7	345	30.2	17.3	58.2	0.12	75.9	34.4	24.8	11.2
B23	05/12/2011	311.32	12.0	5.4	7.38	686	20.4	40.1	334	28.8	17.3	53.8	0.11	78.1	32.6	22.9	9.8
B23	19/12/2011	310.94	11.2	4.6	7.48	940	18.3	17.1	238	23.7	12.9	37.4	0.12	52.9	21.1	22.0	8.6
B23	03/01/2012	312.12	12.3	4.3	7.53	949	19.6	9.0	204	21.6	10.6	30.0	0.08	43.6	17.9	17.7	6.1
B23	16/01/2012	311.78	10.4	5.0	7.51	603	19.8	17.6	286	26.0	14.9	45.2	0.09	64.1	25.6	21.2	7.9
B23	30/01/2012	313.34	10.5	4.3	7.54	550	20.4	24.9	255	23.4	13.5	39.9	0.09	56.4	24.7	21.1	9.3
B23	13/02/2012	310.82	9.8	5.2	7.37	635	20.4	22.2	292	29.6	16.4	48.7	0.05	66.4	29.6	22.4	9.1
B23	27/02/2012	311.28	11.8	5.6	7.45	525	19.2	16.4	236	22.8	12.6	37.6	0.07	50.8	20.9	19.3	7.3
B23	12/03/2012	311.56	13.2	5.8	7.34	637	19.9	23.7	288	26.5	14.7	48.7	<0.05	61.7	25.1	22.8	10.5
B23	26/03/2012	311.68	12.7	6.1	7.36	765	21.4	30.3	350	30.5	17.8	55.0	0.09	81.4	34.2	24.5	10.2
B23	10/04/2012	311.54	11.1	6.4	7.34	788	18.4	30.1	361	34.4	20.8	63.4	0.10	83.2	36.3	25.7	10.2
B23	23/04/2012	311.92	10.8	5.6	7.47	613	19.9	24.4	283	28.0	15.8	42.1	0.10	60.8	26.5	20.2	7.9
B23	09/05/2012	312.38	12.2	5.5	7.35	671	20.2	22.6	321	30.3	16.5	50.8	0.16	71.9	28.7	21.2	8.3
B23	21/05/2012	312.18	11.5	5.2	7.24	856	24.7	38.1	393	37.4	21.6	70.4	0.13	92.0	38.2	25.9	9.9
B23	04/06/2012	312.73	12.2	5.5	7.33	794	21.0	30.6	381	35.0	21.3	66.1	<0.05	91.7	35.6	24.0	8.4
B23	18/06/2012	312.31	14.9	5.3	7.27	938	19.2	42.3	461	36.0	22.7	69.3	<0.05	106.2	41.6	26.6	10.9
B23	02/07/2012	311.92	14.9	6.4	7.31	970	34.2	32.3	494	36.0	24.0	68.4	0.13	116.6	41.6	25.6	11.2
B23	16/07/2012	311.17	13.2	6.0	7.29	970	22.7	32.3	526	34.8	24.3	67.6	<0.05	129.6	43.8	27.8	12.2
B23	30/07/2012	311.66	15.1	5.6	7.25	949	23.1	34.2	495	33.5	24.3	60.7	0.13	106.5	42.5	25.8	10.9
B23	13/08/2012	310.68	15.3	5.7	7.30	951	22.7	19.6	476	33.4	23.5	62.8	0.09	106.1	42.4	26.9	11.8
B23	27/08/2012	311.91	14.5	5.5	7.37	944	22.9	46.2	494	33.5	23.7	60.2	0.08	105.2	45.0	26.7	12.4
B23	10/09/2012	311.89	15.4	5.8	7.39	948	22.7	40.3	482	33.5	23.4	59.4	<0.05	116.7	44.4	26.4	12.1
B23	24/09/2012	310.94	14.2	5.3	7.42	950	22.8	30.3	489	35.8	24.7	63.1	<0.05	115.4	41.9	25.1	11.7
B23	08/10/2012	310.3	14.3	5.5	7.46	940	22.9	35.0	471	34.6	22.9	62.1	0.13	113.3	41.7	27.2	11.9
B23	22/10/2012	310.94	15.3	6.1	7.42	908	26.0	28.4	469	33.3	22.3	60.2	<0.05	93.3	44.1	27.0	12.3
B23	05/11/2012	311.65	12.6	5.2	7.54	868	22.4	23.2	433	32.1	20.7	59.4	0.26	101.1	41.2	27.9	12.0
B26	14/02/2011	312.86	7.9	5.6	6.98	197	14.5	11.9	79	12.4	6.1	7.9	0.14	17.8	4.9	11.4	2.6
B26	28/02/2011	312.99	7.0	7.0	7.07	197	14.1	18.3	78	13.8	7.0	8.5	0.15	22.1	5.2	10.3	2.5
B26	14/03/2011	313.04	8.5	6.2	6.97	200	15.1	22.9	78	14.8	7.0	8.9	0.13	18.8	4.9	9.1	2.2
B26	28/03/2011	312.16	7.5	6.0	7.10	202	11.1	14.1	81	14.2	6.2	8.6	0.11	18.8	5.3	9.0	2.4
B26	11/04/2011	313.05	9.4	4.7	6.87	192	13.7	11.6	77	12.7	5.7	7.9	0.09	17.6	5.8	9.4	2.5
B26	26/04/2011	312.8	12.6	4.6	7.34	190	14.5	9.5	81	12.8	5.5	7.8	0.11	17.6	5.0	9.6	2.5
B26	09/05/2011	312.68	10.2	3.0	7.22	204	15.6	7.6	82	14.3	5.0	8.5	0.28	18.1	5.5	9.3	2.5
B26	23/05/2011	312.57	13.3	4.1	7.16	227	15.5	14.1	93	17.7	3.8	9.7	0.14	20.9	6.1	11.4	2.6
B26	06/06/2011	312.65	15.8	1.4	7.07	247	15.8	20.4	98	20.3	3.4	10.5	0.12	24.9	7.2	13.1	3.4
B26	20/06/2011	312.6	16.3	1.5	7.18	240	15.8	27.6	96	19.1	3.6	10.3	0.51	22.7	6.0	12.9	3.2
B26	04/07/2011	312.81	18.0	1.2	7.09	249	16.5	20.4	99	21.2	3.8	11.5	0.14	23.6	6.7	15.0	3.7
B26	18/07/2011	312.83	17.0	2.0	6.95	250	16.2	18.3	104	21.1	2.7	10.7	0.19	22.5	6.2	14.8	4.0
B26	16/08/2011	312.76	18.9	1.9	7.07	238	16.7	12.3	95	18.9	2.0	9.7	0.17	21.4	5.5	13.6	4.7
B26	29/08/2011	312.8	18.5	3.2	7.11	234	19.3	19.0	98	18.2	0.0	9.1	<0.05	21.2	5.9	14.7	3.7
B26	12/09/2011	312.65	19.1	1.6	7.10	228	17.9	13.7	95	18.0	0.0	8.4	0.10	18.2	5.3	14.3	3.8
B26	26/09/2011	312.6	19.5	1.9	7.14	229	20.5	19.0	92	19.7	1.0	10.5	0.11	18.7	5.5	16.3	4.6
B26	10/10/2011	312.6	19.5	1.8	7.08	224	18.4	14.8	85	19.4	1.5	8.3	0.17	18.0	5.1	14.6	3.8
B26	24/10/2011	312.5	17.9	1.3	7.12	226	16.7	27.6	85	20.2	2.3	8.1	0.17	17.7	5.2	13.7	3.9
B26	07/11/2011	312.39	15.4	2.3	7.17	227	15.6	17.4	85	20.8	3.3	10.0	0.15	19.1	5.5	14.1	3.7
B26	21/11/2011	312.89	16.9	3.1	7.29	199	15.0	13.9	76	14.8	3.1	8.8	0.14	16.4	4.9	14.2	4.5
B26	05/12/2011	311.16	12.9	4.8	7.31	157	14.4	25.5	67	13.8	4.2	8.1	0.14	15.7	4.5	11.1	3.1
B26	19/12/2011	311.52	10.3	6.6	7.46	179	12.9	8.6	70	13.6	4.4	7.8	0.15	14.3	4.2	11.2	2.5
B26	03/01/2012	313.44	10.9	6.2	7.53	174	12.8	5.6	65	10.9	4.9	6.4	0.13	13.9	4.1	10.7	2.7
B26	16/01/2012	311.39	8.7	5.9	7.70	154	12.2	9.3	63	9.8	4.9	6.1	0.26	13.5	3.9	10.7	2.8
B26	30/01/2012	311.04	6.6	7.1	7.61	157	12.4	6.5	63	10.2	5.2	6.2	0.13	12.5	3.8	10.3	2.6
B26	27/02/2012	311.05	6.6	9.9	7.62	200	11.4	5.3	73	16.6	7.2	8.6	0.10	17.5	5.2	11.7	2.4
B26	12/03/2012	312.76	6.9	9.1	7.42	190	18.8	18.1	68	14.3	6.7	8.3	0.10	16.3	4.8	11.1	3.1
B26	26/03/2012	312.79	8.8	7.7	7.40	193	11.4	10.0	71	14.1	6.1	8.2	0.14	16.5	5.1	10.7	2.6
B26	10/04/2012	312.74	6.8	5.0	7.41	200	11.9	12.3	76	16.2	6.0	8.6	0.13	17.1	5.5	11.7	2.5
B26	23/04/2012	313.21	7.2	3.8	7.42	209	12.5	18.1	84	16.1	4.9	8.2	0.12	18.8	5.5	11.4	2.4
B26	09/05/2012	313.48	11.3	3.9	7.39	184	13.0	9.3	77	12.8	4.3	7.7	0.16	16.9	5.0	11.4	2.2
B26	05/06/2012	313.51	10.4	3.3	7.50	188	14.0	8.3	84	11.2	4.1	7.4	0.14	15.6	4.9	11.0	2.0
B26	18/06/2012	313.18	11.3	3.5	7.37	195	12.1	16.7	87	11.2	4.1	7.5	<0.05	18.7	5.3	11.4	2.4
B26	02/07/2012	312.87		3.3	7.25	194	12.3	11.1	99	11.7	4.3	7.7	0.15	18.1	5.9	12.6	2.9
B26	16/07/2012	312.86	11.0	2.8	7.42	200	13.8	16.0	103	11.9	3.7	7.9	0.11	18.3	6.0	12.8	3.0
B26	30/07/2012	312.75	12.5	2.2	7.43	207	15.0	7.0	93	12.4	3.0	7.7	0.13	19.8	6.1	13.1	2.6
B26	13/08/2012	311.29	13.0	2.6	7.41	219	14.5	6.3	94	13.7	3.4	8.5	0.15	20.2	5.6	12.0	2.9
B26	27/08/2012	312.86	14.8	1.8	7.31	219	14.8	12.7	101	14.7	2.8	8.4	0.12	19.9	6.3	13.9	3.3
B26	10/09/2012	312.83	15.6	3.0	7.46	226	17.7	22.9	98	14.6	3.2	8.4	<0.05	22.0	6.2	12.8	2.9
B26	24/09/2012	312.83	13.1	3.2	7.41	242	15.6	15.1	105	15.3	4.3	10.2	0.14	21.9	7.2	14.4	3.5
B26	08/10/2012	312.07	16.1	2.1	7.44	217	16.2	12.3	87	17.1	2.2	7.7	0.11	19.1	5.1	12.6	3.1
B26	22/10/2012	312.61	17.1	2.3	7.45	224	17.1	15.5	87	18.2	3.2	8.3	0.15	18.4	6.0	14.2	3.5
B26	05/11/2012	312.77	14.8	2.3	7.68	218	16.1	16.9	85	17.7	3.0	8.1	0.14	17.9	5.1	13.0	3.1

Sample ID	Date	WL	T	Do	pH	EC	SiO_2	CO_2	HCO_3	Cl	NO_3	SO_4	PO_4	Ca	Mg	Na	K
B27	14/02/2011	312.56	11.5	6.5	6.96	480	19.7	25.7	204	24.2	13.2	35.7	0.05	46.1	16.8	21.0	4.6
B27	28/02/2011	312.59	9.3	6.2	7.06	487	21.6	31.4	210	26.0	14.7	38.1	<0.05	57.5	18.4	19.6	4.3
B27	14/03/2011	312.59	12.8	6.4	7.10	491	21.2	22.5	209	26.8	15.5	39.5	<0.05	48.6	17.4	18.0	4.0
B27	28/03/2011	312.92	11.7	6.6	7.04	499	15.5	33.8	210	26.9	16.2	39.5	<0.05	52.8	18.1	17.7	4.2
B27	11/04/2011	312.8	12.6	6.8	6.98	510	20.0	26.6	214	27.3	16.9	39.7	<0.05	51.1	18.9	18.8	4.6
B27	26/04/2011	312.46	13.5	6.8	7.19	518	20.5	24.1	214	28.6	17.7	41.7	<0.05	51.8	18.5	20.7	4.8
B27	09/05/2011	312.36	14.3	6.4	7.14	534	21.1	27.8	225	29.6	18.2	44.8	<0.05	66.4	20.4	16.4	3.9
B27	23/05/2011	312.21	12.6	6.5	7.16	554	19.7	36.1	232	31.8	19.6	47.1	<0.05	59.7	19.6	18.7	4.7
B27	06/06/2011	312.29	12.4	6.7	7.09	555	18.3	41.5	227	30.9	19.2	47.1	<0.05	56.3	18.8	20.7	4.8
B27	20/06/2011	312.09	13.1	6.5	7.14	558	17.7	29.6	231	31.1	19.3	46.7	0.06	63.6	19.2	20.3	4.0
B27	04/07/2011	312.69	13.7	7.4	7.11	545	18.1	38.0	229	31.6	19.6	50.7	<0.05	58.8	20.6	20.9	4.8
B27	18/07/2011	312.71	13.1	7.5	7.10	533	17.9	17.8	227	29.1	17.3	46.1	0.05	54.6	20.2	28.6	5.2
B27	16/08/2011	312.66	14.4	8.6	7.20	478	18.7	17.4	210	25.3	13.8	38.4	<0.05	50.7	16.0	19.7	5.6
B27	29/08/2011	312.28	14.0	9.1	7.13	506	20.8	52.1	217	25.8	14.6	39.0	0.12	52.7	17.4	19.7	5.3
B27	12/09/2011	312.03	14.1	8.1	7.07	594	19.7	31.7	254	31.1	18.4	51.9	<0.05	58.9	21.1	22.5	5.7
B27	26/09/2011	312.03	14.6	7.8	7.08	607	21.4	36.4	259	33.6	18.7	54.8	<0.05	65.2	23.1	23.5	5.8
B27	10/10/2011	311.84	14.3	7.4	7.03	659	21.2	39.8	283	36.8	18.6	57.3	<0.05	73.5	25.7	23.4	5.9
B27	24/10/2011	311.96	13.4	7.7	7.08	682	19.5	26.4	292	38.3	18.0	58.1	<0.05	75.2	26.5	24.4	6.1
B27	07/11/2011	312.82	13.0	8.2	7.04	597	19.2	30.6	251	34.3	17.0	51.1	<0.05	65.3	22.8	21.8	5.5
B27	21/11/2011	312.59	13.4	8.5	7.08	618	19.3	35.2	266	36.6	17.4	56.6	<0.05	67.0	23.3	24.7	7.7
B27	05/12/2011	312.11	11.9	8.8	7.21	562	19.3	36.8	240	30.3	13.1	48.2	<0.05	63.0	21.9	20.4	5.2
B27	19/12/2011	312.55	10.4	9.1	7.21	442	19.0	20.8	194	23.8	8.3	33.5	0.05	46.0	15.6	21.2	4.9
B27	03/01/2012	312.66	11.8	8.9	7.15	469	14.9	18.1	205	25.2	9.2	35.7	<0.05	48.5	16.8	19.5	4.2
B27	16/01/2012	312.42	11.2	8.7	7.22	457	18.7	18.5	200	24.4	8.8	34.5	0.05	48.7	16.8	19.9	5.0
B27	30/01/2012	311.89	11.2	8.6	7.24	468	19.5	26.9	207	24.4	8.7	34.8	<0.05	47.5	17.4	21.5	7.1
B27	13/02/2012	312.17	10.1	8.4	7.14	387	11.5	19.7	172	21.3	6.2	25.6	<0.05	39.7	14.7	18.2	5.2
B27	27/02/2012	312.03	11.7	7.7	7.27	363	18.6	16.0	155	19.5	5.6	20.9	0.05	34.5	12.2	17.4	4.1
B27	12/03/2012	312.33	12.1	7.3	7.24	341	18.4	10.7	146	17.9	5.4	18.8	0.05	30.8	10.7	16.5	4.7
B27	26/03/2012	312.39	12.6	7.5	7.22	350	18.4	15.1	150	17.6	5.5	19.7	0.09	32.3	12.0	16.5	4.4
B27	10/04/2012	312.3	12.3	7.5	7.19	333	15.9	17.1	149	18.5	6.2	19.6	0.07	31.4	11.6	18.4	5.8
B27	23/04/2012	312.68	11.9	7.2	7.29	306	18.3	16.4	135	16.8	5.7	16.4	0.06	27.3	10.0	14.8	3.5
B27	09/05/2012	313.23	12.8	7.1	7.26	284	18.1	15.7	126	15.8	5.6	14.6	<0.05	26.6	9.2	14.2	2.9
B27	21/05/2012	312.96	12.3	7.1	7.13	273	21.8	11.3	118	16.0	5.9	13.9	0.08	25.4	8.8	13.7	2.9
B27	04/06/2012	313.58	13.8	7.3	7.24	265	17.9	13.8	127	15.3	5.9	12.6	0.05	25.6	8.7	13.7	2.9
B27	18/06/2012	313.17	13.7	7.4	7.33	266	16.9	29.2	117	14.4	5.6	12.0	<0.05	25.9	8.5	13.3	3.0
B27	02/07/2012	312.8	14.2	7.6	7.22	290	17.2	16.0	133	15.4	6.0	12.9	0.05	25.4	9.7	14.9	3.6
B27	16/07/2012	312.77	13.8	8.0	7.34	291	18.3	15.3	138	16.2	6.3	13.8	<0.05	29.5	9.5	14.3	3.6
B27	30/07/2012	312.66	14.6	7.9	7.17	310	19.6	9.0	139	16.7	7.1	14.2	<0.05	30.5	10.4	15.0	3.2
B27	13/08/2012	312.7	15.1	7.9	7.22	350	19.7	2.6	154	17.4	8.0	15.7	0.07	31.3	10.7	15.3	3.9
B27	27/08/2012	312.78	14.6	7.8	7.20	321	18.7	22.5	149	17.3	8.0	15.7	0.06	35.2	10.8	15.0	3.6
B27	10/09/2012	312.78	15.1	7.7	7.32	328	19.8	21.3	145	16.7	7.3	14.7	<0.05	32.9	10.4	14.4	3.5
B27	24/09/2012	312.82	15.1	7.7	7.41	319	20.3	14.8	139	17.3	7.4	15.2	<0.05	31.3	10.2	14.2	3.5
B27	08/10/2012	312.06	14.6	7.2	7.47	308	18.4	14.6	138	16.6	6.9	14.0	0.06	30.3	9.9	14.4	3.4
B27	22/10/2012	312.38	14.3	6.9	7.32	298	20.0	15.8	134	16.2	6.2	13.3	<0.05	27.3	10.3	14.4	3.5
B27	05/11/2012	312.55	13.0	7.3	7.49	295	19.1	4.4	132	15.9	5.7	13.1	0.06	28.3	10.5	15.9	3.9
B29	14/02/2011	313.06	11.3	4.7	6.91	968	23.8	36.4	466	45.6	17.2	78.2	<0.05	87.3	47.3	41.2	11.9
B29	28/02/2011	312.96	10.0	6.4	7.02	944	24.6	35.2	472	46.5	18.8	76.4	0.05	103.3	50.6	38.0	11.5
B29	14/03/2011	312.99	13.2	4.6	7.17	940	26.8	42.6	466	42.5	17.3	70.6	<0.05	94.5	47.9	31.9	9.4
B29	28/03/2011	313.31	11.8	4.1	7.20	958	20.9	29.6	465	46.9	18.8	76.4	0.06	99.1	49.1	31.7	9.9
B29	11/04/2011	313.19	12.8	4.6	7.06	974	24.2	30.1	469	46.6	19.8	74.3	0.05	93.0	49.4	35.5	10.9
B29	26/04/2011	312.97	13.3	3.7	7.35	959	25.0	31.0	459	46.9	21.7	78.8	0.05	90.2	47.8	36.3	11.2
B29	09/05/2011	312.81	14.4	4.3	7.31	962	25.7	22.5	480	46.3	21.3	78.9	0.09	98.6	51.6	31.8	9.8
B29	23/05/2011	312.66	12.7	4.2	7.29	964	25.2	44.7	473	48.1	22.3	76.2	<0.05	91.6	48.0	30.2	9.8
B29	06/06/2011	312.63	12.5	4.4	7.31	962	22.5	48.2	469	47.4	22.2	77.1	<0.05	91.3	45.6	36.3	10.5
B29	20/06/2011	312.54	15.6	4.3	7.31	912	21.7	41.9	465	47.9	24.4	76.1	0.08	101.6	48.8	34.7	9.9
B29	04/07/2011	312.85	15.1	6.1	7.33	955	22.5	43.5	484	49.9	24.7	82.4	<0.05	96.6	49.4	39.7	9.6
B29	18/07/2011	312.99	12.8	4.8	7.30	972	21.9	36.8	477	50.0	22.3	75.3	0.05	96.6	49.7	37.4	10.3
B29	16/08/2011	313.02	14.3	5.2	7.29	964	24.7	26.6	480	49.3	22.1	83.5	0.07	104.5	46.4	37.7	13.2
B29	29/08/2011	312.83	14.2	5.5	7.31	968	24.4	28.7	481	47.9	23.3	75.6	<0.05	98.7	46.0	34.9	10.5
B29	12/09/2011	312.6	13.5	5.1	7.27	993	22.9	45.0	499	47.5	26.2	80.7	<0.05	95.5	51.8	38.5	12.2
B29	26/09/2011	312.39	14.4	5.5	7.27	989	28.7	41.3	492	47.8	25.6	81.6	<0.05	98.8	52.0	45.2	13.3
B29	10/10/2011	312.38	13.8	5.9	7.28	1003	23.3	21.3	488	48.0	26.0	75.1	0.07	99.1	51.4	38.0	11.8
B29	24/10/2011	311.19	14.8	6.0	7.25	994	22.7	45.2	503	47.3	24.8	72.3	0.07	99.5	50.8	37.6	12.1
B29	07/11/2011	311.6	13.4	6.6	7.28	985	22.3	42.3	493	49.3	22.9	76.5	0.07	97.3	52.7	37.4	11.9
B29	21/11/2011	313.04	14.7	6.1	7.32	960	23.1	36.2	471	50.6	20.6	74.8	0.09	90.9	52.2	37.8	13.1
B29	05/12/2011	312.56	12.6	6.3	7.34	966	23.8	50.6	486	48.9	21.4	73.8	0.09	99.6	52.5	38.2	11.6
B29	19/12/2011	311.74	11.8	6.3	7.40	960	23.3	29.1	472	49.6	20.2	75.6	0.07	101.9	49.1	40.3	12.1
B29	03/01/2012	312.93	12.7	5.7	7.39	962	23.7	25.9	471	49.6	21.1	73.6	<0.05	94.0	49.3	38.3	9.8
B29	16/01/2012	312.86	11.9	5.6	7.42	966	22.0	28.8	470	48.5	21.2	75.2	0.10	97.9	50.5	39.3	11.9
B29	30/01/2012	312.42	11.4	5.1	7.45	979	23.9	63.3	475	48.2	21.5	71.5	<0.05	93.4	51.5	40.2	14.3
B29	13/02/2012	311.56	9.2	5.2	7.38	972	23.2	30.3	467	50.0	21.7	74.3	<0.05	99.6	55.2	39.1	12.3
B29	27/02/2012	312.28	11.7	5.0	7.36	1002	23.5	23.0	472	49.1	20.4	72.8	<0.05	93.1	50.5	39.9	11.1
B29	12/03/2012	312.62	13.9	5.2	7.32	992	23.5	24.2	464	49.7	19.4	75.5	<0.05	92.2	51.3	39.4	11.0
B29	26/03/2012	312.8	13.7	5.3	7.29	981	23.4	39.4	466	49.2	18.9	72.6	0.06	95.0	50.6	39.0	12.2
B29	10/04/2012	312.35	11.8	5.3	7.29	1005	20.1	41.8	473	53.7	20.8	78.9	<0.05	95.5	52.0	40.7	12.4
B29	23/04/2012	312.9	11.8	5.1	7.38	995	23.3	30.6	466	54.5	21.0	77.5	<0.05	93.6	50.6	40.8	11.0
B29	09/05/2012	313.45	13.4	5.5	7.30	985	22.7	43.4	462	52.9	18.9	81.2	<0.05	100.3	46.7	35.2	11.1
B29	21/05/2012	313.33	12.4	5.2	7.22	993	27.3	34.2	461	54.1	20.0	83.7	<0.05	97.4	50.6	39.3	11.5
B29	04/06/2012	313.96	14.0	4.9	7.30	989	23.5	31.3	460	50.4	21.0	82.0	<0.05	100.8	49.5	37.6	11.4
B29	18/06/2012	313.62	15.4	5.1	7.27	976	20.2	98.3	470	47.4	19.8	73.3	<0.05	103.4	48.2	36.1	11.4
B29	02/07/2012	313.22	15.5	5.6	7.27	979	20.5	38.4	477	48.4	21.0	72.5	0.07	98.0	45.5	33.8	11.1
B29	16/07/2012	312.25	13.5	5.7	7.26	981	22.6	35.4	499	47.8	21.2	72.4	<0.05	102.9	47.8	35.3	12.0
B29	30/07/2012	313.05	15.3	5.3	7.21	983	24.1	30.1	471	47.8	19.7	69.0	<0.05	98.5	49.7	36.8	11.1
B29	13/08/2012	311.95	13.6	5.4	7.32	995	23.2	8.1	480	48.0	18.7	72.2	0.12	98.3	44.7	35.0	11.7
B29	27/08/2012	313.12	14.9	5.8	7.36	993	23.4	41.3	498	48.1	19.1	71.2	<0.05	106.8	50.5	37.4	12.3
B29	10/09/2012	313.14	14.9	5.5	7.39	1009	23.0	37.7	489	47.7	17.5	70.6	<0.05	103.8	49.5	37.6	11.9
B29	24/09/2012	313.06	15.0	5.3	7.37	997	23.5	31.0	483	49.9	17.9	73.0	<0.05	100.7	48.3	36.7	11.8
B29	08/10/2012	311.4	14.5	5.4	7.45	987	22.6	35.2	467	46.8	21.0	68.8	0.08	100.7	47.5	35.4	11.8
B29	22/10/2012	312.71	14.0	5.2	7.44	984	24.6	35.9	462	47.0	18.4	71.2	<0.05	91.3	53.1	39.0	13.1
B29	05/11/2012	312.83	12.7	5.2	7.52	984	23.2	32.8	469	47.8	17.1	73.8	<0.05	97.6	45.7	37.1	11.1

Sample ID	Date	WL	T	Do	pH	EC	SiO_2	CO_2	HCO_3	Cl	NO_3	SO_4	PO_4	Ca	Mg	Na	K
B33	14/02/2011	314.67	8.9	5.9	7.07	180	14.8	16.0	67	12.3	6.4	7.6	0.08	14.2	4.8	12.4	2.9
B33	28/02/2011	314.77	7.9	6.8	6.85	182	12.7	16.7	67	13.6	6.8	8.2	0.11	15.4	5.2	10.5	2.6
B33	14/03/2011	314.89	8.5	6.8	6.96	189	14.5	25.2	67	14.5	6.8	8.7	0.11	14.8	5.3	10.3	2.4
B33	28/03/2011	315.07	7.8	7.3	7.07	181	14.0	17.4	67	13.4	6.6	8.2	0.13	15.0	4.3	10.2	2.6
B33	11/04/2011	314.83	8.8	7.1	7.11	178	13.9	10.0	66	12.5	5.8	7.5	0.12	13.8	5.5	10.1	2.8
B33	26/04/2011	314.58	9.3	5.1	7.17	179	15.0	12.3	68	13.0	5.5	7.7	0.08	14.4	5.1	10.1	2.6
B33	09/05/2011	314.52	11.2	3.5	7.03	191	15.4	18.3	72	14.4	6.6	8.7	0.13	15.6	5.4	10.1	2.6
B33	23/05/2011	314.18	14.1	2.5	7.22	219	15.4	27.8	82	17.9	5.4	9.9	0.13	18.3	5.8	11.1	3.1
B33	06/06/2011	314.39	15.2	1.7	6.82	242	15.3	26.2	88	20.9	5.8	10.9	0.14	18.2	6.3	14.9	3.7
B33	20/06/2011	314.66	17.8	1.6	6.90	238	14.6	22.5	88	19.9	5.7	10.6	0.20	18.7	6.3	14.5	3.8
B33	04/07/2011	314.25	17.2	1.9	6.87	239	11.3	24.5	90	21.2	4.6	11.0	0.18	18.7	6.2	15.6	3.8
B33	18/07/2011	314.44	16.9	1.8	6.89	234	15.8	15.7	87	20.5	3.6	9.9	0.18	18.4	6.0	17.5	3.8
B33	16/08/2011	314.5	19.2	1.5	6.86	223	16.3	22.9	87	18.1	2.8	9.2	0.18	18.4	5.8	15.0	3.8
B33	29/08/2011	314.71	18.2	2.2	6.96	222	17.4	16.4	88	18.2	2.1	8.7	0.13	17.2	5.5	14.4	3.9
B33	12/09/2011	314.61	18.5	1.8	6.90	218	13.1	18.3	87	17.7	1.6	8.1	0.13	15.2	5.3	15.1	4.0
B33	26/09/2011	314.45	19.4	2.8	6.91	219	17.7	22.0	85	19.1	2.6	8.7	0.15	16.5	5.6	16.3	4.3
B33	10/10/2011	314.51	19.3	1.5	6.87	215	17.6	21.5	81	19.1	2.8	8.3	0.15	16.1	5.4	15.0	4.1
B33	24/10/2011	314.38	17.4	1.7	6.88	215	17.1	18.5	81	19.8	3.2	8.7	0.13	16.1	5.3	15.1	4.3
B33	07/11/2011	316.69	16.2	4.5	7.01	212	15.1	18.1	78	19.2	4.4	9.0	0.13	15.2	5.7	15.0	4.8
B33	21/11/2011	314.35	16.4	3.8	6.91	189	14.4	15.1	73	14.0	4.4	7.9	0.12	13.9	4.8	12.2	3.2
B33	05/12/2011	314.26	13.6	4.5	7.32	185	14.5	30.1	70	14.0	4.4	8.1	0.10	13.1	4.9	11.9	3.2
B33	19/12/2011	314.97	11.2	6.2	7.19	180	13.6	16.0	70	13.9	4.4	8.0	0.12	14.4	4.7	13.9	4.0
B33	03/01/2012	315.47	10.6	6.6	7.30	164	13.6	9.7	63	11.7	5.1	6.8	0.09	13.2	4.6	11.5	2.9
B33	16/01/2012	314.7	8.0	6.4	7.34	155	13.5	7.4	61	10.6	4.9	6.5	0.11	12.8	4.4	11.1	2.6
B33	30/01/2012	314.36	8.0	6.9	7.55	157	13.2	12.5	61	10.8	5.1	6.4	0.11	11.5	4.1	10.2	2.6
B33	13/02/2012	314.17	6.2	7.2	7.19	168	12.8	5.8	63	13.2	5.6	7.2	0.08	13.8	5.0	11.8	3.3
B33	27/02/2012	314.26	6.9	9.1	7.33	190	12.6	8.3	66	15.5	6.5	8.1	0.08	14.9	5.2	11.7	2.8
B33	12/03/2012	314.72	7.3	9.0	7.18	201	11.8	9.0	66	14.6	6.5	8.1	0.07	14.1	4.8	11.7	2.6
B33	26/03/2012	314.4	7.8	8.0	7.22	183	12.3	11.1	66	14.2	6.0	7.9	0.12	14.1	5.1	10.7	2.4
B33	10/04/2012	314.43	6.8	6.7	7.14	194	12.3	15.1	67	15.7	6.0	8.5	0.05	14.7	5.5	11.0	2.4
B33	23/04/2012	315.17	7.6	5.6	7.19	191	13.6	12.5	74	15.4	4.8	7.9	0.11	14.6	5.3	11.8	2.5
B33	09/05/2012	315.29	10.1	5.2	7.10	155	13.2	15.3	63	10.3	4.3	6.7	0.12	12.6	4.4	10.9	2.1
B33	21/05/2012	315.1	9.2	3.5	6.99	155	16.0	15.5	65	10.0	4.0	6.7	0.13	11.9	4.3	10.7	2.0
B33	04/06/2012	315.3	10.8	4.2	6.92	169	14.4	10.9	76	9.2	5.0	7.2	0.19	13.6	4.4	11.6	2.5
B33	18/06/2012	314.9	12.9	2.8	7.09	179	14.9	19.9	74	9.5	3.5	6.9	0.07	15.2	4.9	11.6	2.6
B33	02/07/2012	312.98	13.6	1.6	6.93	175	14.2	12.0	83	10.0	2.9	6.8	0.15	13.9	5.1	12.1	3.1
B33	16/07/2012	314.61	14.1	1.6	7.05	182	15.6	13.4	83	12.5	3.0	7.7	0.12	16.2	5.0	11.7	3.1
B33	30/07/2012	314.51	16.4	1.7	6.81	196	16.5	16.9	81	13.9	2.8	7.8	0.14	16.3	5.5	12.3	2.9
B33	13/08/2012	314.62	16.9	2.0	6.97	214	17.5	7.4	79	16.0	2.7	8.8	0.13	17.8	5.6	12.6	3.6
B33	27/08/2012	314.64	18.5	1.1	6.83	201	17.4	28.0	81	16.4	2.6	8.3	0.14	17.8	5.4	12.7	3.5
B33	10/09/2012	314.34	19.6	1.2	7.04	208	18.3	29.9	73	15.6	2.2	7.1	<0.05	16.6	5.1	12.5	3.5
B33	24/09/2012	314.23	19.1	1.7	6.84	199	17.9	17.6	74	18.2	3.4	7.8	0.15	15.3	4.9	12.5	3.5
B33	08/10/2012	314.34	18.9	1.8	7.03	234	16.4	15.1	77	18.4	3.3	7.7	0.13	16.9	5.1	12.8	3.5
B33	22/10/2012	312.82	17.6	2.3	7.35	210	17.6	24.3	76	18.7	3.8	8.1	0.12	15.3	5.9	13.6	3.6
B33	05/11/2012	314.47	16.0	2.7	7.27	207	15.9	19.9	79	18.2	3.2	8.2	0.11	15.8	5.6	14.4	3.7
B39	14/02/2011	315.21	10.4	4.2	7.23	204	19.0	13.2	90	13.0	1.2	6.6	0.09	17.6	5.8	13.6	3.5
B39	28/02/2011	315.03	9.8	3.4	7.12	198	17.5	12.8	89	12.7	1.1	6.6	0.11	21.0	5.3	11.6	3.1
B39	14/03/2011	315.01	10.6	3.8	6.91	195	20.0	9.7	87	13.0	1.1	7.0	0.10	15.5	5.4	11.8	3.2
B39	28/03/2011	315.20	10.4	2.5	7.20	194	19.1	16.4	85	13.2	1.2	7.2	0.11	19.6	5.5	9.9	3.0
B39	11/04/2011	315.11	10.9	3.6	7.08	195	19.3	9.0	85	13.1	1.2	7.1	0.08	16.1	6.2	10.4	3.0
B39	26/04/2011	314.96	10.6	1.4	7.28	194	19.7	10.0	84	13.1	1.1	6.9	<0.05	16.0	5.5	10.2	3.0
B39	09/05/2011	314.88	11.9	1.5	7.25	193	18.9	10.9	84	13.1	0.0	6.7	0.10	16.5	5.6	9.7	2.9
B39	23/05/2011	314.82	11.4	1.0	7.31	201	17.3	20.8	85	13.5	0.0	6.3	0.07	16.9	5.5	8.9	2.7
B39	06/06/2011	314.80	10.7	1.8	7.35	202	15.7	19.7	92	13.6	0.0	5.8	0.10	17.0	5.6	10.8	2.9
B39	20/06/2011	314.78	11.5	1.6	7.37	216	14.1	21.1	95	14.4	0.0	5.9	0.10	17.5	6.1	11.3	2.7
B39	04/07/2011	314.66	12.3	1.5	7.34	204	13.4	15.5	93	14.5	0.0	6.2	0.08	19.4	5.9	10.7	2.8
B39	18/07/2011	314.81	12.6	1.9	7.58	213	15.4	14.8	98	15.0	0.0	5.4	0.07	18.6	6.1	10.8	2.7
B39	16/08/2011	314.80	12.5	1.3	7.48	252	17.0	16.4	112	18.0	0.0	5.2	0.12	21.4	6.9	13.5	4.3
B39	29/08/2011	314.84	14.4	1.8	7.42	244	11.6	8.8	112	17.4	0.0	5.4	<0.05	23.0	6.5	12.9	3.3
B39	12/09/2011	314.89	15.8	1.5	7.34	252	16.0	15.3	116	17.8	0.0	5.2	<0.05	21.5	7.2	12.9	3.6
B39	26/09/2011	314.84	15.0	1.7	7.37	252	20.5	19.7	111	18.1	0.0	4.9	0.47	18.3	7.1	14.2	4.0
B39	10/10/2011	314.74	16.0	1.8	7.33	249	21.9	22.5	107	18.6	0.0	5.1	0.40	18.5	7.0	13.5	4.0
B39	24/10/2011	314.62	15.6	2.1	7.10	239	21.0	14.4	104	18.9	1.2	5.1	0.19	18.4	6.8	13.8	4.1
B39	07/11/2011	315.75	15.5	1.6	7.12	232	20.3	18.8	103	19.9	1.5	5.3	0.35	16.7	6.9	14.8	4.8
B39	21/11/2011	314.93	15.5	2.6	7.19	217	19.6	15.7	89	18.1	1.2	6.1	0.12	16.1	6.4	14.2	4.5
B39	05/12/2011	314.72	13.3	2.9	7.38	208	20.5	18.3	85	16.2	1.3	6.1	0.20	14.7	5.8	13.5	4.6
B39	19/12/2011	315.02	13.1	2.3	7.37	201	20.2	8.1	85	15.7	1.3	6.2	0.16	15.9	5.6	14.9	3.8
B39	03/01/2012	315.2	11.6	2.5	7.51	197	15.0	9.3	83	15.1	1.3	6.5	0.10	16.2	5.9	13.2	3.7
B39	16/01/2012	314.99	10.0	2.8	7.60	189	19.8	9.3	79	14.1	1.4	6.7	0.18	15.8	5.5	13.3	3.5
B39	30/01/2012	314.8	9.9	3.1	7.78	188	19.6	11.3	79	13.4	1.2	6.4	0.15	14.1	5.0	11.7	3.4
B39	13/02/2012	314.65	9.8	3.7	7.31	181	18.7	8.6	79	12.9	1.2	6.3	0.12	14.8	5.3	12.6	3.6
B39	27/02/2012	314.81	10.3	3.4	7.47	181	18.8	3.2	79	12.4	1.2	6.4	0.12	14.0	4.9	11.9	3.2
B39	12/03/2012	314.7	11.0	3.6	7.30	182	17.8	5.6	74	12.5	4.0	6.7	0.11	13.9	4.5	11.4	3.1
B39	26/03/2012	314.75	10.7	2.6	7.30	187	18.0	4.4	74	12.9	1.0	7.1	0.13	13.9	5.0	11.0	3.0
B39	10/04/2012	314.67	10.9	2.1	7.23	186	17.6	13.2	73	14.4	1.2	7.9	<0.05	14.3	5.3	11.4	3.5
B39	23/04/2012	314.88	10.7	2.0	7.33	188	17.4	15.5	78	14.8	0.0	7.5	0.08	15.7	5.3	10.3	2.7
B39	09/05/2012	315.29	10.8	1.4	7.15	194	16.1	15.3	79	15.2	1.2	7.7	0.05	17.0	6.0	11.2	2.4
B39	21/05/2012	315.07	10.4	3.4	7.27	186	18.8	15.8	81	14.0	1.3	7.5	0.08	15.9	5.7	11.0	2.2
B39	05/06/2012	315.52	11.9	5.5	7.50	192	12.4	7.2	82	13.8	1.0	6.8	0.05	16.7	5.5	11.1	2.8
B39	18/06/2012	315.32	11.1	1.7	7.30	192	14.8	20.4	81	11.0	1.1	6.8	<0.05	16.8	5.5	10.5	2.5
B39	02/07/2012	315.03	12.9	2.3	7.00	194	14.2	15.3	92	10.9	1.2	6.9	0.06	17.0	5.5	10.6	2.5
B39	16/07/2012	315	11.4	1.5	7.31	189	15.3	20.8	93	11.3	1.2	6.7	0.09	17.1	5.3	10.5	2.7
B39	30/07/2012	314.84	13.3	1.7	7.16	192	15.5	12.7	90	10.7	0.0	6.1	0.05	17.4	5.6	11.0	2.4
B39	13/08/2012	314.85	12.6	1.4	7.38	193	15.6	6.7	92	10.6	0.0	6.0	0.07	17.8	6.0	11.7	3.1
B39	27/08/2012	314.78	12.9	0.8	7.43	200	15.5	15.3	103	10.8	0.0	5.6	0.05	19.0	5.6	10.8	2.7
B39	10/09/2012	314.73	14.3	1.6	7.47	202	15.7	17.2	96	10.6	0.0	5.4	<0.05	18.5	5.4	10.5	2.7
B39	24/09/2012	314.65	14.9	1.4	7.60	226	16.7	10.0	109	14.1	0.0	5.3	0.23	20.6	6.5	11.9	3.0
B39	08/10/2012	314.62	14.2	1.2	7.58	232	17.7	10.7	105	15.0	0.0	5.1	0.33	20.6	6.2	12.0	3.0
B39	22/10/2012	313.6	14.5	2.1	7.45	232	20.7	18.8	103	16.5	0.0	5.1	0.48	17.7	6.8	13.0	3.3
B39	05/11/2012	314.68	12.8	2.5	7.47	225	19.7	11.8	99	17.0	0.0	5.1	0.36	17.9	6.8	13.9	3.6

Sample ID	Date	WL	T	Do	pH	EC	SiO_2	CO_2	HCO_3	Cl	NO_3	SO_4	PO_4	Ca	Mg	Na	K
B50	14/02/2011	312.33	8.7	9.0	6.83	808	21.4	29.2	345	43.1	35.4	62.0	0.12	68.9	35.7	38.1	16.3
B50	14/03/2011	312.91	8.1	8.9	7.10	218	14.9	25.7	84	16.3	7.3	10.9	0.12	19.8	6.0	10.2	2.6
B50	28/03/2011	313.17	8.5	6.4	7.01	179	12.3	17.4	72	12.3	6.0	8.5	0.10	17.3	4.9	8.8	2.7
B50	11/04/2011	312.85	11.5	7.6	7.04	220	15.4	16.2	89	14.5	6.5	11.3	0.07	21.3	7.7	11.7	3.5
B50	26/04/2011	312.62	13.1	7.7	7.13	220	15.8	15.8	88	15.6	5.2	9.6	0.10	19.1	5.9	11.9	3.2
B50	09/05/2011	311.43	12.8	6.4	7.34	598	22.2	20.8	284	35.6	26.8	48.5	0.12	59.9	27.4	25.1	11.9
B50	23/05/2011	313.12	14.3	6.8	7.08	306	16.1	24.1	124	21.3	8.1	15.5	0.09	29.6	8.4	12.6	3.7
B50	06/06/2011	313.26	13.8	5.3	7.08	375	15.9	25.7	153	24.7	10.8	21.0	0.05	37.6	10.2	17.0	4.7
B50	20/06/2011	312.8	15.2	5.3	7.24	488	16.8	32.4	200	30.3	18.4	30.8	0.08	51.5	14.4	22.7	5.8
B50	04/07/2011	312.86	15.8	5.1	7.25	489	17.5	26.4	209	32.8	18.9	32.0	0.07	50.5	15.4	23.5	6.3
B50	18/07/2011	313.11	14.9	4.7	7.26	459	17.0	20.8	189	29.6	16.4	29.5	0.08	44.4	13.9	20.4	6.1
B50	16/08/2011	313.02	17.0	4.9	7.19	495	17.5	25.2	206	31.4	17.9	32.6	0.08	51.7	14.9	22.0	8.4
B50	29/08/2011	313.11	18.3	5.2	7.15	443	16.1	27.4	184	28.4	14.2	28.2	<0.05	44.6	12.6	19.7	5.9
B50	12/09/2011	313.03	18.2	5.0	7.18	511	18.8	29.6	214	31.5	18.0	37.5	0.06	50.3	15.8	23.5	7.3
B50	26/09/2011	312.59	17.2	4.9	7.18	513	19.5	21.8	210	32.3	18.0	37.8	0.06	52.5	16.2	25.4	8.0
B50	10/10/2011	312.97	16.7	4.8	7.16	500	18.0	22.0	200	31.8	16.6	30.2	0.12	49.4	15.1	22.9	7.1
B50	24/10/2011	312.9	16.1	4.7	7.19	492	17.2	55.6	199	31.7	16.5	28.9	0.11	48.2	15.1	23.6	7.3
B50	07/11/2011	315.44	15.2	7.1	6.98	257	16.4	15.5	94	16.7	15.1	14.5	0.11	23.2	6.7	14.2	4.3
B50	21/11/2011	313.4	15.0	6.0	7.20	347	16.4	18.5	143	21.0	10.4	21.6	0.10	37.5	11.4	17.3	6.0
B50	05/12/2011	313.14	13.7	5.3	7.28	468	17.0	22.2	190	27.8	17.0	31.3	0.09	49.5	15.2	22.3	6.7
B50	19/12/2011	313.97	11.0	6.6	7.13	229	15.4	17.1	95	13.8	5.6	10.6	0.10	21.8	5.7	15.9	3.5
B50	03/01/2012	314.2	11.7	6.6	7.17	196	15.2	11.3	81	11.4	4.6	7.8	0.07	17.9	5.0	13.1	2.7
B50	16/01/2012	313.72	10.0	6.8	7.34	279	16.6	10.9	120	14.3	7.9	14.9	0.11	26.4	8.3	14.7	5.0
B50	30/01/2012	313.39	8.6	6.9	7.35	354	16.5	13.9	150	19.5	12.6	21.8	0.08	35.2	11.6	16.1	4.8
B50	27/02/2012	313.23	9.5	8.2	7.32	305	14.6	6.3	112	19.9	10.4	15.8	0.09	27.9	8.3	15.2	3.6
B50	12/03/2012	313.02	11.0	6.6	7.33	405	16.3	6.3	161	23.1	15.5	25.9	0.07	38.4	12.0	18.8	5.5
B50	26/03/2012	313.17	11.2	6.0	7.26	337	15.6	13.4	135	20.1	11.6	19.7	<0.05	31.8	10.3	16.9	4.9
B50	23/04/2012	313.76	9.8	5.1	7.13	210	14.6	16.2	87	14.6	4.6	9.0	0.07	17.8	5.6	13.4	2.7
B50	09/05/2012	313.99	11.5	5.6	7.18	198	16.0	19.2	89	10.5	3.7	8.6	0.12	19.3	5.8	12.0	2.5
B50	05/06/2012	314.12	12.9	5.5	7.01	250	18.1	23.3	120	10.0	4.5	10.5	0.08	23.3	7.3	12.9	2.8
B50	18/06/2012	313.88	15.2	5.4	7.09	328	17.6	25.2	151	13.6	7.5	15.7	<0.05	35.6	9.8	15.1	4.6
B50	02/07/2012	313.08	13.3	5.2	7.15	460	17.2	17.8	200	24.2	15.1	28.6	<0.05	49.0	13.4	18.6	5.1
B50	16/07/2012	313.18	14.3	5.2	7.20	479	18.3	27.9	231	25.8	15.8	30.7	<0.05	53.6	15.1	20.8	6.7
B50	30/07/2012	313.06	15.5	5.0	7.08	518	19.1	7.4	225	29.4	17.6	30.1	<0.05	53.3	17.5	23.6	6.1
B50	13/08/2012	313.08	16.4	4.8	7.22	455	18.5	15.5	192	25.8	13.7	27.2	0.11	47.7	12.3	19.4	5.7
B50	27/08/2012	312.99	16.4	4.7	7.21	503	18.7	29.6	215	29.0	16.6	31.5	0.06	56.0	15.9	22.0	6.4
B50	10/09/2012	312.94	17.1	4.5	7.33	480	19.3	30.8	201	27.4	15.1	28.1	<0.05	51.6	14.7	21.5	6.2
B50	24/09/2012	312.85	17.3	4.4	7.26	449	18.2	18.3	184	28.0	13.5	26.1	0.11	45.1	14.5	23.0	6.9
B50	08/10/2012	312.9	16.3	4.5	7.43	484	17.9	16.7	199	29.3	15.7	28.8	0.12	51.9	13.8	21.2	6.9
B50	22/10/2012	312.94	16.8	4.8	7.39	455	18.4	24.6	187	27.8	13.5	25.9	0.10	43.5	14.8	22.4	6.8
B50	05/11/2012	313.04	15.4	4.4	7.52	435	17.3	19.5	172	27.3	12.7	25.5	<0.05	42.5	13.4	21.6	6.6
B56	14/02/2011	316.31	9.7	4.3	6.69	459	18.6	29.9	190	25.0	17.4	28.4	0.09	43.9	16.9	17.4	5.6
B56	28/02/2011	316.28	9.7	3.8	6.95	470	18.8	36.1	198	26.1	17.6	33.1	0.08	54.2	19.4	16.2	4.9
B56	14/03/2011	316.32	8.9	3.0	6.86	346	19.1	19.2	143	19.8	9.9	23.1	0.09	35.4	12.1	11.6	3.4
B56	28/03/2011	316.34	8.9	4.0	7.13	309	19.2	24.1	131	17.1	8.9	19.5	0.11	31.3	11.1	10.9	3.8
B56	11/04/2011	316.3	9.9	4.4	7.06	451	21.2	28.0	185	23.9	15.3	31.7	0.08	45.7	18.7	14.3	5.1
B56	26/04/2011	316.21	9.3	3.6	7.11	366	19.9	22.9	151	20.7	10.3	25.1	0.06	35.3	13.3	12.3	4.1
B56	09/05/2011	315.91	11.6	3.5	7.05	420	20.6	31.7	185	24.8	14.9	34.9	0.09	46.0	16.9	14.4	4.5
B56	23/05/2011	315.98	11.3	3.6	7.10	552	21.3	39.4	233	30.2	21.0	36.9	0.07	57.0	22.3	15.5	5.5
B56	06/06/2011	315.99	10.5	3.2	7.06	446	17.9	34.5	185	24.5	13.0	32.0	0.09	42.3	15.8	15.8	4.8
B56	20/06/2011	315.69	11.5	2.5	7.08	369	15.6	39.1	157	22.3	8.6	23.6	0.10	40.7	13.2	14.3	3.9
B56	04/07/2011	315.74	11.8	2.9	7.08	432	13.6	33.8	185	25.5	12.2	31.6	0.11	43.2	15.8	16.3	5.0
B56	18/07/2011	315.84	11.6	2.9	7.07	380	18.8	24.8	165	22.7	7.7	23.1	0.08	36.2	13.3	14.5	4.3
B56	16/08/2011	315.93	13.4	3.3	7.02	340	18.3	33.3	149	21.5	4.7	16.3	0.14	34.1	11.0	16.2	6.7
B56	29/08/2011	316.06	14.3	3.2	7.04	282	14.9	28.9	127	19.3	1.5	9.1	0.13	26.3	8.4	14.7	4.7
B56	12/09/2011	315.92	14.0	3.0	7.03	329	16.3	30.3	146	20.9	4.3	13.5	0.10	29.7	10.8	15.2	4.8
B56	26/09/2011	315.93	14.1	3.1	7.09	405	20.7	29.9	178	24.9	9.0	20.9	0.10	39.3	14.4	18.7	6.9
B56	10/10/2011	315.86	15.0	2.5	7.00	337	20.6	27.3	148	22.1	4.7	13.3	0.14	32.1	11.5	14.9	5.0
B56	24/10/2011	315.78	13.6	2.9	7.09	388	20.2	24.5	167	24.2	7.3	17.3	0.10	36.9	13.6	15.7	5.3
B56	07/11/2011	316.97	15.1	5.3	7.18	198	17.5	22.7	83	13.7	4.4	7.2	0.14	15.6	5.9	14.0	4.9
B56	21/11/2011	316.16	13.8	3.9	7.32	174	16.0	15.7	72	12.3	2.3	7.1	0.13	14.0	4.7	10.7	3.1
B56	05/12/2011	315.83	13.1	2.5	7.23	283	17.6	15.1	120	18.2	4.6	13.0	0.11	25.5	9.1	12.2	4.2
B56	19/12/2011	316.3	12.0	3.3	7.15	201	16.0	15.5	85	13.7	2.1	7.8	0.14	17.6	6.3	13.6	4.4
B56	03/01/2012	316.61	11.1	5.3	7.43	182	12.0	8.8	74	12.2	3.0	7.2	0.09	17.4	5.6	10.7	3.7
B56	16/01/2012	316.16	10.2	4.5	7.44	226	20.1	10.2	100	13.2	3.9	9.3	0.27	20.9	7.7	11.8	4.1
B56	30/01/2012	315.34	9.7	4.1	7.59	260	18.7	16.4	110	14.8	5.7	12.1	0.11	22.5	8.4	11.9	4.2
B56	13/02/2012	315.59	7.4	3.1	7.13	275	17.9	20.8	120	16.7	6.7	14.6	0.11	27.1	10.2	15.2	4.3
B56	27/02/2012	316.52	9.1	4.9	7.29	207	16.1	8.6	85	13.0	2.8	9.9	0.11	18.2	6.3	11.9	3.7
B56	12/03/2012	315.74	11.2	4.9	7.15	348	19.0	46.3	146	19.5	8.9	19.3	0.09	31.6	11.1	14.9	5.2
B56	26/03/2012	315.81	10.1	3.9	7.13	327	18.5	14.1	133	18.6	8.0	18.0	0.13	30.0	11.6	13.7	4.7
B56	10/04/2012	315.99	9.7	3.5	7.15	229	15.5	17.8	94	17.4	3.5	13.2	0.08	19.6	7.4	11.8	3.4
B56	23/04/2012	316.22	10.0	3.6	7.22	269	18.1	17.1	111	17.8	4.9	14.7	0.12	24.7	9.2	12.7	3.8
B56	09/05/2012	316.36	10.6	4.6	7.13	180	16.4	14.6	74	11.3	3.1	8.5	0.14	16.0	5.8	9.8	2.5
B56	21/05/2012	316.29	10.4	3.5	7.12	219	21.9	14.3	93	13.7	3.8	11.2	0.13	19.8	7.5	10.9	2.9
B56	05/06/2012	316.54	12.1	3.6	7.20	159	18.0	15.7	68	9.4	3.6	7.9	0.13	14.1	5.1	9.2	2.5
B56	18/06/2012	316.34	12.5	3.1	7.09	229	16.2	22.9	82	10.6	2.4	8.4	<0.05	17.7	5.8	9.8	2.8
B56	02/07/2012	316.13	12.7	3.4	7.06	233	16.4	12.7	100	12.9	3.4	10.9	0.14	23.4	7.2	10.5	3.1
B56	16/07/2012	316.17	12.2	3.4	7.23	279	18.2	23.4	126	15.5	5.6	14.0	0.12	27.4	9.1	11.7	3.9
B56	30/07/2012	315.95	13.0	3.3	7.06	338	19.1	25.9	148	18.7	8.3	19.1	0.08	34.6	12.3	13.4	3.8
B56	13/08/2012	315.89	13.1	2.9	7.00	350	18.8	16.0	157	18.8	7.4	19.0	0.12	33.6	11.4	13.0	4.3
B56	27/08/2012	315.87	13.4	1.8	7.07	219	17.2	24.1	103	14.2	1.1	8.9	0.12	21.8	7.2	11.5	3.3
B56	10/09/2012	315.88	14.7	1.6	7.15	254	18.3	28.9	111	15.5	1.7	9.6	0.11	24.9	7.8	12.1	3.5
B56	24/09/2012	315.7	15.7	1.9	7.06	245	17.6	21.8	120	18.2	3.4	13.2	0.14	29.5	10.4	14.4	4.2
B56	08/10/2012	315.68	14.6	2.3	7.28	347	19.4	24.6	143	20.5	5.8	18.1	0.12	34.8	11.3	13.4	4.2
B56	22/10/2012	315.63	15.4	1.9	7.28	253	19.3	19.9	117	18.6	2.8	12.6	0.12	24.3	8.4	12.6	3.7
B56	05/11/2012	315.76	14.4	2.1	7.34	264	18.4	15.1	111	18.6	2.5	12.2	0.12	23.7	8.9	14.0	4.1

Sample ID	Date	WL	T	Do	pH	EC	SiO_2	CO_2	HCO_3	Cl	NO_3	SO_4	PO_4	Ca	Mg	Na	K
B65	14/02/2011	316.6	12.2	5.3	6.84	441	20.6	25.9	210	21.5	1.2	27.0	0.09	41.5	15.3	21.1	5.1
B65	28/02/2011	316.72	11.1	5.2	6.94	435	21.0	29.6	207	22.2	1.2	27.9	0.09	50.3	16.7	19.4	4.8
B65	14/03/2011	316.77	12.7	4.8	6.80	430	23.0	18.3	209	22.2	1.3	28.4	0.09	42.4	15.4	17.8	4.3
B65	28/03/2011	316.88	11.7	5.3	7.16	433	23.3	25.9	206	21.9	1.5	27.8	0.11	44.7	15.3	18.2	4.8
B65	11/04/2011	316.74	12.6	5.9	7.05	441	23.1	22.5	210	21.7	1.4	27.1	0.10	47.1	18.5	19.3	5.0
B65	26/04/2011	316.54	13.1	5.3	7.21	445	24.5	24.1	209	22.2	1.2	27.4	0.06	42.9	15.5	17.6	4.6
B65	09/05/2011	316.41	13.5	4.8	7.19	446	23.6	27.6	211	22.0	1.1	28.1	0.08	43.1	15.3	17.3	4.5
B65	23/05/2011	316.4	14.5	4.5	7.17	449	21.5	32.7	210	22.7	1.3	28.2	0.07	44.8	15.1	17.0	4.6
B65	06/06/2011	316.48	13.0	4.3	7.12	438	20.4	32.2	210	21.9	1.2	27.5	0.09	41.5	14.6	20.1	4.8
B65	20/06/2011	316.3	14.1	4.6	7.20	454	18.2	27.6	211	22.9	1.2	27.1	0.10	48.5	15.3	20.2	4.5
B65	04/07/2011	316.17	13.6	4.5	7.16	440	22.0	27.8	210	23.4	1.2	29.0	0.10	42.6	14.9	19.7	4.9
B65	18/07/2011	316.34	12.9	5.1	7.13	448	19.8	24.1	212	23.2	0.0	28.0	0.11	46.2	15.6	21.2	5.6
B65	16/08/2011	316.29	13.9	6.8	7.07	467	21.2	31.5	223	24.2	0.0	28.9	0.12	49.5	18.3	20.2	5.2
B65	29/08/2011	316.07	13.5	7.3	7.09	462	21.8	29.9	221	23.8	0.0	29.0	0.10	53.4	15.7	19.2	5.2
B65	12/09/2011	316.23	14.3	7.2	7.08	455	17.8	31.7	220	23.8	0.0	28.2	0.09	42.9	16.4	20.3	5.7
B65	26/09/2011	316.28	14.1	6.7	7.08	456	22.2	29.9	222	24.2	0.0	28.8	0.11	44.7	16.7	21.6	6.1
B65	10/10/2011	316.29	13.8	7.2	7.07	462	22.3	33.8	218	24.4	0.0	28.6	0.15	45.8	16.7	19.9	5.6
B65	24/10/2011	316.32	13.3	7.0	7.12	459	21.4	27.6	218	24.1	0.0	28.1	0.12	45.4	16.8	19.5	5.6
B65	07/11/2011	317.26	13.4	8.8	7.17	392	19.8	21.8	166	20.3	10.1	31.2	0.11	35.9	14.1	18.6	6.3
B65	21/11/2011	314.98	13.0	7.3	7.17	412	18.9	25.5	188	21.8	3.0	28.5	0.11	39.7	14.9	16.9	5.4
B65	05/12/2011	315.24	12.5	7.7	7.28	422	20.3	20.8	198	21.8	1.9	27.4	0.10	42.3	15.4	17.9	5.1
B65	19/12/2011	317.14	11.9	8.4	7.21	394	19.3	19.2	185	19.7	3.1	26.1	0.12	38.9	13.9	19.1	5.0
B65	03/01/2012	317.24	11.5	8.7	7.28	338	20.1	17.6	161	15.8	3.7	19.7	0.10	34.5	12.1	15.8	4.2
B65	16/01/2012	316.47	10.6	8.4	7.35	350	20.9	18.8	166	16.2	3.3	20.6	0.11	35.4	13.1	17.7	4.6
B65	30/01/2012	316.62	11.5	7.4	7.29	397	20.9	23.4	187	19.7	2.0	23.9	0.10	39.1	14.7	19.1	5.9
B65	13/02/2012	317.03	10.4	6.3	7.16	397	20.1	23.4	187	19.9	2.2	23.9	0.07	39.5	15.2	20.7	5.5
B65	27/02/2012	316.92	11.4	7.0	7.25	428	21.3	7.2	194	20.5	1.8	20.6	0.08	40.8	15.0	20.2	5.7
B65	12/03/2012	316.43	12.6	5.4	7.17	436	19.9	26.2	198	21.7	1.5	26.3	0.06	40.2	14.0	20.6	6.4
B65	26/03/2012	316.52	12.3	5.4	7.18	439	21.2	18.5	200	21.4	1.4	26.0	0.11	41.3	14.9	19.7	6.1
B65	10/04/2012	316.49	12.2	5.6	7.13	441	20.0	25.9	200	23.5	1.5	28.6	0.05	40.5	15.8	20.6	5.2
B65	23/04/2012	316.97	12.0	5.9	7.21	430	20.8	27.6	199	22.5	1.8	27.3	0.11	39.9	15.2	18.3	4.7
B65	09/05/2012	317.22	12.9	6.6	7.17	381	20.6	18.3	178	19.5	2.7	23.0	0.15	38.6	13.9	18.1	3.9
B65	21/05/2012	316.84	12.5	5.3	7.06	412	24.3	28.4	190	21.9	2.2	26.4	0.11	39.1	14.3	18.2	3.8
B65	05/06/2012	317.19	14.0	6.5	7.12	367	20.8	13.8	176	18.4	2.9	22.7	0.12	36.8	13.2	17.0	4.1
B65	18/06/2012	316.74	13.9	5.3	7.16	409	20.6	30.1	190	18.9	2.2	23.1	0.06	41.4	13.7	17.7	4.2
B65	02/07/2012	315.48	13.3	5.4	7.10	421	17.8	28.9	193	20.8	1.7	25.0	0.11	42.7	14.0	17.4	4.2
B65	16/07/2012	316.52	13.1	5.5	7.31	442	20.9	26.9	227	22.2	1.6	26.3	0.12	43.5	16.8	20.4	5.3
B65	30/07/2012	316.35	14.6	5.1	7.03	451	21.3	21.9	214	22.0	1.3	26.3	0.11	45.5	15.9	19.4	4.3
B65	13/08/2012	316.33	13.6	6.6	7.12	474	22.1	22.7	231	23.0	1.2	27.4	0.12	47.8	16.1	18.9	5.3
B65	27/08/2012	316.35	13.5	5.6	7.17	453	19.8	32.2	226	22.4	1.2	26.6	0.05	48.5	15.8	18.6	4.6
B65	10/09/2012	316.28	13.8	7.2	7.20	482	20.8	40.3	228	22.8	0.0	26.1	0.12	50.7	17.3	19.4	5.0
B65	24/09/2012	316.24	14.1	6.8	7.20	468	21.3	26.6	222	23.9	0.0	27.1	0.13	49.1	16.5	18.7	4.8
B65	08/10/2012	314.74	14.2	7.0	7.24	482	21.2	26.9	221	24.3	0.0	28.0	0.11	51.4	16.9	19.5	5.1
B65	22/10/2012	315.22	13.7	7.9	7.31	472	22.4	34.7	221	24.1	0.0	27.7	<0.05	45.2	17.9	20.2	5.2
B65	05/11/2012	316.31	13.1	7.2	7.40	469	21.1	26.6	217	24.8	0.0	28.9	0.10	47.8	16.8	20.5	5.3
B66	14/02/2011	313.27	9.1	2.7	7.15	266	16.5	10.9	118	14.3	6.1	12.0	0.09	25.2	8.5	13.8	3.3
B66	28/02/2011	313.34	8.8	2.1	7.17	224	16.4	22.2	120	15.0	6.7	12.5	0.09	27.9	8.5	12.1	2.9
B66	14/03/2011	313.34	9.8	3.1	6.94	284	17.4	12.0	126	15.7	6.9	13.3	0.10	28.3	9.1	11.2	2.8
B66	28/03/2011	313.5	9.4	2.4	7.16	286	14.2	21.5	123	15.9	7.0	13.5	0.05	28.7	9.3	10.6	2.9
B66	11/04/2011	313.4	11.8	3.4	7.29	298	17.0	11.3	132	15.9	7.1	14.1	0.11	29.9	11.1	12.5	3.4
B66	26/04/2011	312.4	10.5	2.6	7.37	306	17.0	12.5	131	16.3	7.4	14.3	0.06	28.0	9.6	12.4	3.3
B66	09/05/2011	312.74	12.4	3.0	7.19	308	17.7	14.1	137	17.7	9.2	14.9	0.11	32.2	11.5	11.5	2.8
B66	23/05/2011	311.8	12.0	2.3	7.26	334	17.8	22.0	149	19.4	9.1	16.2	0.09	30.5	11.9	13.3	3.3
B66	06/06/2011	313.48	13.4	2.4	7.36	285	16.1	17.8	131	18.3	1.0	8.9	0.15	26.3	7.9	13.1	3.4
B66	20/06/2011	312.92	12.9	1.6	7.27	346	16.1	22.0	153	20.9	6.7	15.8	0.10	33.5	12.1	14.4	3.0
B66	04/07/2011	313.31	13.7	1.8	7.28	351	17.7	23.9	154	22.6	8.2	17.2	0.09	32.8	12.9	16.0	3.6
B66	18/07/2011	314.5	12.3	3.9	7.17	325	17.8	21.5	144	20.8	6.5	14.0	0.08	30.3	12.6	15.6	3.5
B66	16/08/2011	312.69	17.8	2.3	7.15	255	17.9	11.3	116	18.3	0.0	7.3	0.20	27.3	6.4	18.4	5.2
B66	29/08/2011	312.91	18.2	2.6	7.17	249	19.0	15.7	112	18.3	0.0	6.5	0.06	23.7	6.5	13.7	4.5
B66	12/09/2011	312.77	18.8	2.6	7.07	247	19.7	15.5	114	17.7	0.0	5.4	0.17	22.2	6.5	14.7	4.5
B66	26/09/2011	312.8	19.2	2.6	7.15	250	21.0	19.2	110	19.2	0.0	5.9	0.13	23.5	6.5	16.2	5.1
B66	10/10/2011	312.05	18.8	2.6	7.13	250	19.7	20.1	109	19.5	0.0	6.7	0.21	23.0	6.2	14.7	4.2
B66	24/10/2011	312.68	19.3	2.6	7.05	245	18.6	54.2	104	20.0	0.0	7.0	0.19	21.5	6.2	14.3	4.1
B66	07/11/2011	314.17	16.7	2.6	7.17	244	17.4	12.3	101	19.6	1.4	9.1	0.16	22.1	6.5	14.5	4.1
B66	21/11/2011	312.34	17.0	2.6	7.15	236	17.6	10.9	99	16.9	0.0	8.6	0.45	21.9	6.6	13.3	4.5
B66	05/12/2011	311.72	14.8	2.6	7.18	236	18.3	21.8	104	16.1	1.1	8.8	0.15	21.7	6.8	13.6	4.1
B66	19/12/2011	313.1	13.4	2.6	7.25	242	17.5	11.6	106	16.2	1.5	9.4	0.14	24.6	6.9	15.0	3.6
B66	03/01/2012	312.37	13.0	2.6	7.35	236	17.4	7.2	103	14.6	2.0	8.7	0.10	21.1	7.0	14.1	3.0
B66	16/01/2012	313.1	11.6	2.6	7.34	237	16.9	14.1	107	14.4	2.9	9.2	0.14	22.7	7.2	13.9	3.6
B66	30/01/2012	312.92	11.0	2.6	7.47	234	16.9	10.2	104	13.5	3.1	9.1	0.10	20.2	7.3	13.4	3.5
B66	27/02/2012	313	11.1	2.4	7.45	236	16.5	4.9	99	14.2	3.9	9.2	0.10	20.6	7.0	14.0	2.9
B66	12/03/2012	313.17	10.8	3.1	7.38	263	15.3	8.1	110	15.0	5.3	11.0	0.08	23.8	8.0	14.7	4.5
B66	26/03/2012	312.75	11.6	2.0	7.29	254	16.5	10.4	107	15.5	5.4	10.9	0.13	22.8	8.6	13.5	3.0
B66	10/04/2012	312.76	9.8	2.1	7.35	250	15.8	13.2	106	16.9	4.7	10.5	0.10	24.2	7.8	12.9	2.7
B66	23/04/2012	313.18	9.7	1.9	7.42	244	15.4	13.2	106	16.2	3.5	9.5	0.10	21.7	7.4	12.7	2.7
B66	09/05/2012	313.48	10.9	2.3	7.36	226	15.0	13.2	99	14.3	3.0	9.1	0.14	21.3	7.2	11.9	2.2
B66	21/05/2012	313.3	10.1	1.6	7.31	230	18.1	7.0	103	13.8	3.5	9.5	0.10	21.5	7.2	11.9	2.3
B66	05/06/2012	312.93	10.7	2.1	7.21	231	17.4	16.7	103	12.9	3.3	9.1	0.16	22.7	7.2	11.9	2.4
B66	18/06/2012	313.07	12.1	2.1	7.43	251	14.7	14.1	117	12.6	4.6	10.3	0.05	25.0	8.0	12.0	2.6
B66	02/07/2012	311.94	14.4	2.4	7.17	229	15.1	9.0	117	11.9	2.7	8.5	0.15	22.6	6.7	11.5	2.7
B66	16/07/2012	312.91	13.7	1.9	7.40	237	16.2	15.8	126	13.4	1.7	8.6	0.11	24.9	7.1	12.4	3.1
B66	30/07/2012	312.72	16.2	1.8	7.16	263	17.2	0.0	124	15.1	2.0	9.3	0.12	25.6	7.9	13.3	2.9
B66	13/08/2012	312.94	15.9	1.4	7.39	275	17.1	7.0	129	16.0	1.0	9.3	0.16	27.2	7.8	14.0	3.6
B66	27/08/2012	311.78	17.1	1.5	7.21	242	18.3	22.7	107	16.7	0.0	6.9	0.16	25.2	6.6	13.9	3.5
B66	10/09/2012	312.66	18.8	2.2	7.24	230	19.6	25.5	103	15.9	0.0	5.8	0.19	23.2	6.1	13.8	3.6
B66	24/09/2012	312.54	19.0	2.3	7.20	225	18.2	12.0	95	17.7	0.0	7.0	0.25	20.8	5.4	12.7	3.4
B66	08/10/2012	311.84	18.8	2.0	7.30	232	19.6	13.4	95	18.1	0.0	7.4	0.21	22.0	5.4	12.8	3.4
B66	22/10/2012	312.59	18.1	3.3	7.39	234	18.9	11.4	100	18.4	0.0	7.9	0.19	20.7	6.3	13.4	3.5
B66	05/11/2012	312.73	16.7	1.8	7.82	237	16.8	13.9	100	18.1	0.0	7.9	0.18	20.1	5.7	13.0	3.4

Sample ID	Date	WL	T	Do	pH	EC	SiO_2	CO_2	HCO_3	Cl	NO_3	SO_4	PO_4	Ca	Mg	Na	K
B71	28/02/2011	315.5	8.4	2.9	7.03	378	19.9	30.6	160	26.6	14.6	37.5	<0.05	40.4	13.6	15.3	3.7
B71	14/03/2011	315.52	9.5	4.0	6.89	422	22.2	24.5	185	22.0	11.8	26.8	<0.05	46.1	15.2	14.4	4.1
B71	28/03/2011	315.73	9.7	3.7	7.00	364	17.0	27.6	155	19.6	9.5	21.8	<0.05	37.8	12.4	12.4	3.4
B71	11/04/2011	315.56	11.3	4.3	6.85	418	20.5	26.4	183	21.4	10.3	26.6	<0.05	44.4	17.8	16.4	4.9
B71	26/04/2011	315.27	12.3	2.2	7.19	410	20.9	25.2	177	21.4	10.0	26.0	<0.05	38.1	14.3	16.2	4.7
B71	09/05/2011	311.15	12.6	5.2	7.22	265	22.4	10.9	118	15.5	3.2	10.9	0.06	26.9	7.8	11.2	2.9
B71	23/05/2011	310.71	12.4	7.1	7.22	273	24.8	17.6	123	16.1	3.6	11.0	0.06	27.1	8.2	10.1	2.5
B71	06/06/2011	311.27	11.8	5.7	7.21	268	19.9	22.7	123	15.4	3.5	10.5	0.05	26.6	7.8	13.4	2.5
B71	20/06/2011	311.25	13.6	4.6	7.18	417	19.0	35.7	178	23.1	11.4	25.6	0.07	45.7	14.8	16.5	4.0
B71	04/07/2011	310.98	12.6	6.2	7.32	273	19.9	21.3	126	17.0	4.6	12.4	0.06	28.2	8.5	14.6	3.7
B71	18/07/2011	311.29	12.5	5.4	7.17	271	19.6	21.1	121	15.8	3.9	10.3	0.10	27.5	7.9	16.8	2.5
B71	16/08/2011	311.16	14.0		7.21	263	20.2	15.1	116	15.4	3.9	10.2	0.08	27.5	7.3	13.3	2.8
B71	29/08/2011	311.35	13.2	5.5	7.21	258	20.4	18.1	117	15.2	3.6	9.7	0.16	26.6	7.1	11.8	2.5
B71	12/09/2011	311.22	13.4	5.0	7.19	254	20.4	15.3	116	15.0	3.4	9.2	<0.05	22.8	7.0	13.5	2.8
B71	26/09/2011	311.25	13.2	4.6	7.13	252	21.4	18.1	114	15.3	3.6	9.3	<0.05	25.3	7.3	14.2	3.2
B71	10/10/2011	311.26	13.3	5.1	7.43	260	21.6	18.5	111	15.5	3.5	9.2	0.09	24.9	7.0	13.1	2.8
B71	24/10/2011	311.16	12.6	5.2	7.17	253	20.7	56.0	114	15.2	3.4	9.0	0.06	24.0	7.0	13.2	2.7
B71	07/11/2011	312.97	14.2	1.7	7.02	269	17.9	15.5	118	19.8	0.0	8.7	0.10	23.7	8.3	15.4	5.0
B71	21/11/2011	311.79	14.3	2.4	7.28	268	18.1	11.3	114	18.5	0.0	8.8	0.08	24.1	7.8	13.1	3.5
B71	05/12/2011	311.33	12.1	5.5	7.21	264	20.8	15.1	112	15.7	3.3	9.7	0.06	24.3	7.1	12.9	3.1
B71	19/12/2011	314.87	11.0	5.5	7.37	252	20.6	16.9	114	14.9	3.6	10.0	0.07	29.1	7.2	13.7	2.7
B71	03/01/2012	311.65	11.3	5.1	7.43	267	20.7	12.0	112	15.3	3.4	9.5	0.05	26.1	7.5	14.6	3.0
B71	16/01/2012	311.25	9.1	5.4	7.46	254	20.1	9.7	115	16.2	3.2	10.1	0.08	29.0	7.1	15.4	4.3
B71	30/01/2012	311.56	9.6	6.4	7.54	252	20.9	15.5	111	16.4	2.7	9.5	<0.05	24.5	7.2	13.6	3.0
B71	27/02/2012	311.18	9.7	4.5	7.34	253	19.7	6.5	107	16.0	3.0	9.6	0.07	23.8	7.1	13.6	2.7
B71	12/03/2012	311.68	10.2	5.8	7.28	388	18.8	20.4	166	20.4	8.9	23.5	0.08	35.5	14.0	17.3	6.4
B71	26/03/2012	311.24	11.7	5.6	7.22	258	20.7	11.9	111	16.1	2.8	9.8	0.11	24.3	7.5	14.9	2.7
B71	10/04/2012	311.44	11.4	5.7	7.16	258	20.5	12.3	114	17.5	3.2	10.3	0.06	25.2	7.6	15.0	4.5
B71	23/04/2012	311.98	11.0	4.9	7.29	261	22.1	15.3	112	17.0	3.1	9.8	0.06	23.8	7.2	13.3	2.5
B71	09/05/2012	312.3	11.5	3.9	7.31	240	18.0	11.1	106	15.2	3.1	9.7	0.09	23.8	7.3	12.4	2.1
B71	05/06/2012	312.23	13.1	5.2	7.25	272	21.6	14.1	122	16.4	3.2	11.5	0.08	25.8	7.8	12.5	2.0
B71	18/06/2012	311.79	13.6	5.2	7.23	269	19.9	23.6	123	15.6	3.1	10.5	<0.05	28.8	7.6	12.4	2.3
B71	02/07/2012	311.33	13.0	5.3	7.15	273	19.5	11.3	122	16.0	2.9	10.4	0.06	28.1	7.3	12.1	2.3
B71	16/07/2012	311.48	13.6	5.7	7.34	265	20.6	17.4	134	15.9	2.6	10.2	<0.05	28.3	7.4	12.8	2.6
B71	30/07/2012	311.21	13.7	5.2	7.21	273	21.6	2.6	131	15.6	2.9	9.9	<0.05	28.4	7.9	13.1	2.2
B71	13/08/2012	311.3	15.2	1.7	7.37	259	17.2	9.0	123	15.1	1.4	9.0	0.13	25.8	7.8	13.2	3.3
B71	27/08/2012	311.28	13.9	6.1	7.25	278	20.5	17.6	126	15.8	3.3	10.9	0.06	30.0	8.3	13.3	2.7
B71	10/09/2012	311.25	14.5	5.3	7.38	268	20.1	21.8	133	15.0	3.1	9.6	<0.05	28.8	7.8	12.9	2.5
B71	24/09/2012	311.08	13.9	5.4	7.69	267	20.7	16.4	126	15.6	3.3	10.0	0.08	27.8	7.5	12.4	2.4
B71	08/10/2012	311.13	13.4	5.5	7.52	270	21.9	14.1	121	15.3	3.2	9.6	<0.05	28.9	7.4	12.7	2.4
B71	22/10/2012	311.14	13.4	5.1	7.45	267	21.7	13.2	122	15.2	3.2	9.8	0.06	26.3	8.0	12.9	2.5
B71	05/11/2012	311.25	12.6	5.1	7.61	267	21.2	21.3	123	15.2	3.2	9.9	0.05	26.2	7.3	13.1	2.5
Allier	14/02/2011	28.378	5.8	11.7	7.60	350	13.7	4.60	78	16.2	6.9	9.8	<0.05	17.0	5.9	14.4	3.3
Allier	28/02/2011	41.858	6.6	11.8	7.55	149	13.7	13.90	67	14.3	5.4	8.1	<0.05	14.5	4.9	10.5	2.6
Allier	14/03/2011	65.127	8.0	11.0	7.70	185	14.4	19.70	71	14.9	5.9	7.5	<0.05	15.1	5.2	10.4	2.9
Allier	28/03/2011	62.345	10.2	10.5	7.60	159	13.9	12.00	60	12.6	5.3	7.7	<0.05	14.1	4.4	8.7	2.5
Allier	11/04/2011	36.785	16.4	9.2	7.50	180	10.0	4.20	70	14.1	4.1	8.3	<0.05	13.8	4.8	10.9	3.1
Allier	26/04/2011	18.903	16.3	9.6	7.50	226	10.0	10.70	89	18.5	4.7	9.8	<0.05	18.2	6.2	14.4	3.7
Allier	09/05/2011	13.623	18.6	9.0	7.80	236	9.3	8.80	90	18.6	4.3	10.0	<0.05	18.1	6.2	13.1	3.5
Allier	23/05/2011	14.925	19.0	8.3	7.85	229	12.3	11.80	88	18.9	5.4	9.7	0.09	18.1	5.9	12.7	3.5
Allier	06/06/2011	19.473	18.5	8.1	7.70	196	12.6	11.80	73	15.7	4.8	8.3	0.11	14.1	4.8	14.0	3.5
Allier	20/06/2011	13.864	18.5	8.7	7.50	248	12.0	9.00	98	20.3	5.4	10.4	0.26	20.2	6.8	17.5	4.4
Allier	04/07/2011	12.506	20.3	8.6	7.70	217	8.2	13.20	84	20.1	3.9	9.7	0.12	17.0	6.1	16.8	4.2
Allier	18/07/2011	16.602	18.4	8.4	7.50	231	12.8	4.90	85	20.4	5.7	9.1	0.21	16.5	5.7	14.8	3.8
Allier	16/08/2011	15.148	21.2	7.9	7.70	178	7.2	4.90	73	18.0	3.3	7.7	0.08	16.0	4.8	14.4	4.6
Allier	29/08/2011	16.992	17.9	9.0	7.50	170	10.6	8.60	73	16.4	3.9	7.1	0.12	15.6	4.8	13.8	3.9
Allier	12/09/2011	13.951	19.5	8.4	7.50	228	8.5	9.30	85	20.8	3.8	9.0	0.16	20.3	6.0	17.9	4.5
Allier	26/09/2011	15.315	17.4	8.8	7.65	192	6.2	13.00	71	18.7	2.5	7.7	<0.05	13.7	4.8	16.3	4.3
Allier	10/10/2011	15.899	14.9	9.0	7.40	207	7.5	10.20	76	20.0	3.4	7.8	0.06	15.2	5.2	16.5	6.2
Allier	24/10/2011	13.768	10.9	10.3	7.45	211	8.0	11.60	79	19.7	2.8	7.8	0.06	15.6	5.4	16.5	4.1
Allier	07/11/2011	261.46	11.4	9.8	7.50	79	8.0	9.00	24	6.7	3.7	7.6	0.09	6.2	2.2	5.6	3.4
Allier	21/11/2011	32.761	9.8	10.6	7.50	160	11.9	15.70	56	13.8	4.7	8.1	0.10	12.0	4.1	10.3	2.7
Allier	05/12/2011	30.71	9.5	11.0	7.75	208	13.5	12.30	81	17.0	5.0	9.0	0.06	15.6	5.7	14.0	3.5
Allier	19/12/2011	68.613	4.9	12.4	7.10	126	15.1	4.60	49	9.5	5.2	5.4	0.11	10.3	3.7	10.1	3.6
Allier	03/01/2012	115.89	6.6	12.3	7.70	105	8.7	7.40	38	7.4	4.3	4.5	0.05	7.4	3.7	8.1	2.4
Allier	16/01/2012	43.626	2.5	13.0	7.65	149	16.3	8.30	55	11.6	5.7	6.9	0.09	11.6	4.5	10.6	2.4
Allier	30/01/2012	34.506	4.4	13.2	7.45	167	15.2	7.20	61	13.0	5.1	7.0	0.11	12.3	4.7	11.4	2.9
Allier	13/02/2012	27.1	0.6	13.8	7.55	209	9.9	8.80	77	17.1	6.9	9.9	0.07	15.9	6.2	14.5	3.6
Allier	27/02/2012	52.427	3.3	12.5	7.50	143	13.6	3.00	51	11.8	5.7	6.6	0.09	10.8	4.3	10.2	2.8
Allier	12/03/2012	28	6.2	11.9	7.55	174	12.7	5.90	62	14.4	5.2	8.3	<0.05	12.9	4.7	12.9	3.1
Allier	26/03/2012	25.717	10.0	10.5	7.50	182	12.2	9.50	70	15.4	4.1	8.3	0.06	13.4	4.9	13.5	3.7
Allier	10/04/2012	23.082	10.2	10.3	7.55	183	9.6	8.60	70	16.1	3.3	8.4	0.05	13.4	4.9	13.6	3.4
Allier	23/04/2012	79.487	8.9	10.7	7.35	120	13.5	11.80	46	9.3	3.4	5.0	0.06	9.3	3.7	8.2	2.3
Allier	09/05/2012	84.38	12.3	9.6	7.40	122	13.7	5.30	48	9.7	3.7	6.5	0.05	10.0	3.7	7.5	1.7
Allier	21/05/2012	93.044	12.4	9.3	7.45	141	17.5	5.10	60	10.0	3.9	6.0	0.08	13.3	4.8	8.6	2.8
Allier	04/06/2012	83.288	16.2	8.7	7.30	139	14.0	<0.5	50	10.4	4.7	7.5	0.10	11.7	4.5	8.7	2.1
Allier	18/06/2012	40.089	19.3	8.4	7.10	163	14.7	9.70	65	12.0	4.4	8.1	0.06	14.7	4.9	10.2	2.5
Allier	02/07/2012	29.331	18.7	8.3	7.20	193	11.9	8.10	74	15.2	4.6	8.8	0.07	16.4	5.4	12.7	3.2
Allier	16/07/2012	19.55	17.3	9.2	7.65	198	14.0	4.20	84	16.0	4.5	8.6	0.09	16.8	5.5	12.8	3.4
Allier	30/07/2012	14.35	20.6	7.8	7.50	203	11.0	2.80	78	17.3	3.7	8.3	0.12	15.8	5.7	14.7	3.2
Allier	13/08/2012	16.65	21.3	7.9	7.50	178	10.1	6.50	68	16.0	3.6	7.6	0.13	13.1	4.9	13.2	3.4
Allier	27/08/2012	17.55	18.5	8.6	7.40	174	9.6	9.00	74	16.3	3.3	7.0	0.12	14.7	5.0	13.2	3.0
Allier	10/09/2012	15.95	18.6	8.5	7.50	181	7.1	13.40	70	16.3	2.7	6.9	<0.05	14.7	4.8	13.6	3.0
Allier	24/09/2012	16.85	17.8	8.6	7.60	218	8.2	2.80	82	21.6	3.5	8.3	<0.05	16.5	5.5	16.1	3.5
Allier	08/10/2012	14.05	16.6	8.8	7.60	220	10.1	0.50	84	20.4	3.6	8.3	0.18	17.2	5.7	16.5	3.6
Allier	22/10/2012	16.25	15.5	8.7	7.60	204	8.8	17.10	78	18.1	1.9	7.4	0.07	14.1	5.6	15.1	3.4
Allier	05/11/2012	23.75	9.9	10.3	7.70	194	13.0	9.00	70	15.8	3.3	7.5	<0.05	13.7	5.3	13.8	3.5

Sample ID	Date	Flow	T	Do	pH	EC	SiO_2	CO_2	HCO_3	Cl	NO_3	SO_4	PO_4	Ca	Mg	Na	K
Cognet	14/02/2011	N.A	11.8	9.1	6.85	957	38.0	41.0	482	37.9	50.1	37.0	0.20	119.9	37.3	17.3	19.5
Cognet	28/02/2011	31.63	11.1	9.2	7.11	1061	37.9	36.6	487	36.4	49.9	36.6	0.25	137.9	38.0	16.1	18.0
Cognet	14/03/2011	32.62	11.5	8.7	7.18	937	44.2	44.7	486	34.0	50.2	37.4	0.26	117.7	37.2	14.4	16.3
Cognet	28/03/2011	31.33	12.0	8.9	7.25	940	42.8	43.1	477	33.1	49.9	37.2	0.17	129.0	38.1	14.3	16.7
Cognet	11/04/2011	26.34	12.5	9.0	7.09	964	43.4	29.9	499	33.1	49.1	36.0	0.24	124.0	40.4	15.8	18.1
Cognet	26/04/2011	20.39	12.3	9.3	7.31	970	46.8	32.2	494	31.7	49.1	35.9	0.19	122.8	37.8	14.3	18.2
Cognet	09/05/2011	18.14	13.1	9.3	7.26	939	44.7	34.3	503	31.3	50.0	37.3	0.26	121.2	37.3	14.5	16.0
Cognet	23/05/2011	16.23	13.0	9.3	7.31	960	41.6	42.8	494	32.7	50.7	36.5	0.21	129.6	39.9	16.0	17.0
Cognet	06/06/2011	14.12	13.3	9.0	7.25	946	40.9	43.3	505	31.8	49.8	36.2	0.18	117.6	36.4	16.1	17.5
Cognet	20/06/2011	13.38	13.4	9.2	7.28	957	33.4	35.7	506	32.3	51.1	36.7	0.27	127.4	38.8	15.7	17.4
Cognet	04/07/2011	11.23	13.7	9.5	7.29	973	39.8	45.2	521	33.6	50.3	36.2	0.16	125.1	38.7	15.8	15.3
Cognet	18/07/2011	14.97	13.6	8.9	7.29	968	38.0	30.6	499	33.5	52.7	36.2	0.17	126.2	38.1	15.1	17.1
Cognet	16/08/2011	10.35	14.5	9.2	7.27	974	39.2	39.6	498	32.8	52.3	36.5	0.17	126.2	36.5	15.6	20.9
Cognet	29/08/2011	9.26	14.3	9.8	7.24	945	41.7	31.3	503	32.6	49.8	34.6	0.00	139.7	39.5	16.0	19.5
Cognet	12/09/2011	9.06	14.6	9.4	7.29	943	42.5	37.5	489	32.8	50.7	40.7	0.24	117.3	37.7	15.9	19.0
Cognet	26/09/2011	6.58	14.8	9.4	7.22	933	41.5	33.4	503	32.7	51.8	41.9	0.26	122.4	38.9	16.9	19.8
Cognet	10/10/2011	5.6	14.7	9.2	7.24	951	42.4	35.0	497	32.6	51.4	36.1	0.26	125.1	38.8	16.6	19.3
Cognet	24/10/2011	5.09	14.0	9.3	7.31	943	41.5	26.2	498	32.4	50.5	35.4	0.38	127.8	39.0	16.5	19.5
Cognet	07/11/2011	9.44	14.1	9.0	7.30	952	40.1	46.1	500	34.1	50.0	36.7	0.23	117.3	39.1	16.7	22.9
Cognet	21/11/2011	5.94	13.7	9.2	7.39	928	38.4	36.8	495	34.0	51.9	36.4	0.20	122.7	38.4	15.5	18.3
Cognet	05/12/2011	5.35	13.7	9.5	7.48	918	39.5	27.3	477	32.4	49.3	36.3	0.25	115.4	37.9	16.1	19.4
Cognet	19/12/2011	5.84	12.8	9.9	7.63	908	40.1	9.0	473	32.9	50.0	35.9	0.25	125.9	38.3	19.6	19.9
Cognet	03/01/2012	6.62	12.6	9.7	7.63	879	42.2	21.5	458	32.1	51.8	38.8	0.19	119.4	38.4	16.1	16.4
Cognet	16/01/2012	5.69	10.9	9.6	7.66	880	40.0	17.4	454	31.1	44.5	34.4	0.19	116.7	37.2	17.4	18.1
Cognet	30/01/2012	5.7	11.6	10.2	7.65	860	39.2	21.5	455	31.0	42.7	33.2	0.20	108.8	35.1	15.0	18.7
Cognet	13/02/2012	8.82	9.6	9.7	7.54	818	37.1	26.4	429	30.8	39.1	32.1	0.16	109.0	35.9	16.7	17.7
Cognet	27/02/2012	9.54	11.2	9.7	7.48	865	36.9	20.8	421	31.3	39.0	32.8	0.17	103.5	33.3	15.4	15.9
Cognet	12/03/2012	7.85	11.6	9.7	7.47	888	34.6	25.7	433	29.6	38.3	31.7	0.15	102.8	32.3	15.7	17.8
Cognet	26/03/2012	8.12	11.6	9.9	7.48	926	38.2	21.1	456	32.7	44.0	34.5	0.09	118.4	38.0	14.9	16.9
Cognet	10/04/2012	8.37	12.4	9.7	7.34	976	38.7	27.8	473	36.2	50.2	37.4	0.29	119.5	39.0	16.3	17.3
Cognet	23/04/2012	8.99	12.2	9.5	7.39	959	39.3	36.1	483	38.0	50.0	35.7	0.30	121.5	38.6	15.7	17.8
Cognet	09/05/2012	10.56	13.0	9.1	7.23	978	38.6	42.4	475	39.0	50.5	40.0	0.14	125.3	39.0	15.9	14.5
Cognet	21/05/2012	9.88	12.9	9.4	7.20	988	47.7	29.5	487	39.9	53.9	41.6	0.26	129.2	39.2	15.7	16.9
Cognet	05/06/2012	16.58	14.2	9.0	7.23	1007	42.0	37.4	497	47.3	55.0	39.9	0.28	122.4	39.5	15.5	15.8
Cognet	18/06/2012	15.54	13.3	8.9	7.22	1037	39.9	41.7	500	45.0	52.1	39.2	0.21	142.3	40.3	15.7	18.0
Cognet	02/07/2012	16.16	13.5	8.8	7.21	1031	36.6	32.7	501	45.9	54.0	39.3	0.31	144.1	38.8	14.9	17.5
Cognet	16/07/2012	19.69	13.4	8.8	7.16	1044	38.9	0.5	515	49.5	53.8	38.4	0.30	148.4	40.2	15.4	18.9
Cognet	30/07/2012	19.2	13.9	8.5	7.16	1047	39.6	29.1	487	50.2	53.8	36.6	0.14	127.4	41.8	16.0	17.8
Cognet	13/08/2012	16.59	14.3	8.6	7.24	1032	40.6	44.2	499	44.0	53.4	38.1	0.26	132.0	39.7	15.4	18.9
Cognet	27/08/2012	15.23	14.1	8.7	7.25	1026	40.1	41.2	527	41.5	54.4	38.4	0.20	146.7	40.3	15.6	18.4
Cognet	10/09/2012	9.48	14.9	9.1	7.36	1015	40.1	44.0	512	38.0	51.1	35.6	0.21	142.0	40.0	15.4	18.6
Cognet	24/09/2012	7.96	15.1	8.9	7.36	1023	41.5	38.9	498	39.0	52.9	37.3	0.27	136.9	40.4	15.9	19.4
Cognet	08/10/2012	6.43	15.2	8.8	7.35	1003	39.9	41.7	523	38.6	52.5	35.7	0.27	136.9	37.0	14.8	18.3
Cognet	22/10/2012	6.5	15.2	8.7	7.41	986	43.8	42.2	494	38.4	49.4	35.8	0.19	120.8	40.8	15.9	19.7
Cognet	05/11/2012	7.72	14.4	10.0	7.55	959	40.7	31.3	481	37.5	47.1	36.0	0.24	124.0	40.6	17.3	20.0
Jallat	14/02/2011	N.A	10.2	9.5	6.80	802	45.5	31.0	409	22.0	46.9	33.0	<0.05	111.4	29.5	8.4	3.8
Jallat	28/02/2011	3.82	9.1	9.3	6.95	947	43.9	39.6	393	21.1	46.7	32.6	<0.05	121.9	30.5	7.9	3.8
Jallat	14/03/2011	3.63	11.4	8.9	7.19	773	50.6	48.9	408	20.0	45.9	32.7	<0.05	108.7	29.9	7.6	3.6
Jallat	28/03/2011	3.43	10.8	8.4	6.97	776	49.8	40.1	422	19.0	42.8	30.7	<0.05	116.1	30.8	7.4	3.5
Jallat	26/04/2011	3.28	12.4	8.9	7.29	787	53.8	41.2	415	18.6	41.3	29.5	<0.05	110.7	29.4	7.7	3.8
Jallat	09/05/2011	3.21	13.1	9.0	7.23	770	51.5	38.9	421	18.3	41.8	30.3	<0.05	110.2	28.9	7.7	3.4
Jallat	23/05/2011	3.21	14.3	9.1	7.22	767	46.4	45.2	411	18.8	42.6	29.7	<0.05	107.0	29.5	7.3	3.5
Jallat	06/06/2011	3.39	13.4	9.2	7.21	768	43.5	44.7	412	18.7	42.7	30.0	<0.05	104.5	27.9	8.6	3.7
Jallat	20/06/2011	3.52	13.9	9.4	7.25	775	38.2	35.8	419	18.4	42.3	29.6	<0.05	117.7	29.7	9.2	3.8
Jallat	04/07/2011	3.09	14.4	9.5	7.29	765	36.3	35.2	432	18.0	46.4	32.4	<0.05	109.1	29.7	8.3	4.0
Jallat	18/07/2011	2.85	14.0	9.1	7.26	773	42.1	31.7	421	16.8	42.7	27.2	0.05	106.5	31.6	8.9	4.4
Jallat	16/08/2011	2.5	14.8	8.4	7.22	758	43.7	31.3	432	15.1	38.7	27.4	<0.05	112.6	28.4	8.5	4.7
Jallat	29/08/2011	2.48	14.8	8.6	7.20	744	45.0	37.7	423	14.6	37.0	26.7	<0.05	109.6	28.5	9.6	4.4
Jallat	12/09/2011	2.24	15.1	8.0	7.20	735	36.4	39.6	423	14.0	36.7	25.9	<0.05	101.1	29.4	8.8	4.1
Jallat	26/09/2011	1.29	14.4	8.5	7.21	739	47.3	37.5	421	14.2	36.7	26.3	<0.05	104.8	30.2	9.4	4.5
Jallat	10/10/2011	1.64	14.6	8.5	7.20	745	47.5	45.6	427	13.7	36.3	25.7	<0.05	107.5	30.9	9.3	4.3
Jallat	24/10/2011	5.57	14.0	9.1	7.14	728	45.3	34.0	421	13.8	35.5	25.7	<0.05	111.5	31.3	8.8	4.1
Jallat	07/11/2011	2.86	12.8	8.6	7.24	778	41.8	45.4	411	19.4	46.1	31.0	<0.05	104.9	31.2	9.1	5.4
Jallat	21/11/2011	5.54	11.8	8.5	7.28	745	40.6	29.4	420	18.8	40.2	29.1	<0.05	108.8	30.2	11.1	4.1
Jallat	05/12/2011	1.57	11.1	8.9	7.11	715	47.8	35.4	425	16.4	38.2	26.8	<0.05	104.5	30.0	9.3	5.0
Jallat	19/12/2011	1.3	9.2	9.7	7.38	735	42.7	32.0	422	15.7	37.5	27.4	<0.05	111.5	31.2	10.2	5.0
Jallat	03/01/2012	1.31	9.5	9.0	7.25	732	45.6	30.1	420	15.5	37.9	26.4	<0.05	110.6	30.8	9.6	4.3
Jallat	16/01/2012	1.75	7.9	8.5	7.24	748	45.0	34.0	414	19.6	40.8	29.7	<0.05	114.8	30.4	11.1	5.9
Jallat	30/01/2012	1.72	8.0	8.7	7.29	745	44.4	36.1	412	19.4	39.3	28.5	<0.05	107.0	30.6	8.4	4.7
Jallat	13/02/2012	1.8	6.5	9.8	7.11	765	44.3	34.0	415	18.8	39.6	28.6	<0.05	113.8	32.5	9.0	4.8
Jallat	27/02/2012	2.65	7.5	8.5	7.30	833	44.7	29.4	406	26.3	46.8	31.9	<0.05	113.0	29.9	9.2	5.3
Jallat	12/03/2012	1.61	9.2	8.2	7.28	822	41.9	43.5	410	24.9	44.9	31.3	<0.05	109.0	27.5	8.7	4.9
Jallat	26/03/2012	3.42	9.8	7.6	7.26	809	45.1	26.4	406	22.6	41.5	29.4	0.06	111.7	30.3	9.0	5.0
Jallat	10/04/2012	2	11.0	8.1	7.06	811	45.2	37.5	411	22.9	43.0	29.8	<0.05	112.0	30.8	10.0	4.5
Jallat	23/04/2012	1.71	10.2	7.3	7.20	804	47.6	42.2	421	21.7	41.5	32.2	<0.05	112.0	30.5	8.5	4.5
Jallat	09/05/2012	1.58	12.1	7.4	7.10	800	46.3	34.7	409	21.3	39.7	31.7	<0.05	119.0	31.9	9.2	3.9
Jallat	21/05/2012	1.54	12.3	8.0	7.06	799	54.5	31.9	419	20.2	41.9	31.7	<0.05	119.2	30.8	8.9	3.8
Jallat	05/06/2012	2.97	14.3	7.3	7.14	800	45.7	37.2	426	18.4	43.4	29.9	<0.05	123.7	30.1	8.3	3.1
Jallat	18/06/2012	4.29	14.0	7.4	7.04	828	49.3	46.1	421	22.5	49.5	31.9	<0.05	123.7	30.2	8.1	3.5
Jallat	02/07/2012	5.23	13.6	7.9	7.06	843	40.4	39.6	411	26.3	53.9	34.4	<0.05	133.8	29.9	7.9	3.4
Jallat	16/07/2012	4.55	13.7	7.9	6.99	843	44.6	44.2	447	25.8	52.7	34.4	<0.05	136.0	29.5	7.9	3.6
Jallat	30/07/2012	3.85	14.6	7.7	6.98	835	45.3	29.3	415	23.8	52.8	33.1	<0.05	128.6	32.0	8.5	3.6
Jallat	13/08/2012	3.71	14.6	7.6	7.09	837	46.0	35.7	438	21.6	50.3	33.7	0.06	124.5	31.0	8.2	3.8
Jallat	27/08/2012	3.58	14.7	7.7	7.08	822	46.2	46.9	448	19.9	49.1	33.0	0.05	135.3	32.6	8.5	3.6
Jallat	10/09/2012	4.28	14.5	8.6	7.15	817	45.4	50.6	437	18.1	43.6	31.2	<0.05	129.3	32.0	8.3	3.5
Jallat	24/09/2012	3.9	14.4	8.7	7.11	810	46.0	44.5	427	17.7	44.1	31.1	<0.05	120.0	31.1	8.1	3.4
Jallat	08/10/2012	3.34	14.2	8.7	7.23	807	50.0	43.8	422	16.6	42.7	30.3	<0.05	118.0	30.0	8.1	3.4
Jallat	22/10/2012	3.15	13.9	8.5	7.29	800	48.0	46.3	447	15.8	40.6	29.2	0.05	119.6	33.1	8.6	3.6
Jallat	05/11/2012	2.97	12.4	9.2	7.23	792	45.8	36.6	426	15.4	39.4	29.1	0.05	116.0	34.1	9.5	3.9

Sample ID	Date	WL	T	Do	pH	EC	SiO_2	CO_2	HCO_3	Cl	NO_3	SO_4	PO_4	Ca	Mg	Na	K
P13	14/02/2011	317.14	10.6	5.4	6.62	1290	31.8	51.1	498	64.0	35.7	115.7	0.09	135.8	51.9	36.6	11.1
P13	28/02/2011	317.03	9.7	4.6	6.75	1241	29.5		492	78.2	47.7	143.3	0.10	153.6	51.8	32.3	10.5
P13	14/03/2011	316.99	10.4	4.1	7.13	1197	35.1	44.7	497	65.0	38.2	117.6	0.11	137.2	52.8	28.6	9.7
P13	28/03/2011	317.05	10.8	3.4	7.11	1193	32.9	47.2	514	71.6	45.5	124.4	0.15	147.8	53.1	30.1	9.7
P13	11/04/2011	317.04	11.3	5.2	7.11	1247	33.1	35.2	523	67.3	46.7	131.9	0.13	142.9	54.2	31.8	10.3
P13	26/04/2011	316.96	12.2	4.7	7.19	1251	35.2	45.2	527	67.5	49.8	133.3	0.08	149.3	54.7	33.7	9.7
P13	09/05/2011	316.89	12.7	4.3	6.73	1220	34.6	31.2	522	64.7	49.7	138.7	0.09	150.3	54.5	31.2	10.0
P13	23/05/2011	316.82	12.7	3.2	7.11	1165	33.5	56.2	514	65.9	46.2	135.9	0.14	148.0	55.7	31.1	9.9
P13	06/06/2011	316.76	12.3	3.8	7.08	1231	29.9	48.4	526	74.7	51.2	143.8	0.11	149.4	55.7	37.2	10.3
P13	20/06/2011	316.69	13.5	4.3	7.10	1225	25.3	56.5	528	74.8	47.5	132.8	0.13	155.1	54.6	37.6	9.3
P13	04/07/2011	316.6	13.2	2.5	7.03	1111	26.7	57.9	521	62.2	32.8	118.0	0.10	134.4	50.1	33.0	10.2
P13	18/07/2011	316.58	12.5	3.0	7.07	1185	29.2	61.6	509	61.8	35.7	122.8	0.09	139.3	51.1	31.4	10.3
P13	16/08/2011	316.56	13.1	3.7	7.07	1154	31.2	51.8	516	57.6	41.5	132.5	0.10	144.0	51.6	35.5	14.3
P13	29/08/2011	316.55	13.0	3.5	7.02	1128	31.3	57.9	505	60.0	36.6	119.7	<0.05	157.8	51.5	33.4	11.3
P13	12/09/2011	316.54	14.0	2.5	7.05	1107	24.4	76.3	519	57.2	37.7	129.9	<0.05	130.8	51.7	33.2	11.6
P13	26/09/2011	316.51	14.4	3.1	7.06	1159	33.6	54.5	523	76.0	36.3	125.1	0.13	142.7	52.1	40.6	11.8
P13	10/10/2011	316.46	13.5	2.6	7.02	1113	32.8	51.8	510	58.9	35.8	119.3	0.13	139.3	52.9	33.8	12.1
P13	24/10/2011	316.44	13.6	2.9	7.05	1176	31.7	68.7	515	60.6	34.3	113.7	0.14	141.0	51.5	31.3	11.4
P13	07/11/2011	316.46	14.7	3.5	7.10	1199	30.8	62.8	531	63.8	35.9	120.1	<0.05	132.9	55.6	35.9	14.2
P13	21/11/2011	316.61	12.8	2.6	7.11	1099	33.3	60.4	525	63.6	35.9	118.8	0.09	137.5	52.6	30.6	10.7
P13	05/12/2011	316.55	13.4	4.4	7.27	1131	30.0	71.4	516	64.9	36.0	114.5	0.12	137.5	53.8	31.9	12.1
P13	19/12/2011	316.52	11.9	3.3	7.21	1106	31.3	52.3	499	62.7	29.4	103.3	0.09	135.9	50.0	36.1	12.0
P13	03/01/2012	316.61	11.5	3.2	7.22	1118	32.8	45.2	508	64.1	33.7	105.2	<0.05	142.0	55.4	34.2	11.3
P13	16/01/2012	316.67	10.1	2.4	7.27	1127	31.9	63.3	516	65.2	34.7	108.8	0.14	141.0	54.4	33.7	9.8
P13	30/01/2012	316.64	10.7	4.1	7.24	1147	32.3	56.5	510	66.4	34.4	107.8	0.09	134.2	53.3	35.7	12.1
P13	13/02/2012	316.6	9.1	3.0	7.14	1171	32.0	74.3	527	65.3	34.4	109.7	0.12	148.8	58.5	37.6	12.1
P13	27/02/2012	316.65	10.7	2.7	7.15	1196	31.7	65.5	495	65.3	33.4	103.3	0.07	132.9	51.7	33.5	10.9
P13	12/03/2012	316.64	11.2	4.2	7.13	1244	30.8	60.4	522	68.2	35.4	111.9	0.07	133.7	49.5	34.2	10.8
P13	26/03/2012	316.57	10.5	3.7	7.13	1223	31.6	61.1	509	70.5	34.9	109.2	0.07	143.3	54.6	43.5	11.8
P13	10/04/2012	316.52	10.9	3.5	7.08	1226	31.3	76.8	512	74.1	37.9	118.0	0.07	141.8	55.2	33.3	10.3
P13	23/04/2012	316.56	12.0	2.6	7.14	1190	42.4	70.6	523	69.0	35.2	112.5	0.12	155.1	49.0	29.7	11.6
P13	09/05/2012	316.7	13.4	2.5	7.07	1173	31.6	74.2	498	68.1	32.5	103.5	<0.05	139.9	48.9	29.8	11.3
P13	21/05/2012	316.72	12.0	3.1	7.00	1213	37.9	73.8	515	76.9	40.8	118.5	0.13	141.6	53.2	33.3	10.0
P13	04/06/2012	316.96	12.5	2.0	7.07	1199	30.8	70.6	503	69.5	32.4	109.3	0.18	129.3	50.0	31.1	9.7
P13	18/06/2012	316.96	13.1	4.1	7.07	1238	30.1	70.9	489	90.5	40.3	91.8	0.05	136.9	50.4	37.2	9.4
P13	02/07/2012	316.84	13.3	2.5	7.04	1169	28.7	74.6	506	67.9	31.4	105.4	0.14	139.2	49.4	30.2	11.3
P13	16/07/2012	316.78	13.3	4.0	7.04	1280	31.7	0.0	522	109.0	37.7	92.8	<0.05	168.9	49.7	44.1	10.5
P13	30/07/2012	316.71	14.1	2.9	7.02	1233	31.4	76.8	554	68.7	31.9	102.5	0.15	140.1	49.7	42.2	9.3
P13	13/08/2012	316.62	14.5	3.6	7.08	1268	31.5	39.6	530	75.0	35.7	110.2	0.16	164.3	44.5	34.7	10.1
P13	27/08/2012	316.55	14.7	2.3	7.07	1244	31.3	19.9	541	67.8	32.3	103.0	0.06	139.3	53.5	32.8	11.7
P13	10/09/2012	316.51	16.1	3.5	7.07	1229	33.1	77.7	534	76.4	39.6	98.5	<0.05	153.4	51.5	38.3	10.5
P13	24/09/2012	316.45	16.2	3.1	7.09	1212	29.9	60.9	515	69.0	32.5	99.2	<0.05	138.5	49.0	30.4	11.4
P13	08/10/2012	316.41	15.5	5.2	7.17	1225	31.3	68.4	531	67.7	33.5	100.4	0.18	143.6	52.4	32.9	11.4
P13	22/10/2012	316.36	14.3	2.5	7.27	1195	35.2	63.6	527	65.4	30.3	94.0	0.06	137.8	52.9	37.0	10.6
P13	05/11/2012	316.36	14.3	2.8	7.22	1175	32.8	64.5	523	68.2	34.5	97.4	0.09	140.5	52.6	39.2	10.8

Campaigns December 2010

Sample ID	WL	T	Do	pH	EC	SiO_2	CO_2	HCO_3	Cl	NO_3	SO_4	PO_4	Ca	Mg	Na	K	$\delta^{18}O$	$\delta^{2}H$
B01	314.91	10.9	5.7	6.92	216	17.4	14.4	92	15.1	3.4	9.3	0.05	21.1	6.0	12.1	3.2	-8.46	-56.22
B02	314.92	11.5	5.6	7.06	213	17.5	13.4	92	15.1	3.0	8.8	0.06	20.1	5.8	12.2	3.2	-8.26	-56.12
B03	314.80	11.3	5.8	7.04	214	17.0	13.2	90	15.1	3.0	8.9	0.00	20.7	5.8	12.2	3.2	-8.40	-55.91
B04	314.96	11.5	5.2	7.3	218	17.0	17.2	92	15.2	3.2	9.0	0.08	19.0	6.4	11.7	3.1	-8.45	-57.00
B05	314.73	12.4	6.3	7.27	177	14.7	13.0	70	12.6	5.3	8.4	0.12	17.0	4.5	11.0	3.0	-8.40	-55.52
B06	314.91	11.9	5.4	7.29	217	16.6	15.9	92	15.3	3.2	9.2	0.06	21.7	5.8	11.7	3.1	-8.50	-56.60
B07	315.00	12.0	5.4	7.3	189	15.5	15.5	77	13.5	4.7	8.4	0.06	17.7	4.9	11.0	2.9	-8.59	-56.20
B08	314.78	11.9	5.5	7.28	234	17.4	15.5	98	15.9	3.8	10.8	0.00	23.3	6.5	12.1	3.1	-8.49	-55.78
B09	314.91	12.0	6.6	7.32	194	16.0	12.8	79	13.8	4.1	8.5	0.05	19.4	5.1	11.5	3.0	-8.29	-55.59
B10	314.87	12.5	6.9	7.21	321	19.0	19.8	134	19.3	8.1	19.8	0.07	31.2	10.0	14.3	3.8	-8.38	-56.28
B11	315.00	12.6	5.6	7.27	182	15.5	13.4	72	12.6	4.5	8.4	0.13	16.5	4.6	11.4	3.1	-8.58	-57.15
B12	314.86	12.2	7.3	7.25	310	19.4	17.1	133	18.5	6.5	17.7	0.00	30.0	9.4	14.0	3.6	-8.27	-55.71
B13	314.86	12.2	6.4	7.24	186	15.5	12.5	76	12.4	5.1	8.4	0.11	17.9	4.6	10.7	2.9	-8.42	-56.16
B14	314.92	12.3	7.2	7.08	248	19.8	28.2	109	15.9	3.0	10.1	0.00	26.0	6.9	12.7	3.6	-8.36	-55.85
B15	314.86	11.7	6.4	7.31	208	15.4	21.1	78	14.7	4.6	9.0	0.06	18.7	5.2	12.3	3.3	-8.68	-57.29
B16	315.17	12.3	6.1	7.1	225	19.3	27.6	100	15.4	1.3	7.9	0.06	20.8	6.4	11.8	3.2	-8.18	-55.82
B17	315.39	12.4	5.8	7.1	204	17.7	23.6	85	14.1	3.9	8.7	0.09	17.7	5.6	11.8	3.2	-8.35	-56.22
B18	315.44	12.1	6.0	7.12	219	19.2	25.9	99	15.4	1.1	7.7	0.07	21.1	6.0	11.8	3.0	-8.22	-55.02
B19	315.92	12.3	5.4	7.08	204	17.5	27.1	85	14.1	4.1	8.9	0.11	18.1	5.5	11.9	3.1	-8.39	-56.50
B20	314.26	11.7	5.7	6.97	211	16.7	15.5	90	14.7	2.6	9.0	0.05	20.3	5.6	11.9	3.3	-8.46	-56.53
B21	313.82	12.0	7.2	7.05	301	17.6	18.5	129	17.9	5.3	17.3	0.00	29.0	9.1	14.1	3.8	-8.39	-55.86
B22	314.01	12.3	6.8	7.11	686	20.0	17.4	322	34.4	13.1	55.0	0.00	73.4	30.1	26.5	9.5	-7.82	-53.10
B23	313.64	12.0	4.9	7.15	955	21.9	19.6	473	42.0	17.4	78.8	0.00	112.1	46.1	28.5	11.8	-7.18	-50.36
B24	313.93	11.3	5.4	7.26	828	22.3	26.6	403	34.5	22.2	67.1	0.34	94.1	35.3	29.3	10.2	-7.01	-49.99
B25	319.36	10.8	5.1	7.26	270	15.1	7.2	129	15.6	3.6	9.9	0.08	28.0	7.7	12.1	3.3	-8.58	-56.94
B26	314.45	9.8	5.6	7.35	199	13.8	9.7	87	13.0	4.6	8.4	0.12	20.3	5.4	10.4	2.8	-8.58	-58.39
B27	314.15	12.4	7.9	7.28	439	18.8	18.3	192	23.5	17.0	33.6	0.06	47.0	16.0	19.4	4.6	-8.23	-54.87
B28	314.79	12.2	6.5	7.2	734	21.8	25.7	326	39.0	14.7	64.1	0.05	73.1	33.3	29.5	8.6	-7.07	-51.48
B29	314.86	12.2	4.8	7.23	947	22.0	21.8	451	49.0	12.8	80.2	0.00	91.3	47.9	38.4	11.5	-5.96	-45.14
B30	316.04	11.1	6.6	7.27	193	16.0	26.4	77	13.7	5.1	8.7	0.11	17.3	5.0	11.5	3.0	-8.27	-55.52
B31	316.82	12.2	7.0	7.03	220	17.0	19.8	89	16.6	3.8	9.5	0.05	19.8	6.0	12.4	3.1	-8.28	-54.32
B31BIS	315.62	10.7	6.3	7.15	195	16.3	22.0	78	13.0	6.6	9.1	0.07	17.7	5.4	10.2	2.8	-8.37	-56.79
B32	315.89	12.5	6.3	7.1	201	16.0	17.6	81	14.2	4.8	9.1	0.13	17.1	5.5	11.6	3.1	-8.53	-57.50
B33	316.61	12.6	5.1	7.43	188	14.9	19.2	72	13.5	5.0	8.6	0.15	17.9	4.9	11.8	3.1	-8.36	-56.17
B34	316.68	11.0	5.4	7.53	230	15.4	13.7	99	15.4	2.8	8.7	0.10	24.7	6.8	11.3	3.2	-8.24	-54.97
B35	315.69	10.5	2.5	7.56	222	18.1	9.5	89	18.1	3.4	8.1	0.07	19.9	6.6	12.4	2.8	-8.50	-57.23
B36	315.82	11.8	3.8	7.53	190	14.5	13.0	73	14.2	4.2	8.8	0.13	17.8	4.9	11.8	3.0	-8.37	-56.25
B37	316.52	11.4	3.2	7.52	215	15.9	11.6	93	16.4	3.6	8.7	0.05	20.9	6.1	12.2	3.4	-8.77	-57.65
B38	317.18	9.2	4.5	7.52	199	18.7	9.4	83	14.9	1.7	7.7	0.00	23.3	4.6	10.0	3.0	-8.48	-56.22
B39	316.86	10.6	3.2	7.41	227	18.7	13.9	99	15.9	3.7	5.9	0.00	25.0	6.4	11.4	3.2	-8.52	-56.68
B40	317.30	10.0	3.7	7.73	198	19.7	11.3	83	13.4	0.0	6.5	0.22	17.1	6.2	10.0	2.8	-8.37	-55.35
B41	315.31	9.6	7.3	7.21	269	18.0	11.2	112	16.1	8.5	16.3	0.07	23.5	8.4	14.6	4.6	-7.87	-53.54
B42	315.18	9.7	7.2	7.1	269	17.5	11.3	112	15.8	8.2	16.1	0.08	23.5	8.5	13.9	4.5	-8.25	-56.02
B43	315.24	9.5	7.0	7.04	257	16.2	8.8	107	15.4	8.2	15.2	0.08	22.9	7.9	13.2	4.3	-8.21	-56.13
B44	315.31	8.9	7.3	7.19	275	15.1	10.3	115	16.5	8.8	15.8	0.07	30.8	9.7	12.8	3.9	-8.34	-56.92
B45	315.31	9.5	6.6	7.21	283	16.4	10.2	118	15.0	9.9	18.7	0.05	26.3	9.4	14.8	3.8	-8.22	-55.47
B46	315.33	11.1	5.3	7.17	268	19.0	11.4	118	15.7	4.3	15.1	0.08	25.4	10.5	15.6	4.5	-8.10	-55.05
B47	315.60	11.1	4.0	7.2	191	16.7	13.4	81	12.5	5.4	9.3	0.06	17.6	5.4	11.3	3.3	-8.36	-56.26
B48	315.70	10.4	7.2	7.08	272	17.3	15.2	111	16.6	13.6	17.6	0.07	25.7	9.2	14.7	4.5	-8.37	-55.19
B49	315.70	10.2	7.9	7.26	185	16.9	11.8	72	12.0	7.4	9.1	0.07	18.5	5.2	9.3	2.8	-8.42	-55.74
B50	315.61	8.7	8.1	7.15	270	16.2	11.7	112	16.0	9.1	15.8	0.10	27.0	8.3	13.1	5.3	-8.52	-55.48
B51	317.62	10.9	4.0	7.49	176	14.4	14.3	67	13.1	4.3	8.3	0.17	15.9	4.6	10.4	2.8	-8.50	-56.55
B52	317.68	10.1	5.3	7.4	168	13.7	11.6	61	13.2	5.7	8.4	0.12	15.9	4.5	9.8	2.6	-8.40	-55.96
B53	317.93	13.1	3.5	7.26	179	17.2	11.6	71	12.9	3.1	8.4	0.17	16.7	4.7	10.8	3.0	-8.46	-56.59
B54	318.08	10.8	5.9	7.56	188	17.8	19.4	77	12.1	2.0	8.2	0.13	17.8	5.3	10.2	3.2	-8.45	-56.56
B55	318.01	11.1	4.4	7.6	200	17.9	21.3	82	13.6	1.3	8.5	0.11	16.9	5.8	11.1	3.2	-8.33	-55.86
B56	318.02	10.2	5.1	7.49	214	17.1	15.0	77	12.8	4.3	8.8	0.13	17.4	5.9	9.4	3.2	-8.46	-56.70
B57	317.89	11.6	2.4	7.37	214	17.9	15.3	96	14.5	3.7	8.0	0.18	22.8	6.7	10.0	3.2	-8.03	-55.17
B58	317.93	10.7	5.4	7.34	226	20.5	23.6	79	12.9	4.8	9.4	0.13	15.1	5.9	10.6	3.9	-7.79	-54.08
B59	317.95	11.8	3.8	7.36	216	19.4	14.8	96	12.8	1.7	9.0	0.15	22.6	6.7	10.0	3.6	-6.94	-49.47
B60	318.00	11.4	5.2	7.24	309	25.5	22.6	137	16.1	7.0	14.8	0.18	30.5	10.9	10.7	5.2	-7.28	-51.70
B61	318.02	10.9	4.7	7.24	290	23.1	18.5	120	15.4	8.9	15.0	0.10	28.2	9.8	10.8	3.8	-6.09	-45.09
B62	318.78	10.2	4.9	7.27	284	20.2	19.2	114	16.4	6.2	14.8	0.06	26.7	8.9	11.1	3.2	-7.43	-51.23
B63	318.58	10.7	4.9	7.27	285	19.8	29.2	120	14.9	12.1	17.2	0.11	28.3	9.3	11.9	3.4	-6.84	-48.02
B64	318.69	11.4	7.7	7.13	323	20.9	23.6	145	16.4	2.9	19.3	0.15	32.5	10.9	13.2	3.8	-5.97	-44.95
B65	318.65	11.9	8.0	7.23	383	21.4	26.2	172	19.1	8.4	24.3	0.17	39.2	13.7	15.0	4.2	-5.81	-44.07
B66	315.48	12.7	3.7	7.19	226	15.9	7.0	98	14.0	1.9	9.4	0.12	22.5	6.4	11.6	3.1	-8.58	-57.64
B69	313.08	10.4	3.3	7.35	213	14.7	7.3	98	13.1	0.0	8.2	0.14	20.1	6.1	10.7	2.8	-8.52	-56.82
B70	313.31	11.2	2.6	7.33	220	15.9	8.6	98	13.5	3.6	9.5	0.12	20.9	6.4	11.2	3.0	-8.01	-54.87
B71	316.60	10.7	6.2	7.31	257	19.5	13.7	116	15.8	2.6	10.6	0.07	26.6	7.2	12.2	2.6	-8.28	-55.77
Allier		2.3	12.7	7.78	138	15.8	4.8	48	10.7	6.6	7.5	0.00	12.9	4.4	7.5	2.2	-8.32	-55.9
P13	318.08	11.8	3.2	7.09	1105	31.2	57.2	494	64.8	44.2	115.6	0.00	141.8	52.4	29.4	10.7	-6.38	-45.33

Campaign June 2012

Sample ID	WL	T°C	DO	pH	EC	SiO_2	CO_2	HCO_3	Cl	NO_3	SO_4	PO_4	Ca	Mg	Na	K	$\delta^{18}O$	$\delta^{2}H$
B01	314.96	11.0	5.3	7.24	194	12.4	12.5	79	14.4	5.2	10.2	0.00	17.5	5.3	11.9	2.8	-8.45	-55.92
B02	315.24	12.1	5.4	7.00	204	16.3	14.8	87	14.7	3.3	7.9	0.06	19.1	5.8	11.7	2.3	-8.26	-56.62
B03	315.01	11.4	3.1	7.19	161	13.7	7.5	66	9.1	4.7	7.5	0.12	14.0	4.5	10.3	2.4	-8.42	-56.83
B04	314.92	12.2	6.0	7.23	180	14.3	13.4	74	12.5	4.9	7.9	0.00	16.0	5.0	11.0	2.3	-8.15	-56.79
B05	314.95	10.3	4.4	7.17	168	12.0	12.7	68	11.3	5.3	7.5	0.08	14.4	4.8	11.1	2.3	-8.70	-57.52
B06	314.94	12.6	6.6	7.14	172	16.3	13.0	66	13.2	5.4	7.8	0.00	14.9	4.5	11.1	2.4	-8.60	-56.65
B07	315.14	10.5	5.7	7.04	172	14.5	12.5	66	11.9	5.1	7.6	0.06	15.5	4.8	11.0	2.3	-8.68	-57.30
B08	315.07	12.2	7.0	7.16	195	17.7	12.8	79	13.5	5.3	8.4	0.05	17.7	5.7	11.1	2.4	-8.47	-55.96
B09	315.18	11.8	5.8	7.06	198	16.7	13.9	84	13.6	3.7	7.8	0.07	18.4	5.5	11.4	2.3	-8.47	-56.65
B10	315.17	11.9	7.1	7.11	245	19.3	17.1	105	16.1	5.1	11.5	0.00	23.5	7.8	12.6	2.7	-8.16	-54.99
B11	315.27	10.4	5.1	7.12	176	14.7	11.2	76	12.0	4.3	7.4	0.07	15.7	5.0	10.9	2.2	-8.38	-56.96
B12	315.13	12.8	3.5	7.15	259	21.3	14.7	106	16.9	3.2	10.6	0.00	25.6	8.0	13.7	2.8	-7.99	-55.29
B13	315.10	10.3	6.3	7.18	176	14.1	14.6	74	11.0	5.0	7.5	0.08	15.4	4.9	11.0	2.2	-8.59	-57.19
B14	315.20	12.1	6.8	6.89	211	17.7	18.1	94	14.6	3.9	8.3	0.00	20.6	5.9	11.4	2.4	-8.23	-56.29
B15	315.26	12.0	4.6	7.26	188	12.8	6.0	76	14.4	5.9	8.3	0.08	15.8	5.0	11.3	2.4	-8.29	-56.02
B16	315.33	13.0	7.3	7.04	233	17.9	15.6	99	16.6	2.2	8.0	0.00	21.9	6.4	12.1	2.5	-8.49	-56.95
B17	316.30	11.8	5.9	7.14	181	13.7	7.6	67	14.8	7.1	8.1	0.00	16.3	4.7	10.5	2.4	-8.43	-56.96
B18	315.68	12.2	7.5	7.01	220	18.0	21.8	92	16.2	1.9	7.5	0.00	20.0	6.1	12.0	2.3	-8.23	-56.06
B19	316.11	11.2	8.4	6.95	190	15.5	12.0	77	13.5	4.2	8.0	0.07	16.3	5.2	11.3	2.2	-8.22	-56.17
B20	314.84	11.8	5.7	7.07	194	15.6	12.3	79	13.7	4.3	8.5	0.08	18.2	5.4	11.4	2.4	-8.38	-56.72
B21	314.41	13.5	7.4	7.09	231	17.9	14.1	94	15.0	5.4	11.1	0.05	22.3	7.0	12.3	2.6	-8.14	-55.30
B22	314.60	13.5	7.3	7.35	484	19.5	16.7	218	24.4	11.3	30.7	0.12	49.4	20.1	18.4	6.4	-6.84	-48.92
B23	314.21	12.2	5.5	7.33	794	21.0	30.6	381	35.0	21.3	66.1	0.00	91.7	35.6	24.0	8.4	-6.63	-47.81
B24	314.31	13.6	6.6	7.28	671	21.0	22.2	299	35.3	15.5	51.7	0.08	61.2	29.4	25.1	6.9	-7.23	-51.36
B25	314.41	12.4	6.0	7.72	231	15.7	2.6	103	14.2	5.0	8.7	0.13	22.0	6.3	11.5	2.2	-8.37	-56.88
B26	314.63	10.4	3.3	7.50	188	14.0	8.3	84	11.2	4.1	7.4	0.14	15.6	4.9	11.0	2.0	-8.84	-59.39
B27	314.72	13.8	7.3	7.24	265	9.9	13.8	127	15.3	5.9	12.6	0.05	25.6	8.7	13.7	2.9	-7.38	-51.69
B28	315.45	13.3	6.9	7.24	661	10.7	29.8	288	35.8	16.5	57.6	0.09	65.7	29.5	26.3	7.4	-6.06	-45.37
B29	315.41	14.0	4.9	7.30	989	11.3	31.3	460	50.4	21.0	82.0	0.00	100.8	49.5	37.6	11.4	-5.80	-44.05
B30	315.81	11.2	7.6	7.00	173	15.1	18.0	73	9.6	3.8	7.4	0.13	15.0	5.0	11.2	2.4	-8.66	-58.23
B31	316.52	11.9	6.4	6.85	207	16.4	14.1	83	15.3	4.2	9.4	0.00	17.9	5.9	12.9	2.5	-8.32	-55.72
B31BIS	315.29	9.7	6.8	6.98	212	14.6	18.3	98	12.7	5.0	9.3	0.11	19.8	6.4	11.8	2.3	-8.96	-60.04
B32	315.59	9.8	7.4	7.13	188	13.3	10.6	78	11.7	4.7	7.6	0.00	15.7	5.2	11.4	2.9	-8.31	-54.65
B33	316.19	10.8	4.2	6.92	169	24.7	10.9	76	9.2	5.0	7.2	0.19	19.0	4.6	11.4	2.3	-8.43	-56.66
B34	316.30	11.2	3.0	7.10	193	15.4	12.7	89	11.0	2.7	7.3	0.08	17.3	6.2	11.3	2.5	-7.98	-54.48
B35	315.83	13.0	1.7	7.49	186	11.3	10.4	68	16.2	1.8	9.0	0.13	14.0	5.5	11.8	2.3	-8.20	-56.20
B36	316.56	10.1	3.1	7.16	193	4.1	15.6	82	10.7	4.7	7.6	0.08	16.9	5.7	12.8	2.5	-8.39	-56.85
B37	316.65	9.9	1.2	7.30	190	9.4	12.3	76	14.2	1.9	9.1	0.05	16.3	5.9	11.0	2.3	-8.16	-54.93
B38	316.93	11.0	1.2	7.32	198	9.8	12.0	73	15.7	2.7	12.1	0.00	17.5	5.0	11.7	2.7	-8.60	-58.49
B39	316.65	11.9	5.5	7.50	192	12.4	7.2	82	13.8	1.0	6.8	0.05	16.7	5.5	11.1	2.8	-8.17	-55.60
B40	317.01	11.5	1.0	7.38	201	16.9	7.6	89	13.5	0.0	6.7	0.20	17.1	6.8	11.2	2.5	-8.82	-59.65
B41	314.47	13.2	3.7	7.19	492	23.2	27.8	233	22.1	9.7	31.2	0.12	41.8	22.0	21.9	3.9	-8.52	-57.60
B42	314.64	12.3	4.9	7.32	271	15.2	14.8	123	13.3	6.3	13.5	0.12	24.3	9.5	15.0	3.2	-8.60	-58.72
B43	314.54	12.2	4.8	7.29	270	15.3	16.4	124	12.1	6.7	12.9	0.11	24.6	8.2	13.1	2.7	-8.58	-58.55
B44	314.80	11.8	3.5	7.43	255	13.6	13.7	117	12.1	5.9	13.1	0.12	26.3	7.7	13.2	2.5	-8.74	-58.88
B45	314.90	12.1	4.1	7.23	378	23.1	18.0	178	18.1	10.9	29.6	0.10	36.0	14.6	20.0	3.4	-8.57	-57.07
B46	314.98	12.7	4.4	7.15	470	19.4	16.9	203	23.8	15.6	36.4	0.14	38.0	20.2	25.0	4.8	-8.53	-56.78
B47	315.48	11.9	3.8	7.15	291	15.4	11.1	101	13.9	7.9	13.1	0.07	19.7	8.0	14.2	3.0	-8.77	-58.48
B48	315.67	13.8	5.6	7.43	170	15.9	4.9	67	10.3	4.2	6.9	0.00	13.3	4.3	10.4	2.8	-8.47	-56.80
B49	315.45	12.5	4.2	6.95	220	18.5	22.2	105	9.3	3.2	8.5	0.08	20.3	6.8	11.5	2.6	-8.87	-58.41
B50	315.74	12.9	5.5	7.01	250	18.1	23.3	120	10.0	4.5	10.5	0.08	23.3	7.3	12.9	2.8	-8.85	-59.76
B51	317.32	11.9	2.4	7.17	164	15.5	13.0	66	10.8	3.9	7.4	0.13	13.3	4.4	10.4	2.2	-8.64	-57.76
B52	317.35	12.5	2.2	7.01	151	15.0	16.9	62	9.0	3.8	7.4	0.16	12.7	4.3	9.9	2.3	-8.59	-57.67
B53	317.53	10.6	3.5	7.24	171	16.0	16.0	72	10.1	4.3	7.5	0.15	14.0	4.9	10.6	2.2	-8.49	-56.43
B54	317.48	12.1	3.3	7.07	220	18.8	16.3	88	14.8	5.8	12.1	0.07	20.2	7.2	11.7	3.0	-8.72	-58.98
B55	317.11	11.6	3.1	7.17	225	20.4	16.0	93	13.9	4.6	11.8	0.11	20.4	7.4	11.3	3.2	-8.54	-57.32
B56	317.49	12.1	3.6	7.20	159	18.0	15.7	68	9.4	3.6	7.9	0.13	14.1	5.1	9.2	2.5	-8.73	-58.73
B57	317.49	11.2	2.2	7.07	211	19.5	14.6	92	12.6	3.3	10.7	0.12	19.6	6.9	10.9	2.8	-8.47	-56.78
B58	317.57	11.9	4.7	7.15	244	21.5	13.8	107	13.7	5.7	13.0	0.14	21.3	8.5	11.7	3.4	-8.34	-56.45
B59	317.70	13.0	5.6	7.15	323	27.8	15.0	142	16.7	10.2	16.4	0.18	29.9	11.9	12.7	6.2	-8.21	-54.58
B60	317.77	14.7	8.3	7.29	306	22.6	14.7	143	15.1	5.1	14.0	0.13	30.5	10.8	13.3	4.2	-7.49	-52.64
B61	317.68	13.2	5.2	7.10	358	26.5	27.0	159	18.1	14.2	20.0	0.11	32.6	13.8	15.2	4.3	-7.76	-54.10
B62	318.21	13.0	4.2	7.11	275	22.2	21.3	122	15.0	6.7	15.0	0.00	27.5	9.5	12.8	3.0	-7.90	-55.46
B63	317.95	12.5	5.7	7.02	335	23.3	25.7	149	16.3	8.5	19.6	0.12	30.9	12.0	14.9	3.2	-7.88	-53.82
B64	318.11	12.8	5.8	7.11	357	7.3	22.0	167	19.0	4.4	21.7	0.12	33.2	12.8	16.1	3.4	-6.45	-47.38
B65	318.03	14.0	6.5	7.12	367	20.8	13.8	176	18.4	2.9	22.7	0.12	33.7	12.8	16.9	3.5	-5.24	-42.20
B66	314.87	10.7	2.1	7.21	231	17.4	16.7	103	12.9	3.3	9.1	0.16	22.7	7.2	11.9	2.4	-8.43	-56.60
B69	312.10	11.3	4.2	7.01	233	18.5	22.0	100	13.7	2.8	9.0	0.05	19.9	6.7	11.5	2.2	-8.50	-56.62
B70	312.91	11.3	3.6	7.15	210	17.8	14.1	95	10.3	1.9	7.1	0.16	19.0	5.8	10.6	2.0	-8.58	-57.42
B71	316.42	13.1	5.6	7.15	272	21.6	14.1	122	16.4	3.2	11.5	0.08	25.8	7.8	12.5	2.0	-8.19	-54.63
Allier		16.2	8.7	7.30	139	14.0	0.0	50	10.4	4.7	7.5	0.10	11.7	4.5	8.7	2.1	-8.79	-59.91
P13	317.90	12.5	2.0	7.07	1199	30.8	70.6	503	69.5	32.4	109.3	0.18	129.3	50.0	31.1	9.7	-5.82	-46.19

Rainfall

Sampme ID	Date	pH	EC	HCO3	Cl	NO3	SO4	PO4	Ca	Mg	Na	K	**amount (mm)**
Rainfall	14-21/2/2011			43	1.0	1.7	1.0	0.10	0.40	<0.1	0.60	<0.25	7
Rainfall	21-28/2/2011			37	<1	1.0	<1	<0.05	0.30	<0.1	<0.5	<0.25	10
Rainfall	7-14/3/2011			24	<1	<1	<1	<0.05	<0.2	<0.1	<0.5	<0.25	14.4
Rainfall	14-21/3/2011			10	<1	2.1	<4	<0.05	2.50	0.10	<0.5	<0.25	9.6
Rainfall	21-28/3/2011			10	<1	<1	<4	<0.05	<0.2	<0.1	<0.5	<0.25	18
Rainfall	28/3-4/4/2011	7.50	16	5	<1	<1	<5	<0.05	0.90	<0.1	<0.5	<0.25	6.4
Rainfall	26/4-9/5/2011	7.70	22	5	<1	3.4	2.0	0.13	0.26	<0.1	<0.5	<0.25	12
Rainfall	2/5-9/5/2011	7.40	11	6	<1	<1	<1	0.05	<0.2	<0.1	<0.5	<0.25	45.4
Rainfall	16-23/5/2011	7.85	11	9	<1	1.6	<1	<0.05	0.30	<0.1	<0.5	<0.25	5
Rainfall	31/5-6/6/2011	7.55	19	7	<1	2.9	1.1	<0.05	0.50	<0.1	<0.5	<0.25	14.3
Rainfall	06/06/2011	7.30	24	7	<1	2.9	1.6	0.11	1.30	0.20	0.50	0.40	12.3
Rainfall	6-20/6/2011	7.45	23	11	1.0	2.2	2.4	1.31	0.70	<0,1	<0.5	0.50	12.3
Rainfall	4-18/7/2011	7.50	26		2.5	2.2	1.4		2.20	0.20	1.60	0.80	24
Rainfall	22-29/8/2011				1.0	2.7	1.7		3.10	0.30	0.60	0.60	36.4
Rainfall	29/8-5/9/2011	7.20	12	7	<1	1.8	<1	<0.05	0.85	<0.1	<0.5	<0.25	41.4
Rainfall	12-19/09/2011	7.50	10	10	<1	1.1	1.1	<0.05	0.32	0.04	0.10	0.04	6.6
Rainfall	3-10/10/2011	7.45	12	5	<1	1.3	<1	<0.05	1.00	0.04			8.8
Rainfall	17-24/10/2011	7.30	15	6	1.0	2.3	1.0	<0.05	0.90	0.08	0.40	0.08	7.4
Rainfall	24-31/10/2011	7.60	11	2	1.3	<1	<1	0.12	0.12	0.07	0.66	0.05	20.2
Rainfall	31/10-7/11/2011	8.50	13	2	<1	<1	<4	<0.05	0.18	0.03	0.17	0.04	43.2
Rainfall	7-14/11/2011	7.35	4	6	<1	<1	0.2	0.05	<0.2	<0.1	<0.5	<0.25	5.6
Rainfall	28/11-5/12/2011	6.75	3	5	<1	<1	0.3	<0.05	<0.2	<0.1	<0.5	<0.25	2
Rainfall	5-12/12/2011	7.40	12	4	<1	2.0	<1	<0.05	2.10	<0.1	0.17	0.09	4.2
Rainfall	19/12-3/1/2012	6.95	6		<1	<1	<1	0.06					20.2
Rainfall	3-10/01/2012	7.45	6	2	<1	<1	<1	<0.05	0.20	<0.1	0.20	<0.1	2
Rainfall	13/02/2012	7.25	7	4	1.0	<1	<1	<0.05	0.20	<0.1	0.50	<0.1	6
Rainfall	20-27/02/2012	7.45	12	2	<1	<1	<1	<0.05	<0.2	<0.1	0.40	<0.1	4
Rainfall	5-12/03/2012	7.40	19		3.5	1.6	1.2	<0.05	0.40	0.20	1.70	0.11	4
Rainfall	12-26/03/2012	6.40	8		<1	1.6	<1	0.05	<0.2	<0.1	<0.5	<0.25	13
Rainfall	19-26/03/2012	5.60	7	2	<1	1.0	<1	<0.05	<0.2	<0.1	<0.5	<0.25	2.8
Rainfall	26/3-3/4/2012	6.20	26	2	2.1	6.4	1.7	<0.05	0.80	0.20	1.30	0.10	23
Rainfall	3-10/04/2012	7.05	29		4.0	<4	<4	<0.05	0.80	0.10	0.70	0.20	24
Rainfall	23-30/04/2012	6.90	17	4	<1	1.7	<1	<0.05	0.20	<0.1	0.20	0.10	9.4
Rainfall	30/04-07/05/2012				1.5	2.4	<1	<0.05	0.40	0.20	1.20	0.10	8.8
Rainfall	9-15/05/2012	6.70	19	4	<1	4.5	<1	0.05	<0.2	<0.1	0.20	<0.1	12.5
Rainfall	15-22/05/2012	6.80	32	5	<1	7.5	1.9	<0.05	0.40	0.10	0.20	0.10	20
Rainfall	22-29/05/2012	5.80	10	6	<1	1.4	<1	<0.05	0.50	<0.1	0.20	<0.1	20
Rainfall	29/5-4/6/2012	6.70	11	4	<1	1.3	1.0	<0.05	0.90	0.10	0.30	<0.1	20
Rainfall	4-11/06/2012	7.30	19	7	<1	2.4	1.6	<0.05	1.30	0.09	0.26	0.08	20
Rainfall	11-18/06/2012	6.75	4	5	<1	<1	<1	<0.05	0.20	0.03	0.10	0.04	3.2
Rainfall	09-16/07/2012	6.35	14	2	<1	2.7	1.8	<0.05	0.20	0.03	0.08	0.04	22
Rainfall	23-30/07/2012	6.30	11	5	<1	1.6	1.0	<0.05	0.40	0.04	0.07	0.06	18.4
Rainfall	30/7-6/8/2012	6.50	5	2	<1	<1	<1	<0.05	0.20	0.03	0.08	0.03	5
Rainfall	13-20/8/2012	6.20	12		<1	1.7	<1	<0.05	0.30	0.06	0.20	0.10	22
Rainfall	20-27/8/2012	7.00	8	5	<1	1.3	<1	<0.05	0.26	0.04	0.10	0.05	17.2
Rainfall	27/8-3/9/2012	7.05	28	6	<1	1.6	<1	<0.05	0.90	0.10	0.18	0.08	9.6
Rainfall	10-17/9/2012	7.70	15	10	<1	1.2	1.0	0.09	1.30	0.13	0.22	0.09	26
Rainfall	17-24/9/2012	7.50	19	9	<1	2.1	1.3	<0.05	1.50	0.11	0.18	0.10	10.6
Rainfall	24/9-1/10/2012	6.35	10	6	<1	1.3	1.0	0.06	0.40	0.04	0.12	0.04	4.6
Rainfall	1-8/10/2012	6.45	19	7	<1	4.1	1.4	<0.05	0.73	0.10	0.25	0.07	10
Rainfall	8-15/10/2012	6.80	23	5	<1	3.6	0.5	0.05					9
Rainfall	22-29/10/2012	6.55	10	4	<1	<1	<1	0.08	0.26	0.03	0.09	0.05	35.4
Rainfall	29-10/5-11/2012	6.30	7	5	<1	<1	<1	<0.05	0.11	0.01	0.02	<0.02	3.6

APPENDIX B

Stable isotopes data (‰ VSMOW)

Sample ID	Date	$\delta^{18}O$	$\delta^{2}H$	Sample ID	Date	$\delta^{18}O$	$\delta^{2}H$	Sample ID	Date	$\delta^{18}O$	$\delta^{2}H$
B10	14/02/2011	-7.45	-53.19	**B18**	14/02/2011	-8.29	-56.92	**B23**	14/02/2011	-6.57	-48.43
B10	28/02/2011	-7.56	-52.99	**B18**	28/02/2011	-8.22	-56.64	**B23**	28/02/2011	-6.70	-48.38
B10	14/03/2011	-7.48	-52.97	**B18**	14/03/2011	-8.48	-56.87	**B23**	14/03/2011	-6.69	-46.79
B10	28/03/2011	-7.59	-52.99	**B18**	28/03/2011	-8.26	-55.80	**B23**	28/03/2011	-5.22	-45.13
B10	11/04/2011	-7.43	-51.93	**B18**	11/04/2011	-8.33	-55.82	**B23**	11/04/2011	-6.80	-48.73
B10	26/04/2011	-7.36	-52.20	**B18**	26/04/2011	-8.38	-57.19	**B23**	26/04/2011	-6.63	-48.54
B10	09/05/2011	-7.14	-51.20	**B18**	09/05/2011	-8.4	-56.95	**B23**	09/05/2011	-6.57	-47.99
B10	23/05/2011	-7.36	-51.79	**B18**	23/05/2011	-8.31	-56.60	**B23**	23/05/2011	-7.02	-49.84
B10	06/06/2011	-7.78	-53.69	**B18**	06/06/2011	-8.26	-56.31	**B23**	06/06/2011	-7.29	-51.84
B10	20/06/2011	-7.51	-52.24	**B18**	20/06/2011	-8.70	-57.47	**B23**	20/06/2011	-7.24	-50.19
B10	04/07/2011	-7.47	-51.09	**B18**	04/07/2011	-8.54	-57.59	**B23**	04/07/2011	-7.40	-51.48
B10	18/07/2011	-7.35	-51.51	**B18**	18/07/2011	-8.29	-55.67	**B23**	18/07/2011	-6.90	-49.81
B10	16/08/2011	-8.19	-55.45	**B18**	16/08/2011	-8.36	-56.95	**B23**	16/08/2011	-6.69	-48.52
B10	29/08/2011	-7.78	-53.89	**B18**	29/08/2011	-8.17	-56.37	**B23**	29/08/2011	-6.56	-48.41
B10	12/09/2011	-7.81	-54.25	**B18**	12/09/2011	-8.19	-56.63	**B23**	12/09/2011	-6.64	-47.95
B10	26/09/2011	-7.88	-54.01	**B18**	26/09/2011	-8.42	-56.85	**B23**	26/09/2011	-7.27	-51.26
B10	10/10/2011	-8.11	-55.51	**B18**	10/10/2011	-8.45	-56.88	**B23**	10/10/2011	-7.25	-51.42
B10	24/10/2011	-8.15	-54.77	**B18**	24/10/2011	-8.47	-58.05	**B23**	24/10/2011	-7.41	-52.06
B10	07/11/2011	-8.01	-54.73	**B18**	07/11/2011	-8.36	-57.01	**B23**	07/11/2011	-7.65	-52.17
B10	21/11/2011	-8.08	-54.80	**B18**	21/11/2011	-8.53	-56.63	**B23**	21/11/2011	-7.14	-50.42
B10	05/12/2011	-8.05	-55.11	**B18**	05/12/2011	-8.28	-56.92	**B23**	05/12/2011	-7.06	-49.29
B10	19/12/2011	-8.15	-55.38	**B18**	19/12/2011	-8.06	-55.37	**B23**	19/12/2011	-7.36	-50.55
B10	03/01/2012	-8.01	-54.62	**B18**	03/01/2012	-8.24	-55.49	**B23**	03/01/2012	-7.37	-51.29
B10	16/01/2012	-8.0	-54.6	**B18**	16/01/2012	-7.75	-55.36	**B23**	16/01/2012	-7.3	-50.69
B10	30/01/2012	-7.8	-54.1	**B18**	30/01/2012	-7.93	-54.89	**B23**	30/01/2012	-7.47	-52.22
B10	13/02/2012	-8.21	-55.06	**B18**	13/02/2012	-8.13	-54.97	**B23**	13/02/2012	-7.49	-51.43
B10	27/02/2012	-8	-55.1	**B18**	27/02/2012	-8.18	-54.29	**B23**	27/02/2012	-7.75	-52.41
B10	12/03/2012	-8.1	-55.8	**B18**	12/03/2012	-8.18	-55.14	**B23**	12/03/2012	-7.46	-51.46
B10	26/03/2012	-8.2	-54.6	**B18**	26/03/2012	-8.47	-54.41	**B23**	26/03/2012	-7.1	-50.81
B10	10/04/2012	-8.6	-54.8	**B18**	10/04/2012	-7.93	-54.12	**B23**	10/04/2012	-6.76	-50.46
B10	23/04/2012	-8.4	-55.5	**B18**	23/04/2012	-8.24	-54.93	**B23**	23/04/2012	-7.57	-51.27
B10	09/05/2012	-8.4	-56.4	**B18**	09/05/2012	-8.27	-54.56	**B23**	09/05/2012	-7.6	-51.73
B10	21/05/2012	-8.2	-55	**B18**	21/05/2012	-8.15	-54.84	**B23**	21/05/2012	-6.88	-49.13
B10	04/06/2012	-8.4	-56.3	**B18**	04/06/2012	-8.22	-55.02	**B23**	04/06/2012	-7.18	-50.36
B10	18/06/2012	-8.1	-54.6	**B18**	18/06/2012	-8.14	-55.13	**B23**	18/06/2012	-6.69	-47.96
B10	02/07/2012	-8.02	-55.18	**B18**	02/07/2012	-8.29	-55.19	**B23**	02/07/2012	-6.49	-46.47
B10	16/07/2012	-7.96	-54.58	**B18**	16/07/2012	-8.25	-54.77	**B23**	16/07/2012	-6.34	-45.18
B10	30/07/2012	-8.01	-53.74	**B18**	30/07/2012	-8.22	-54.92	**B23**	30/07/2012	-6.39	-45.60
B10	13/08/2012	-7.99	-53.82	**B18**	13/08/2012	-8.19	-55.08	**B23**	13/08/2012	-6.38	-45.86
B10	27/08/2012	-8.08	-55.64	**B18**	27/08/2012	-8.14	-56.24	**B23**	27/08/2012	-6.31	-45.61
B10	10/09/2012	-8.04	-54.68	**B18**	10/09/2012	-8.25	-55.58	**B23**	10/09/2012	-6.39	-46.51
B10	24/09/2012	-8.16	-54.22	**B18**	24/09/2012	-8.29	-54.93	**B23**	24/09/2012	-6.11	-44.88
B10	08/10/2012	-7.93	-55.26	**B18**	08/10/2012	-8.25	-56.34	**B23**	08/10/2012	-6.49	-47.18
B10	22/10/2012	-7.91	-55.14	**B18**	22/10/2012	-8.30	-56.46	**B23**	22/10/2012	-6.84	-45.18
B10	05/11/2012	-8.09	-55.16	**B18**	05/11/2012	-8.28	-56.26	**B23**	05/11/2012	-6.68	-47.79
B11	14/02/2011	-8.75	-59.37	**B20**	14/02/2011	-8.52	-58.44	**B26**	14/02/2011	-8.95	-60.34
B11	28/02/2011	-8.81	-59.39	**B20**	28/02/2011	-8.59	-57.73	**B26**	28/02/2011	-8.56	-59.15
B11	14/03/2011	-8.78	-58.80	**B20**	14/03/2011	-8.67	-58.58	**B26**	14/03/2011	-8.94	-60.14
B11	28/03/2011	-8.69	-57.91	**B20**	28/03/2011	-8.72	-58.65	**B26**	28/03/2011	-8.57	-58.17
B11	11/04/2011	-8.86	-59.13	**B20**	11/04/2011	-8.79	-58.97	**B26**	11/04/2011	-9.01	-60.47
B11	26/04/2011	-8.80	-59.03	**B20**	26/04/2011	-8.70	-59.13	**B26**	26/04/2011	-8.77	-59.26
B11	09/05/2011	-8.45	-58.60	**B20**	09/05/2011	-8.65	-58.33	**B26**	09/05/2011	-8.70	-58.19
B11	23/05/2011	-8.56	-58.34	**B20**	23/05/2011	-8.69	-58.30	**B26**	23/05/2011	-8.23	-55.73
B11	06/06/2011	-8.61	-58.06	**B20**	06/06/2011	-8.63	-57.93	**B26**	06/06/2011	-7.94	-55.06
B11	20/06/2011	-8.30	-55.49	**B20**	20/06/2011	-8.62	-57.71	**B26**	20/06/2011	-7.81	-53.85
B11	04/07/2011	-8.52	-57.02	**B20**	04/07/2011	-8.37	-56.04	**B26**	04/07/2011	-7.86	-53.53
B11	18/07/2011	-8.37	-56.67	**B20**	18/07/2011	-8.34	-56.52	**B26**	18/07/2011	-7.73	-54.82
B11	16/08/2011	-8.02	-56.13	**B20**	16/08/2011	-8.16	-55.53	**B26**	16/08/2011	-7.53	-52.54
B11	29/08/2011	-8.01	-54.89	**B20**	29/08/2011	-7.87	-54.44	**B26**	29/08/2011	-7.59	-52.87
B11	12/09/2011	-7.37	-52.03	**B20**	12/09/2011	-8.13	-55.80	**B26**	12/09/2011	-7.68	-52.77
B11	26/09/2011	-7.21	-49.98	**B20**	26/09/2011	-8.10	-55.16	**B26**	26/09/2011	-7.29	-50.22
B11	10/10/2011	-7.45	-51.29	**B20**	10/10/2011	-7.93	-54.36	**B26**	10/10/2011	-7.25	-50.02
B11	24/10/2011	-7.11	-50.54	**B20**	24/10/2011	-7.72	-54.37	**B26**	24/10/2011	-6.99	-50.54
B11	07/11/2011	-7.40	-51.20	**B20**	07/11/2011	-7.66	-52.66	**B26**	07/11/2011	-7.54	-51.51
B11	21/11/2011	-7.90	-53.75	**B20**	21/11/2011	-7.41	-51.83	**B26**	21/11/2011	-7.69	-50.63
B11	05/12/2011	-7.43	-50.35	**B20**	05/12/2011	-7.33	-51.13	**B26**	05/12/2011	-8.02	-52.23
B11	19/12/2011	-7.61	-50.66	**B20**	19/12/2011	-7.36	-50.84	**B26**	19/12/2011	-8.18	-53.80
B11	03/01/2012	-8.18	-54.08	**B20**	03/01/2012	-7.53	-51.61	**B26**	03/01/2012	-8.38	-55.58
B11	16/01/2012	-8.2	-55.2	**B20**	16/01/2012	-7.73	-52.32	**B26**	16/01/2012	-8.59	-56.72
B11	30/01/2012	-8.2	-54.9	**B20**	30/01/2012	-7.68	-53.13	**B26**	30/01/2012	-8.24	-56.8
B11	13/02/2012	-8.5	-55.6	**B20**	13/02/2012	-8.17	-54.72	**B26**	27/02/2012	-8.5	-57.86
B11	27/02/2012	-8.6	-56.6	**B20**	27/02/2012	-8.27	-55.11	**B26**	12/03/2012	-8.6	-57.87
B11	12/03/2012	-8.5	-56.5	**B20**	12/03/2012	-8.19	-55.17	**B26**	26/03/2012	-8.48	-58.1
B11	26/03/2012	-8.5	-57.1	**B20**	26/03/2012	-8.34	-56.17	**B26**	10/04/2012	-8.42	-56.28
B11	10/04/2012	-8	-56.2	**B20**	10/04/2012	-8.15	-56.15	**B26**	23/04/2012	-8.41	-56.41
B11	23/04/2012	-8.3	-55.1	**B20**	23/04/2012	-8.49	-56.03	**B26**	09/05/2012	-8.64	-57.45
B11	09/05/2012	-8.5	-56.9	**B20**	09/05/2012	-8.52	-56.36	**B26**	05/06/2012	-8.58	-58.39
B11	21/05/2012	-8.4	-56.4	**B20**	21/05/2012	-8.47	-56.96	**B26**	18/06/2012	-8.45	-57.1
B11	04/06/2012	-8.6	-57.2	**B20**	04/06/2012	-8.46	-56.53	**B26**	02/07/2012	-8.44	-56.17
B11	18/06/2012	-8.4	-56.8	**B20**	18/06/2012	-8.37	-55.95	**B26**	16/07/2012	-8.31	-56.32
B11	02/07/2012	-8.21	-55.16	**B20**	02/07/2012	-8.36	-56.91	**B26**	30/07/2012	-8.36	-56.45
B11	16/07/2012	-8.30	-56.70	**B20**	16/07/2012	-8.43	-56.89	**B26**	13/08/2012	-8.20	-55.65
B11	30/07/2012	-8.00	-53.54	**B20**	30/07/2012	-8.28	-55.95	**B26**	27/08/2012	-7.99	-54.92
B11	13/08/2012	-8.28	-55.97	**B20**	13/08/2012	-8.20	-55.63	**B26**	10/09/2012	-7.90	-55.14
B11	27/08/2012	-8.16	-56.29	**B20**	27/08/2012	-7.87	-55.57	**B26**	24/09/2012	-8.09	-53.24
B11	10/09/2012	-8.26	-54.84	**B20**	10/09/2012	-8.03	-54.58	**B26**	08/10/2012	-7.56	-50.48
B11	24/09/2012	-8.21	-54.57	**B20**	24/09/2012	-8.16	-54.10	**B26**	22/10/2012	-7.67	-51.39
B11	08/10/2012	-7.98	-54.74	**B20**	08/10/2012	-7.93	-54.22	**B26**	05/11/2012	-7.67	-52.83
B11	22/10/2012	-8.24	-54.91	**B20**	22/10/2012	-7.63	-51.75				
B11	05/11/2012	-8.04	-54.78	**B20**	05/11/2012	-7.71	-52.84				

Sample ID	Date	$\delta^{18}O$	$\delta^{2}H$	Sample ID	Date	$\delta^{18}O$	$\delta^{2}H$	Sample ID	Date	$\delta^{18}O$	$\delta^{2}H$
B27	14/02/2011	-7.39	-51.70	**B33**	14/02/2011	-8.66	-57.58	**B50**	14/02/2011	-7.62	-53.89
B27	28/02/2011	-7.19	-50.46	**B33**	28/02/2011	-8.46	-58.23	**B50**	14/03/2011	-8.57	-58.69
B27	14/03/2011	-7.17	-51.07	**B33**	14/03/2011	-8.59	-58.63	**B50**	28/03/2011	-8.80	-58.81
B27	28/03/2011	-7.11	-50.86	**B33**	28/03/2011	-8.81	-58.34	**B50**	11/04/2011	-8.75	-59.03
B27	11/04/2011	-7.13	-51.22	**B33**	11/04/2011	-8.69	-58.35	**B50**	26/04/2011	-8.44	-57.93
B27	26/04/2011	-6.99	-50.61	**B33**	26/04/2011	-8.56	-58.71	**B50**	09/05/2011	-7.96	-54.69
B27	09/05/2011	-6.96	-49.67	**B33**	09/05/2011	-8.55	-57.88	**B50**	23/05/2011	-8.08	-54.99
B27	23/05/2011	-6.95	-49.75	**B33**	23/05/2011	-8.23	-56.27	**B50**	06/06/2011	-7.91	-55.51
B27	06/06/2011	-7.12	-50.59	**B33**	06/06/2011	-7.79	-54.81	**B50**	20/06/2011	-7.87	-54.44
B27	20/06/2011	-7.05	-50.58	**B33**	20/06/2011	-7.86	-54.46	**B50**	04/07/2011	-7.71	-53.11
B27	04/07/2011	-7.04	-49.52	**B33**	04/07/2011	-7.70	-53.32	**B50**	18/07/2011	-7.66	-53.28
B27	18/07/2011	-7.07	-50.78	**B33**	18/07/2011	-7.63	-52.50	**B50**	16/08/2011	-7.77	-53.24
B27	16/08/2011	-7.41	-52.54	**B33**	16/08/2011	-7.83	-52.72	**B50**	29/08/2011	-7.34	-51.48
B27	29/08/2011	-7.41	-51.91	**B33**	29/08/2011	-7.71	-53.13	**B50**	12/09/2011	-6.94	-51.03
B27	12/09/2011	-6.87	-49.96	**B33**	12/09/2011	-7.37	-52.09	**B50**	26/09/2011	-7.35	-51.03
B27	26/09/2011	-6.65	-48.97	**B33**	26/09/2011	-7.18	-50.11	**B50**	10/10/2011	-7.20	-51.77
B27	10/10/2011	-6.30	-47.54	**B33**	10/10/2011	-7.00	-50.14	**B50**	24/10/2011	-7.20	-52.05
B27	24/10/2011	-6.33	-47.54	**B33**	24/10/2011	-7.12	-50.95	**B50**	07/11/2011	-7.45	-50.11
B27	07/11/2011	-6.73	-48.49	**B33**	07/11/2011	-7.31	-51.30	**B50**	21/11/2011	-7.83	-52.01
B27	21/11/2011	-6.69	-48.75	**B33**	21/11/2011	-7.38	-51.00	**B50**	05/12/2011	-7.60	-51.25
B27	05/12/2011	-7.03	-50.29	**B33**	05/12/2011	-7.88	-51.73	**B50**	19/12/2011	-8.02	-53.35
B27	19/12/2011	-7.40	-51.41	**B33**	19/12/2011	-7.96	-53.46	**B50**	03/01/2012	-8.51	-55.56
B27	03/01/2012	-7.14	-51.50	**B33**	03/01/2012	-8.22	-55.44	**B50**	16/01/2012	-8.17	-55.4
B27	16/01/2012	-7.34	-51.2	**B33**	16/01/2012	-8.35	-55.8	**B50**	30/01/2012	-8.19	-55.3
B27	30/01/2012	-7.01	-50.2	**B33**	30/01/2012	-8.29	-55.5	**B50**	27/02/2012	-8.38	-56.3
B27	13/02/2012	-7.55	-52.1	**B33**	13/02/2012	-8.55	-56.1	**B50**	12/03/2012	-8.23	-55.4
B27	27/02/2012	-7.76	-52	**B33**	27/02/2012	-8.55	-57	**B50**	26/03/2012	-8.27	-56.1
B27	12/03/2012	-7.58	-53.5	**B33**	12/03/2012	-8.41	-57	**B50**	23/04/2012	-8.5	-57.3
B27	26/03/2012	-7.76	-53.4	**B33**	26/03/2012	-8.53	-57.4	**B50**	09/05/2012	-8.19	-53.9
B27	10/04/2012	-7.96	-52.6	**B33**	10/04/2012	-8.9	-56.9	**B50**	05/06/2012	-8.52	-55.5
B27	23/04/2012	-8.1	-54.7	**B33**	23/04/2012	-8.64	-57.2	**B50**	18/06/2012	-8.19	-55.2
B27	09/05/2012	-8.17	-54.5	**B33**	09/05/2012	-8.7	-58.4	**B50**	02/07/2012	-8.05	-54.76
B27	21/05/2012	-8.08	-54.4	**B33**	21/05/2012	-8.51	-57.4	**B50**	16/07/2012	-7.66	-53.16
B27	04/06/2012	-8.23	-54.9	**B33**	04/06/2012	-8.36	-56.2	**B50**	30/07/2012	-7.68	-52.66
B27	18/06/2012	-8.07	-54.2	**B33**	18/06/2012	-8.33	-55.8	**B50**	13/08/2012	-7.75	-53.06
B27	02/07/2012	-8.26	-55.48	**B33**	02/07/2012	-8.20	-55.84	**B50**	27/08/2012	-7.53	-52.12
B27	16/07/2012	-8.19	-54.69	**B33**	16/07/2012	-8.15	-56.23	**B50**	10/09/2012	-7.56	-51.27
B27	30/07/2012	-8.01	-54.46	**B33**	30/07/2012	-7.94	-54.58	**B50**	24/09/2012	-7.24	-51.70
B27	13/08/2012	-8.16	-55.45	**B33**	13/08/2012	-7.96	-53.83	**B50**	08/10/2012	-7.54	-51.54
B27	27/08/2012	-7.96	-55.91	**B33**	27/08/2012	-7.88	-52.55	**B50**	22/10/2012	-7.74	-51.45
B27	10/09/2012	-8.01	-54.73	**B33**	10/09/2012	-7.71	-52.84	**B50**	05/11/2012	-7.73	-53.07
B27	24/09/2012	-8.04	-54.92	**B33**	24/09/2012	-7.09	-49.89	**B56**	14/02/2011	-7.16	-51.27
B27	08/10/2012	-8.13	-55.12	**B33**	08/10/2012	-7.35	-49.69	**B56**	28/02/2011	-7.51	-53.23
B27	22/10/2012	-8.57	-54.22	**B33**	22/10/2012	-7.37	-50.76	**B56**	14/03/2011	-8.09	-56.33
B27	05/11/2012	-8.30	-56.57	**B33**	05/11/2012	-7.39	-50.82	**B56**	28/03/2011	-8.43	-56.32
B29	14/02/2011	-5.94	-45.56	**B39**	14/02/2011	-8.53	-57.39	**B56**	11/04/2011	-7.77	-53.55
B29	28/02/2011	-6.18	-45.58	**B39**	28/02/2011	-8.78	-58.40	**B56**	26/04/2011	-8.08	-55.82
B29	14/03/2011	-5.94	-46.05	**B39**	14/03/2011	-8.69	-58.53	**B56**	09/05/2011	-7.85	-54.55
B29	28/03/2011	-6.11	-45.65	**B39**	28/03/2011	-8.58	-58.73	**B56**	23/05/2011	-7.62	-52.91
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B29	26/04/2011	-6.15	-46.66	**B39**	26/04/2011	-8.61	-58.56	**B56**	20/06/2011	-8.23	-55.38
B29	09/05/2011	-6.17	-45.97	**B39**	09/05/2011	-8.69	-58.07	**B56**	04/07/2011	-7.84	-53.07
B29	23/05/2011	-6.13	-46.10	**B39**	23/05/2011	-8.78	-59.02	**B56**	18/07/2011	-7.64	-52.79
B29	06/06/2011	-6.19	-45.68	**B39**	06/06/2011	-8.78	-58.64	**B56**	16/08/2011	-7.95	-53.60
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B29	29/08/2011	-6.18	-45.97	**B39**	29/08/2011	-8.16	-55.73	**B56**	24/10/2011	-7.38	-51.20
B29	12/09/2011	-6.29	-46.99	**B39**	12/09/2011	-8.02	-54.18	**B56**	07/11/2011	-7.30	-48.73
B29	26/09/2011	-6.34	-47.12	**B39**	26/09/2011	-7.68	-52.37	**B56**	21/11/2011	-7.59	-51.92
B29	10/10/2011	-6.24	-47.13	**B39**	10/10/2011	-7.31	-50.40	**B56**	05/12/2011	-7.47	-50.93
B29	24/10/2011	-6.18	-47.03	**B39**	24/10/2011	-7.38	-51.24	**B56**	19/12/2011	-7.77	-52.63
B29	07/11/2011	-6.06	-46.54	**B39**	07/11/2011	-7.21	-51.00	**B56**	03/01/2012	-8.20	-54.35
B29	21/11/2011	-5.98	-45.42	**B39**	21/11/2011	-7.15	-50.98	**B56**	16/01/2012	-7.94	-53.6
B29	05/12/2011	-5.87	-45.03	**B39**	05/12/2011	-7.37	-49.71	**B56**	30/01/2012	-7.79	-53
B29	19/12/2011	-6.00	-44.94	**B39**	19/12/2011	-7.48	-50.53	**B56**	13/02/2012	-7.83	-52.8
B29	03/01/2012	-5.81	-45.43	**B39**	03/01/2012	-8.02	-51.52	**B56**	27/02/2012	-8.24	-54.9
B29	16/01/2012	-5.83	-45.1	**B39**	16/01/2012	-8.35	-53.2	**B56**	12/03/2012	-7.56	-52.5
B29	30/01/2012	-5.95	-45	**B39**	30/01/2012	-7.81	-52.7	**B56**	26/03/2012	-7.77	-52.7
B29	13/02/2012	-5.93	-43.5	**B39**	13/02/2012	-8.18	-53.1	**B56**	10/04/2012	-8.23	-54.8
B29	27/02/2012	-5.81	-44.1	**B39**	27/02/2012	-8.23	-54.6	**B56**	23/04/2012	-8.23	-55.1
B29	12/03/2012	-5.75	-44.1	**B39**	12/03/2012	-8.2	-55.4	**B56**	09/05/2012	-8.54	-57
B29	26/03/2012	-5.65	-44.7	**B39**	26/03/2012	-8.26	-55.8	**B56**	21/05/2012	-8.3	-56.4
B29	10/04/2012	-5.64	-43.7	**B39**	10/04/2012	-8.64	-55.4	**B56**	05/06/2012	-8.46	-56.7
B29	23/04/2012	-5.67	-44	**B39**	23/04/2012	-8.56	-56.3	**B56**	18/06/2012	-8.24	-55.4
B29	09/05/2012	-5.82	-44.2	**B39**	09/05/2012	-8.48	-56.9	**B56**	02/07/2012	-8.23	-55.44
B29	21/05/2012	-5.63	-44.1	**B39**	21/05/2012	-8.48	-57.3	**B56**	16/07/2012	-7.89	-52.78
B29	04/06/2012	-5.96	-45.1	**B39**	05/06/2012	-8.52	-56.7	**B56**	30/07/2012	-7.63	-53.29
B29	18/06/2012	-5.78	-44	**B39**	18/06/2012	-8.44	-56.5	**B56**	13/08/2012	-7.66	-53.99
B29	02/07/2012	-5.72	-45.24	**B39**	02/07/2012	-8.44	-56.69	**B56**	27/08/2012	-7.97	-55.22
B29	16/07/2012	-5.74	-42.54	**B39**	16/07/2012	-8.40	-55.53	**B56**	10/09/2012	-7.60	-52.21
B29	30/07/2012	-5.65	-43.19	**B39**	30/07/2012	-8.37	-56.02	**B56**	24/09/2012	-7.69	-52.45
B29	13/08/2012	-5.63	-44.51	**B39**	13/08/2012	-8.53	-57.09	**B56**	08/10/2012	-7.42	-51.98
B29	27/08/2012	-5.55	-42.82	**B39**	27/08/2012	-8.31	-55.90	**B56**	22/10/2012	-7.63	-52.21
B29	10/09/2012	-5.53	-43.71	**B39**	10/09/2012	-8.29	-55.34	**B56**	05/11/2012	-7.54	-51.31
B29	24/09/2012	-5.50	-43.05	**B39**	24/09/2012	-8.04	-53.04				
B29	08/10/2012	-5.80	-44.76	**B39**	08/10/2012	-7.62	-52.73				
B29	22/10/2012	-5.31	-42.81	**B39**	22/10/2012	-7.21	-50.51				
B29	05/11/2012	-5.35	-43.51	**B39**	05/11/2012	-7.44	-51.04				

Sample ID	Date	$\delta^{18}O$	$\delta^{2}H$	Sample ID	Date	$\delta^{18}O$	$\delta^{2}H$	Sample ID	Date	$\delta^{18}O$	$\delta^{2}H$
B65	14/02/2011	-3.30	-32.41	**B71**	28/02/2011	-7.40	-52.94	**Cognet**	14/02/2011	-7.02	-50.11
B65	28/02/2011	-3.05	-32.82	**B71**	14/03/2011	-6.98	-51.33	**Cognet**	28/02/2011	-7.05	-50.75
B65	14/03/2011	-3.44	-33.50	**B71**	28/03/2011	-7.61	-53.55	**Cognet**	14/03/2011	-6.98	-50.52
B65	28/03/2011	-3.58	-34.92	**B71**	11/04/2011	-7.35	-52.30	**Cognet**	28/03/2011	-6.93	-50.33
B65	11/04/2011	-3.48	-32.47	**B71**	26/04/2011	-7.47	-52.67	**Cognet**	11/04/2011	-6.99	-49.83
B65	26/04/2011	-3.25	-33.38	**B71**	09/05/2011	-8.14	-56.21	**Cognet**	26/04/2011	-7.05	-50.46
B65	09/05/2011	-3.17	-32.42	**B71**	23/05/2011	-8.13	-54.96	**Cognet**	09/05/2011	-6.92	-50.59
B65	23/05/2011	-3.45	-33.06	**B71**	06/06/2011	-8.10	-55.44	**Cognet**	23/05/2011	-7.00	-50.06
B65	06/06/2011	-3.25	-33.65	**B71**	20/06/2011	-7.35	-49.76	**Cognet**	06/06/2011	-6.89	-50.71
B65	20/06/2011	-3.27	-32.76	**B71**	04/07/2011	-8.11	-54.78	**Cognet**	20/06/2011	-7.09	-50.19
B65	04/07/2011	-3.26	-31.23	**B71**	18/07/2011	-8.14	-56.03	**Cognet**	04/07/2011	-7.21	-50.47
B65	18/07/2011	-3.18	-30.73	**B71**	16/08/2011	-8.29	-55.46	**Cognet**	18/07/2011	-6.89	-49.61
B65	16/08/2011	-2.69	-30.40	**B71**	29/08/2011	-8.29	-55.55	**Cognet**	16/08/2011	-6.69	-50.79
B65	29/08/2011	-2.66	-29.48	**B71**	12/09/2011	-8.24	-55.45	**Cognet**	29/08/2011	-7.07	-50.01
B65	12/09/2011	-2.47	-29.32	**B71**	26/09/2011	-8.28	-55.76	**Cognet**	12/09/2011	-6.88	-49.34
B65	26/09/2011	-2.76	-29.60	**B71**	10/10/2011	-8.22	-55.33	**Cognet**	26/09/2011	-7.09	-49.92
B65	10/10/2011	-2.43	-29.54	**B71**	24/10/2011	-8.31	-56.02	**Cognet**	10/10/2011	-7.02	-50.29
B65	24/10/2011	-2.51	-29.47	**B71**	07/11/2011	-7.29	-51.22	**Cognet**	24/10/2011	-7.00	-50.30
B65	07/11/2011	-4.85	-39.50	**B71**	21/11/2011	-7.51	-52.23	**Cognet**	07/11/2011	-6.95	-50.65
B65	21/11/2011	-3.98	-35.39	**B71**	05/12/2011	-8.16	-55.78	**Cognet**	21/11/2011	-7.10	-50.81
B65	05/12/2011	-3.63	-34.23	**B71**	19/12/2011	-8.26	-55.00	**Cognet**	05/12/2011	-7.06	-50.65
B65	19/12/2011	-4.37	-37.11	**B71**	03/01/2012	-8.19	-55.56	**Cognet**	19/12/2011	-7.09	-50.24
B65	03/01/2012	-5.85	-43.18	**B71**	16/01/2012	-8.07	-55.5	**Cognet**	03/01/2012	-7.42	-50.25
B65	16/01/2012	-5.83	-43.3	**B71**	30/01/2012	-8.09	-55.1	**Cognet**	16/01/2012	-7.03	-50.9
B65	30/01/2012	-4.33	-38.3	**B71**	27/02/2012	-8.06	-54.7	**Cognet**	30/01/2012	-6.93	-50.3
B65	13/02/2012	-4.75	-37.6	**B71**	12/03/2012	-7.08	-50.8	**Cognet**	13/02/2012	-7.24	-49.9
B65	27/02/2012	-4.19	-36.6	**B71**	26/03/2012	-8	-54.9	**Cognet**	27/02/2012	-7.27	-50.8
B65	12/03/2012	-3.85	-35.2	**B71**	10/04/2012	-7.82	-54.5	**Cognet**	12/03/2012	-7.16	-50.5
B65	26/03/2012	-3.84	-35.4	**B71**	23/04/2012	-8.21	-55.3	**Cognet**	26/03/2012	-7.53	-50.4
B65	10/04/2012	-3.51	-33.73	**B71**	09/05/2012	-8.37	-57	**Cognet**	10/04/2012	-7.07	-50.5
B65	23/04/2012	-4.21	-36.3	**B71**	05/06/2012	-8.28	-55.8	**Cognet**	23/04/2012	-6.97	-50.6
B65	09/05/2012	-5.33	-42	**B71**	18/06/2012	-8.14	-55.4	**Cognet**	09/05/2012	-7.2	-50.8
B65	21/05/2012	-4.81	-39.5	**B71**	02/07/2012	-8.22	-55.12	**Cognet**	21/05/2012	-7.02	-50.5
B65	05/06/2012	-5.81	-44.1	**B71**	16/07/2012	-8.08	-55.11	**Cognet**	05/06/2012	-6.93	-49
B65	18/06/2012	-5.02	-40.5	**B71**	30/07/2012	-8.20	-56.09	**Cognet**	18/06/2012	-6.96	-50.5
B65	02/07/2012	-4.14	-38.51	**B71**	13/08/2012	-7.96	-53.22	**Cognet**	02/07/2012	-7.02	-50.98
B65	16/07/2012	-3.85	-35.41	**B71**	27/08/2012	-8.08	-55.53	**Cognet**	16/07/2012	-6.81	-49.58
B65	30/07/2012	-3.63	-34.00	**B71**	10/09/2012	-8.11	-55.49	**Cognet**	30/07/2012	-6.97	-49.82
B65	13/08/2012	-3.25	-32.31	**B71**	24/09/2012	-8.14	-55.21	**Cognet**	13/08/2012	-7.01	-50.75
B65	27/08/2012	-3.80	-35.81	**B71**	08/10/2012	-8.20	-56.40	**Cognet**	27/08/2012	-7.03	-50.69
B65	10/09/2012	-3.15	-31.98	**B71**	22/10/2012	-8.22	-55.40	**Cognet**	10/09/2012	-6.95	-51.23
B65	24/09/2012	-3.03	-31.67	**B71**	05/11/2012	-8.28	-55.22	**Cognet**	24/09/2012	-7.13	-52.04
B65	08/10/2012	-2.69	-31.50	**Allier**	14/02/2011	-8.61	-59.10	**Cognet**	08/10/2012	-6.91	-50.60
B65	22/10/2012	-2.62	-30.20	**Allier**	28/02/2011	-8.55	-58.78	**Cognet**	22/10/2012	-7.14	-51.29
B65	05/11/2012	-2.58	-31.07	**Allier**	14/03/2011	-9.41	-65.74	**Cognet**	05/11/2012	-7.09	-50.56
B66	14/02/2011	-8.49	-57.07	**Allier**	28/03/2011	-8.75	-58.20	**Jallat**	14/02/2011	-6.50	-47.14
B66	28/02/2011	-8.37	-56.00	**Allier**	11/04/2011	-8.48	-56.50	**Jallat**	28/02/2011	-6.54	-48.59
B66	14/03/2011	-8.03	-56.44	**Allier**	26/04/2011	-8.36	-57.38	**Jallat**	14/03/2011	-6.74	-48.30
B66	28/03/2011	-8.42	-57.05	**Allier**	09/05/2011	-8.01	-54.24	**Jallat**	28/03/2011	-6.61	-47.63
B66	11/04/2011	-8.05	-56.53	**Allier**	23/05/2011	-7.91	-54.24	**Jallat**	26/04/2011	-6.49	-47.44
B66	26/04/2011	-8.34	-57.12	**Allier**	06/06/2011	-7.81	-54.35	**Jallat**	09/05/2011	-6.41	-47.62
B66	09/05/2011	-8.44	-56.85	**Allier**	20/06/2011	-7.78	-54.01	**Jallat**	23/05/2011	-6.71	-49.66
B66	23/05/2011	-8.19	-55.93	**Allier**	04/07/2011	-7.52	-52.84	**Jallat**	06/06/2011	-6.55	-47.28
B66	06/06/2011	-8.07	-55.15	**Allier**	18/07/2011	-7.71	-53.04	**Jallat**	20/06/2011	-6.65	-47.70
B66	20/06/2011	-7.91	-54.49	**Allier**	16/08/2011	-7.23	-51.30	**Jallat**	04/07/2011	-6.63	-47.87
B66	04/07/2011	-7.81	-53.79	**Allier**	29/08/2011	-7.08	-49.52	**Jallat**	18/07/2011	-6.52	-47.68
B66	18/07/2011	-7.94	-54.71	**Allier**	12/09/2011	-6.98	-50.16	**Jallat**	16/08/2011	-6.38	-47.27
B66	16/08/2011	-7.81	-53.12	**Allier**	26/09/2011	-7.15	-49.73	**Jallat**	29/08/2011	-6.58	-47.36
B66	29/08/2011	-7.49	-52.45	**Allier**	10/10/2011	-7.06	-49.78	**Jallat**	12/09/2011	-6.44	-47.11
B66	12/09/2011	-7.52	-51.92	**Allier**	24/10/2011	-7.21	-51.62	**Jallat**	26/09/2011	-6.68	-47.23
B66	26/09/2011	-7.10	-50.25	**Allier**	07/11/2011	-8.25	-52.96	**Jallat**	10/10/2011	-6.56	-47.73
B66	10/10/2011	-7.14	-49.90	**Allier**	21/11/2011	-8.17	-54.25	**Jallat**	24/10/2011	-6.63	-46.53
B66	24/10/2011	-7.19	-50.94	**Allier**	05/12/2011	-8.38	-55.23	**Jallat**	07/11/2011	-6.52	-47.17
B66	07/11/2011	-7.45	-51.78	**Allier**	19/12/2011	-8.50	-57.08	**Jallat**	21/11/2011	-6.66	-47.69
B66	21/11/2011	-7.55	-50.96	**Allier**	03/01/2012	-8.86	-60.44	**Jallat**	05/12/2011	-6.51	-47.42
B66	05/12/2011	-7.63	-50.76	**Allier**	16/01/2012	-8.64	-57.4	**Jallat**	19/12/2011	-6.65	-47.49
B66	19/12/2011	-7.76	-52.27	**Allier**	30/01/2012	-8.25	-57.2	**Jallat**	03/01/2012	-6.69	-47.31
B66	03/01/2012	-7.90	-53.50	**Allier**	13/02/2012	-8.73	-59	**Jallat**	16/01/2012	-6.71	-47.57
B66	16/01/2012	-7.98	-53.8	**Allier**	27/02/2012	-8.74	-58.2	**Jallat**	30/01/2012	-6.36	-47.65
B66	30/01/2012	-7.8	-53.7	**Allier**	12/03/2012	-8.52	-57.1	**Jallat**	13/02/2012	-6.54	-47.27
B66	27/02/2012	-8.27	-55.4	**Allier**	26/03/2012	-8.37	-56.7	**Jallat**	27/02/2012	-6.54	-47.61
B66	12/03/2012	-8.08	-55.2	**Allier**	10/04/2012	-8.24	-55.1	**Jallat**	12/03/2012	-6.48	-46.97
B66	26/03/2012	-8.25	-55.4	**Allier**	23/04/2012	-8.78	-57.9	**Jallat**	26/03/2012	-7.17	-47.27
B66	10/04/2012	-8.26	-55.9	**Allier**	09/05/2012	-8.49	-58.1	**Jallat**	10/04/2012	-7.06	-46.96
B66	23/04/2012	-8.14	-55.9	**Allier**	21/05/2012	-8.08	-54.9	**Jallat**	23/04/2012	-6.64	-47.32
B66	09/05/2012	-8.47	-56.7	**Allier**	04/06/2012	-8.32	-55.9	**Jallat**	09/05/2012	-6.74	-48.3
B66	21/05/2012	-8.48	-56.6	**Allier**	18/06/2012	-8.35	-56.3	**Jallat**	21/05/2012	-6.63	-48.1
B66	05/06/2012	-8.58	-57.6	**Allier**	02/07/2012	-7.74	-53.15	**Jallat**	05/06/2012	-7.03	-49.12
B66	18/06/2012	-8.28	-56	**Allier**	16/07/2012	-7.98	-55.08	**Jallat**	18/06/2012	-6.82	-47.88
B66	02/07/2012	-8.20	-56.19	**Allier**	30/07/2012	-7.55	-52.07	**Jallat**	02/07/2012	-6.54	-47.97
B66	16/07/2012	-8.17	-55.92	**Allier**	13/08/2012	-7.68	-51.19	**Jallat**	16/07/2012	-6.63	-48.82
B66	30/07/2012	-7.90	-53.27	**Allier**	27/08/2012	-6.85	-48.67	**Jallat**	30/07/2012	-6.47	-46.81
B66	13/08/2012	-7.98	-54.30	**Allier**	10/09/2012	-7.27	-50.21	**Jallat**	13/08/2012	-6.73	-48.33
B66	27/08/2012	-7.73	-52.80	**Allier**	24/09/2012	-7.26	-49.41	**Jallat**	27/08/2012	-6.54	-49.60
B66	10/09/2012	-7.33	-50.18	**Allier**	08/10/2012	-7.70	-52.29	**Jallat**	10/09/2012	-6.51	-48.11
B66	24/09/2012	-7.29	-49.15	**Allier**	22/10/2012	-7.50	-51.32	**Jallat**	24/09/2012	-6.64	-48.48
B66	08/10/2012	-7.20	-50.07	**Allier**	05/11/2012	-7.91	-52.80	**Jallat**	08/10/2012	-6.64	-48.70
B66	22/10/2012	-7.40	-50.84					**Jallat**	22/10/2012	-7.05	-46.97
B66	05/11/2012	-7.56	-53.05					**Jallat**	05/11/2012	-6.67	-48.79

Sample ID	**Date**	**$\delta^{18}O$**	**$\delta^{2}H$**	Sample ID	Date	**$\delta^{18}O$**	**$\delta^{2}H$**
P13	14/02/2011	-6.69	-48.01	Rainfall	14-21/2/11	-7.74	-66.37
P13	28/02/2011	-6.39	-47.63	Rainfall	21-28/2/11	-5.27	-43.25
P13	14/03/2011	-6.26	-47.05	Rainfall	7-14/3/11	-17.51	-133.64
P13	28/03/2011	-6.13	-46.10	Rainfall	14-21/3/11	-9.74	-75.19
P13	11/04/2011	-6.21	-46.55	Rainfall	21-28/3/11	-5.76	-47.46
P13	26/04/2011	-6.43	-47.89	Rainfall	28/3-4/4/11	-3.59	-26.40
P13	09/05/2011	-6.35	-47.47	Rainfall	26/4-9/5/11	-8.44	-63.52
P13	23/05/2011	-6.47	-48.78	Rainfall	2/5-9/5/11	-6.92	-47.90
P13	06/06/2011	-6.31	-47.82	Rainfall	16-23/5/11	-2.78	-25.33
P13	20/06/2011	-6.72	-48.47	Rainfall	31/5-6/6/11	-2.31	-15.99
P13	04/07/2011	-5.89	-45.79	Rainfall	06/06/2011	-3.33	-23.36
P13	18/07/2011	-6.26	-46.78	Rainfall	6-20/6/11	-4.42	-33.19
P13	16/08/2011	-5.78	-44.64	Rainfall	4-18/7/11	-5.02	-36.15
P13	29/08/2011	-6.35	-47.33	Rainfall	22-29/8/11	-4.99	-30.63
P13	12/09/2011	-5.91	-44.91	Rainfall	29/8-5/9/11	-4.88	-33.57
P13	26/09/2011	-6.10	-46.00	Rainfall	12-19/09/11	-3.77	-25.75
P13	10/10/2011	-5.92	-45.47	Rainfall	3-10/10/11	-2.37	-12.42
P13	24/10/2011	-5.93	-45.43	Rainfall	17-24/10/11	-10.34	-70.92
P13	07/11/2011	-6.49	-46.92	Rainfall	24-31/10/11	-10.41	-78.25
P13	21/11/2011	-6.20	-46.92	Rainfall	31/10-7/11/11	-8.56	-59.60
P13	05/12/2011	-6.30	-47.30	Rainfall	7-14/11/11	-5.27	-37.68
P13	19/12/2011	-6.05	-46.08	Rainfall	28/11-5/12/11	-9.77	-74.99
P13	03/01/2012	-6.24	-45.50	Rainfall	5-12/12/11	-7.63	-56.55
P13	16/01/2012	-6	-46.28	Rainfall	19/12-3/1/12	-9.15	-68.57
P13	30/01/2012	-6.13	-45.93	Rainfall	3-10/01/12	-4.2	-35.21
P13	13/02/2012	-6.24	-46.78	Rainfall	13/02/2012	-16.93	-126.07
P13	27/02/2012	-6.18	-45.99	Rainfall	20-27/02/12	-6.81	-51.71
P13	12/03/2012	-6.22	-46.55	Rainfall	5-12/03/12	-4.64	-42.04
P13	26/03/2012	-6.78	-45.81	Rainfall	12-26/03/12	-6.55	-50.76
P13	10/04/2012	-6.4	-46.37	Rainfall	19-26/03/12	-2.94	-22.27
P13	23/04/2012	-6.17	-45.51	Rainfall	26/3-3/4/12	-9.42	-70.99
P13	09/05/2012	-6.02	-46.56	Rainfall	3-10/04/12	-4.83	-30.51
P13	21/05/2012	-6.48	-47.62	Rainfall	23-30/04/12	-6.97	-53.48
P13	04/06/2012	-6.18	-45.23	Rainfall	30/04-07/05/12	-6.25	-52.69
P13	18/06/2012	-6.73	-48.19	Rainfall	9-15/05/12	-3.97	-24.12
P13	02/07/2012	-5.79	-45.79	Rainfall	15-22/05/12	-5.94	-44.25
P13	16/07/2012	-6.42	-46.96	Rainfall	22-29/05/12	-4.3	-24.71
P13	30/07/2012	-6.46	-47.19	Rainfall	29/5-4/6/12	-3.89	-24.69
P13	13/08/2012	-6.38	-46.72	Rainfall	4-11/06/12	-5.95	-49.35
P13	27/08/2012	-6.50	-47.59	Rainfall	11-18/06/12	-6.08	-49.81
P13	10/09/2012	-6.48	-47.22	Rainfall	9-16/7/12	-5.35	-35.05
P13	24/09/2012	-6.62	-48.72	Rainfall	23-30/7/12	-1.86	-8.20
P13	08/10/2012	-6.05	-46.05	Rainfall	30/7-6/8/12	-4.04	-31.04
P13	22/10/2012	-6.57	-46.91	Rainfall	13-20/8/12	-1.90	-16.54
P13	05/11/2012	-6.51	-47.85	Rainfall	20-27/8/12	-2.40	-16.52
				Rainfall	27/8-3/9/12	-2.58	-21.44
				Rainfall	10-17/9/12	-4.19	-25.90
				Rainfall	17-24/9/12	-2.05	-16.98
				Rainfall	24/9-1/10/12	-4.76	-36.79
				Rainfall	1-8/10/12	-3.75	-25.94
				Rainfall	8-15/10/12	-4.75	-35.52
				Rainfall	22-29/10/12	-10.57	-74.20
				Rainfall	29-10/5-11/12	-8.81	-70.55

APPENDIX C

Traces data (µg/l)

Sample ID	Date	As	B	Br	Cu	Li	Mn	Se	Sr	Al	Ba	Be	Cd	Co	Cr	F	Fe	Gd	Hg	Mo	Nd	Ni	Pb	Rb	Sb	Sn	U	V	Zn
B10	14/02/2011	1.92	48.24	47.80	14.86	32.09	0.649	0.477	320.8	7.21	27.51	0.004	0.006	0.053	0.16	<100	6.88	0.004	0.000	0.33	0.009	0.29	0.101	9.16	0.75	<0.000	1.59	0.83	3.07
B10	28/02/2011	1.86	46.84	52.00	16.94	32.88	0.511	0.532	343.1	5.01	27.77	0.005	0.003	0.057	0.15	<100	5.09	0.003	0.211	0.31	0.008	0.29	0.053	9.68	0.72	<0.000	1.78	0.80	2.23
B10	14/03/2011	1.91	46.05	50.93	30.44	32.55	0.324	0.514	350.5	3.37	28.31	0.003	0.001	0.050	0.39	<100	4.25	0.003	0.032	0.38	0.006	0.34	0.021	9.46	0.68	<0.000	1.85	0.83	0.30
B10	28/03/2011	1.87	45.65	48.17	18.06	32.18	0.671	0.344	318.5	4.28	25.49	0.001	0.003	0.059	0.13	<100	18.00	0.004	0.340	0.30	0.006	0.13	0.024	8.78	0.71	0.002	1.58	0.80	0.16
B10	11/04/2011	1.82	43.15	54.56	18.02	33.45	0.175	0.530	349.6	0.71	29.15	0.003	0.002	0.048	0.09	<100	0.00	0.001	0.017	0.31	0.001	0.11	<0.000	8.97	0.69	0.023	0.44	0.65	0.06
B10	26/04/2011	1.88	39.73	59.68	17.58	29.91	0.263	0.478	379.0	3.51	29.78	0.005	0.007	0.050	0.38	<100	4.07	0.003	0.155	0.42	0.006	0.38	0.021	9.75	0.68	<0.000	2.25	0.83	0.08
B10	09/05/2011	1.83	50.45	59.53	30.71	37.46	0.450	0.740	383.6	3.32	30.89	0.006	0.005	0.054	0.14	<100	2.24	0.004	0.006	0.31	0.008	0.32	0.030	9.93	0.65	0.004	2.37	0.83	3.09
B10	23/05/2011	1.68	49.11	52.88	107.44	39.50	0.942	0.644	335.1	1.16	22.62	0.008	0.002	0.055	0.13	<100	3.45	0.003	0.008	0.30	0.006	0.23	0.018	9.83	0.59	<0.000	1.82	0.83	0.30
B10	06/06/2011	1.73	42.50	40.28	25.94	31.42	1.687	0.448	282.6	4.78	23.36	0.016	0.003	0.064	2.80	<100	19.73	0.003	0.014	1.35	0.007	1.49	0.052	7.93	0.69	0.001	1.33	0.78	0.95
B10	20/06/2011	1.82	49.47	59.06	45.94	38.58	0.395	0.501	357.4	1.66	27.44	0.007	0.003	0.056	0.12	111	3.69	0.004	<0.000	0.29	0.007	0.24	0.052	10.17	0.68	0.015	2.01	0.82	0.74
B10	04/07/2011	1.63	48.21	57.71	159.30	40.83	3.429	0.676	343.9	1.80	22.56	0.006	0.002	0.055	0.11	<100	26.33	0.003	<0.000	0.29	0.008	0.25	0.019	10.22	0.66	<0.000	2.00	0.76	0.24
B10	18/07/2011	1.52	39.88	44.72	140.04	35.48	7.173	0.620	298.8	3.03	20.51	0.005	0.004	0.073	0.23	<100	99.48	0.004	0.003	0.25	0.010	0.33	0.071	7.69	0.57	0.014	1.77	0.74	0.59
B10	16/08/2011	1.69	41.22	40.75	23.26	27.01	0.702	0.383	259.0	2.57	19.95	0.007	0.003	0.055	0.17	<100	16.08	0.003	0.010	0.34	0.005	0.13	0.022	8.57	0.75	0.017	0.88	0.84	0.58
B10	29/08/2011	1.93	45.95	47.59	10.71	31.17	0.983	0.547	307.0	10.92	28.77	0.036	0.006	0.063	0.20	120	20.13	0.004	0.137	0.32	0.012	0.35	0.158	9.42	0.78	0.005	1.29	0.89	5.15
B10	12/09/2011	1.90	41.29	45.64	7.75	25.43	0.224	0.494	310.0	1.97	27.39	0.008	0.004	0.054	0.09	105	4.58	0.002	<0.000	0.35	0.007	0.24	0.014	9.39	0.66	<0.000	1.31	0.84	0.34
B10	26/09/2011	1.98	50.73	26.05	13.38	35.27	0.665	0.509	298.6	10.90	27.89	0.003	0.004	0.054	0.20	<100	13.74	0.004	<0.000	0.37	0.012	0.22	0.042	9.63	0.83	0.004	1.33	0.90	1.50
B10	10/10/2011	2.22	52.31	37.72	9.12	32.67	2.142	0.443	280.2	4.47	25.17	0.008	0.005	0.059	0.14	<100	1065.7	0.003	0.002	0.37	0.010	0.24	0.055	9.45	0.85	0.007	1.22	1.03	0.88
B10	24/10/2011	2.26	51.52	33.82	12.95	32.11	0.527	0.500	274.8	3.67	25.94	0.005	0.005	0.053	0.13	104	6.66	0.004	0.006	0.38	0.008	0.32	0.030	9.64	0.85	0.025	1.09	0.90	16.16
B10	07/11/2011	1.86	48.58	32.99	25.47	32.60	4.490	0.416	275.9	3.73	25.24	0.004	0.003	0.067	0.88	101	36.10	0.002	0.002	0.62	0.005	0.50	0.015	10.31	0.83	0.005	1.12	0.85	0.77
B10	21/11/2011	1.74	48.56	27.82	45.34	34.96	3.462	0.367	253.7	7.44	20.37	0.004	0.004	0.063	0.12	101	33.10	0.003	0.000	0.34	0.008	0.18	0.026	9.36	0.78	<0.000	1.04	0.81	0.62
B10	05/12/2011	1.85	46.15	24.20	13.43	29.28	0.873	0.194	202.8	2.37	17.92	0.011	0.003	0.058	0.09	101	11.25	0.002	0.002	0.35	0.004	0.10	0.016	7.90	0.88	0.019	0.49	0.83	0.57
B10	19/12/2011	1.87	42.07	25.93	60.45	29.23	8.875	0.201	192.3	2.49	17.08	0.010	0.001	0.053	0.10	<100	44.45	0.002	0.003	0.36	0.003	0.19	0.009	7.24	0.78	0.015	0.59	0.83	0.35
B10	03/01/2012	1.85	37.95	16.55	8.25	25.61	0.379	0.187	187.3	2.13	16.78	0.008	0.001	0.058	0.11	117	5.63	0.002	<0.000	0.35	0.005	0.29	0.013	7.74	0.97	0.085	0.43	0.81	<0.000
B10	16/01/2012	1.98	40.68	24.86	2.45	29.81	0.126	0.223	191.3	<0.00	16.12	0.003	0.001	0.053	0.07	114	0.03	0.001	<0.000	0.39	0.000	0.13	<0.000	7.48	0.93	0.016	0.08	0.83	0.87
B10	30/01/2012	2.10	41.12	31.17	12.13	27.73	0.345	0.248	209.0	7.82	18.24	0.006	<0.000	0.068	0.13	<100	10.96	0.004	0.006	0.38	0.010	0.26	0.042	8.02	0.93	0.034	0.65	0.91	1.93
B10	13/02/2012	1.98	35.64	27.51	13.42	27.41	1.064	0.216	200.3	4.19	19.96	0.005	0.000	0.064	0.55	<100	7.31	0.003	0.000	0.35	0.006	0.42	0.067	7.63	0.86	0.013	0.64	0.88	1.42
B10	27/02/2012	1.66	46.06	25.85	16.13	35.73	0.641	0.212	190.2	1.67	18.28	0.007	<0.000	0.050	0.12	<100	2.63	0.002	0.001	0.36	0.004	0.10	0.006	7.25	0.75	<0.000	0.62	0.86	0.37
B10	12/03/2012	1.87	49.74	22.10	28.09	34.68	0.624	0.209	200.6	2.44	19.27	0.018	0.003	0.057	0.09	106	2.66	0.002	0.002	0.39	0.004	<0.000	0.028	7.83	0.79	0.024	0.66	0.86	1.42
B10	26/03/2012	1.95	39.67	16.13	24.69	24.51	0.183	0.176	181.5	1.60	14.46	0.001	<0.000	0.057	0.03	107	7.87	0.003	0.001	0.37	0.004	0.34	0.026	7.40	0.95	0.062	0.40	0.93	0.56
B10	10/04/2012	2.03	36.40	14.01	16.18	24.68	4.333	0.185	176.1	4.51	14.86	<0.000	0.002	0.059	0.10	111	394.6	0.004	0.001	0.33	0.010	0.12	0.054	7.02	0.90	<0.000	0.44	0.89	1.42
B10	23/04/2012	1.82	32.63	10.25	7.73	21.42	0.179	0.166	160.3	2.16	12.95	<0.000	0.000	0.046	0.07	101	4.28	0.002	0.001	0.33	0.004	0.18	0.022	6.73	0.91	<0.000	0.31	0.75	0.53
B10	09/05/2012	1.75	29.18	11.02	6.98	21.53	1.026	0.090	133.0	2.10	11.13	0.004	0.003	0.053	0.32	<100	7.11	0.002	0.000	0.40	0.004	0.20	0.010	5.96	0.93	<0.000	0.23	0.76	2.13
B10	21/05/2012	1.64	43.12	13.38	22.19	29.52	0.285	0.106	164.1	2.38	13.47	0.009	0.002	0.044	0.07	114	5.16	0.003	<0.000	0.30	0.006	0.30	0.023	6.69	0.79	<0.000	0.35	0.79	0.56
B10	04/06/2012	1.75	36.37	14.64	11.11	24.73	0.127	0.117	146.3	1.23	12.21	0.002	0.002	0.047	0.11	<100	3.23	0.001	<0.000	0.31	0.002	0.04	0.003	5.93	0.75	<0.000	0.32	0.79	0.35
B10	18/06/2012	1.63	42.50	30.75	13.63	26.20	0.378	0.128	192.2	4.60	16.11	0.009	0.001	0.044	0.16	<100	17.37	0.003	0.004	0.47	0.008	<0.000	0.071	6.84	0.86	0.257	0.47	0.87	3.78
B10	02/07/2012	1.78	43.99	32.03	54.29	28.29	0.380	0.137	202.7	2.33	15.01	<0.000	<0.000	0.044	0.11	<100	8.33	0.003	<0.000	0.36	0.006	<0.000	0.079	7.29	0.76	0.002	0.47	0.91	1.84
B10	16/07/2012	1.95	42.28	18.20	13.22	25.28	0.810	0.198	219.3	2.44	20.71	<0.000	<0.000	0.056	0.12	<100	5.15	0.002	0.004	0.37	0.006	0.41	0.083	7.93	0.89	0.032	0.55	0.81	2.83
B10	30/07/2012	1.64	44.84	20.65	27.32	31.13	4.992	0.124	162.8	3.24	12.63	0.008	0.003	0.081	0.09	103	47.81	0.003	0.010	0.36	0.004	<0.000	0.060	6.97	0.80	0.047	0.35	0.68	1.50
B10	13/08/2012	1.50	43.04	17.57	34.36	26.61	7.084	0.133	170.8	3.75	12.95	0.004	0.002	0.070	0.08	<100	34.40	0.003	0.003	0.33	0.004	<0.000	0.030	7.20	0.76	<0.000	0.40	0.62	3.40
B10	27/08/2012	1.56	47.76	22.04	23.15	32.39	9.203	0.089	168.6	5.03	13.23	<0.000	0.001	0.075	0.02	105	47.87	0.002	<0.000	0.33	0.004	0.02	0.056	7.28	0.75	0.003	0.41	0.70	1.17
B10	10/09/2012	1.73	38.53	20.72	31.11	24.25	13.521	0.119	178.7	4.09	15.12	<0.000	<0.000	0.064	0.08	115	45.53	0.002	<0.000	0.37	0.005	0.24	0.031	7.37	0.86	0.031	0.46	0.76	1.21
B10	24/09/2012	1.60	45.21	15.26	13.00	28.84	9.031	0.100	179.1	3.41	13.40	<0.000	0.002	0.063	0.04	<100	35.08	0.002	<0.000	0.35	0.004	0.11	0.056	7.69	0.70	<0.000	0.53	0.71	0.08
B10	08/10/2012	1.74	52.39	20.19	22.03	30.67	1.360	0.193	207.9	1.72	18.89	<0.000	0.004	0.054	0.10	<100	25.31	0.003	0.006	0.33	0.006	0.11	0.026	7.93	0.76	0.037	0.49	0.81	1.47
B10	22/10/2012	1.61	53.20	23.83	40.20	33.94	3.973	0.170	196.0	2.50	16.38	0.003	0.003	0.054	0.10	108	31.45	0.003	0.001	0.31	0.005	0.12	0.028	7.55	0.72	<0.000	0.50	0.74	0.35
B10	05/11/2012	1.66	53.97	22.73	56.09	33.26	17.171	0.115	183.3	3.41	14.80	<0.000	<0.000	0.083	0.10	<100	146.95	0.001	0.009	0.39	0.006	0.10	0.029	7.46	0.80	0.045	0.52	0.75	0.99

Sample ID	Date	As	B	Br	Cu	Li	Mn	Se	Sr	Al	Ba	Be	Cd	Co	Cr	F	Fe	Gd	Hg	Mo	Nd	Ni	Pb	Rb	Sb	Sn	U	V	Zn
B11	14/02/2011	2.29	27.82	16.85	26.54	23.27	0.279	0.053	107.3	8.53	6.51	0.004	0.000	0.045	0.07	<100	6.85	0.003	0.005	0.27	0.010	0.14	0.037	5.68	1.26	<0.000	0.05	0.90	1.17
B11	28/02/2011	2.17	25.48	16.90	19.91	22.25	0.305	0.052	106.7	6.31	6.24	0.004	<0.000	0.037	0.07	<100	3.60	0.002	0.073	0.26	0.007	0.12	0.028	5.49	1.26	<0.000	0.05	0.85	0.55
B11	14/03/2011	2.02	23.92	16.30	27.39	21.64	0.244	0.045	106.8	7.23	6.06	0.004	0.000	0.037	0.29	<100	5.45	0.003	0.004	0.34	0.007	0.24	0.025	5.33	1.15	<0.000	0.05	0.76	0.81
B11	28/03/2011	2.00	23.71	18.66	25.73	22.92	0.142	0.041	109.8	5.15	6.21	0.001	0.002	0.038	0.05	<100	3.76	0.003	0.609	0.24	0.006	0.02	0.013	5.12	1.14	0.002	0.05	0.73	0.32
B11	11/04/2011	0.88	9.45	9.89	18.96	10.08	0.155	0.017	48.9	4.06	2.79	0.001	0.001	0.022	0.04	<100	3.41	0.001	0.022	0.11	0.004	<0.000	0.029	2.23	0.44	0.045	0.03	0.30	0.10
B11	26/04/2011	1.89	19.25	18.10	19.36	19.17	0.568	0.038	105.7	7.67	5.73	0.004	0.002	0.039	0.27	<100	7.55	0.002	0.002	0.33	0.010	0.25	0.039	5.02	1.08	<0.000	0.05	0.70	0.07
B11	09/05/2011	1.92	23.26	21.30	28.00	23.22	0.422	0.050	111.0	5.58	6.14	0.004	0.001	0.038	0.07	<100	7.84	0.003	0.004	0.24	0.008	0.15	0.036	4.85	1.05	0.006	0.07	0.72	0.55
B11	23/05/2011	1.91	23.06	24.52	57.71	24.48	0.918	0.051	118.4	3.73	6.72	0.006	0.000	0.037	0.07	<100	6.43	0.003	0.005	0.22	0.007	0.13	0.034	5.09	1.01	<0.000	0.06	0.66	0.66
B11	06/06/2011	1.84	24.78	24.62	43.90	23.18	0.597	0.048	119.2	5.02	6.86	0.008	0.002	0.038	0.49	<100	15.08	0.003	0.003	0.56	0.006	0.40	0.032	4.98	0.98	<0.000	0.07	0.65	0.61
B11	20/06/2011	0.97	15.22	18.36	42.02	12.85	0.283	0.024	62.1	3.20	4.76	0.005	0.001	0.019	0.05	<100	5.75	0.002	<0.000	0.08	0.005	0.08	0.049	2.81	0.45	0.018	0.04	0.36	0.67
B11	04/07/2011	2.01	34.37	26.30	125.20	27.30	1.095	0.064	138.8	4.72	9.08	0.005	0.001	0.060	0.08	104	21.75	0.003	<0.000	0.24	0.007	0.18	0.045	6.47	0.94	<0.000	0.14	0.80	0.48
B11	18/07/2011	1.99	33.45	25.51	166.35	26.82	2.187	0.056	141.8	4.01	9.67	0.003	0.003	0.059	0.07	<100	27.00	0.002	0.000	0.25	0.007	0.22	0.092	6.57	0.97	<0.000	0.13	0.77	1.14
B11	16/08/2011	2.31	39.85	33.33	79.08	25.46	1.108	0.074	141.4	11.98	10.34	0.045	0.004	0.053	0.05	124	19.12	0.004	0.008	0.23	0.012	0.19	0.020	6.23	1.06	0.011	0.10	0.78	0.44
B11	29/08/2011	2.62	40.81	36.47	52.58	26.41	0.692	0.056	146.4	11.04	10.74	0.021	0.005	0.051	0.06	115	16.79	0.006	0.025	0.23	0.016	0.24	0.094	6.94	1.16	<0.000	0.10	0.88	0.73
B11	12/09/2011	2.59	41.08	30.72	86.31	20.86	0.339	0.046	132.9	4.23	9.54	0.689	0.005	0.112	0.02	<100	5.41	0.005	<0.000	0.24	0.010	0.22	0.036	6.77	1.13	<0.000	0.08	0.92	0.54
B11	26/09/2011	3.42	60.43	18.07	105.31	32.42	1.029	0.056	145.2	14.05	13.10	0.009	0.004	0.065	0.08	104	55.56	0.007	<0.000	0.32	0.019	0.23	0.077	8.45	1.60	0.008	0.08	1.25	1.08
B11	10/10/2011	2.86	53.10	31.90	21.27	30.71	0.092	0.058	142.7	1.41	10.76	0.001	0.003	0.045	0.02	108	0.17	0.002	0.000	0.33	0.001	0.16	<0.000	8.03	1.57	<0.000	0.02	0.99	0.32
B11	24/10/2011	3.42	58.25	29.36	101.38	30.80	0.185	0.069	137.5	4.53	12.69	0.008	0.003	0.051	0.06	103	3.88	0.005	0.016	0.41	0.010	0.22	0.013	8.57	1.76	0.192	0.06	1.22	0.47
B11	07/11/2011	3.04	54.94	28.00	101.48	30.06	1.056	0.077	147.2	8.14	13.78	0.008	0.005	0.053	2.10	<100	15.72	0.005	0.003	1.04	0.009	0.93	0.016	8.76	1.66	0.009	0.10	1.10	0.66
B11	21/11/2011	2.85	43.65	24.15	62.27	30.54	0.498	0.066	150.3	3.70	12.49	0.006	0.002	0.056	0.06	106	2.61	0.004	0.008	0.32	0.006	0.13	0.015	7.73	1.21	0.101	0.11	0.98	0.90
B11	05/12/2011	3.01	48.82	16.55	105.25	28.84	0.979	0.094	126.6	6.10	10.13	0.011	0.002	0.049	0.03	107	9.37	0.004	0.002	0.32	0.010	0.14	0.012	7.61	1.51	0.007	0.07	1.15	1.36
B11	19/12/2011	3.10	44.52	19.00	95.27	26.48	0.590	0.111	118.5	7.29	9.98	0.008	0.003	0.047	0.06	125	9.49	0.005	0.003	0.36	0.009	0.19	0.040	7.11	1.52	0.010	0.06	1.12	2.05
B11	03/01/2012	2.82	36.20	2.87	32.44	25.50	0.241	0.062	107.0	6.66	7.41	0.008	0.001	0.055	0.06	135	7.06	0.005	<0.000	0.36	0.009	0.25	0.017	6.95	1.66	0.084	0.06	1.06	<0.000
B11	16/01/2012	2.60	33.54	7.64	12.92	26.74	0.180	0.054	93.8	0.65	5.67	0.008	0.000	0.049	0.03	<100	0.11	0.003	<0.000	0.39	0.002	0.04	<0.000	5.94	1.51	0.004	0.00	1.00	<0.000
B11	30/01/2012	2.38	29.64	10.31	18.75	22.41	0.429	0.056	93.1	15.44	5.93	0.008	<0.000	0.048	0.06	101	11.84	0.006	0.004	0.34	0.014	0.14	0.038	5.88	1.59	0.031	0.05	0.93	1.05
B11	13/02/2012	2.32	25.80	8.72	51.69	20.75	0.782	0.054	90.6	18.12	5.83	0.010	<0.000	0.056	1.19	<100	16.58	0.006	0.001	0.33	0.014	0.44	0.088	5.76	1.58	0.008	0.04	0.95	2.65
B11	27/02/2012	1.90	31.29	10.23	44.78	26.63	1.099	0.053	88.4	18.41	5.31	0.010	<0.000	0.050	0.10	<100	48.03	0.004	0.001	0.33	0.012	0.09	0.024	5.37	1.36	0.003	0.04	0.88	1.78
B11	12/03/2012	2.35	30.00	8.11	127.96	24.70	0.917	0.061	95.8	35.42	6.69	0.013	0.003	0.058	0.13	106	26.85	0.006	0.009	0.34	0.020	0.03	0.058	5.36	1.24	0.036	0.08	0.80	1.07
B11	26/03/2012	2.19	26.72	3.99	33.46	21.25	0.178	0.079	105.0	5.49	6.42	0.002	<0.000	0.043	<0.000	101	10.12	0.003	0.001	0.32	0.007	0.26	0.013	5.78	1.40	0.031	0.05	0.85	0.35
B11	10/04/2012	2.17	22.89	2.76	28.45	22.07	1.807	0.063	103.7	44.65	6.63	<0.000	0.002	0.061	0.10	106	94.17	0.010	0.001	0.27	0.040	0.16	0.414	5.38	1.26	0.220	0.06	0.78	1.82
B11	23/04/2012	1.96	26.39	6.46	13.75	21.94	0.682	0.058	122.8	15.12	7.35	<0.000	0.001	0.064	0.08	101	25.08	0.005	0.001	0.26	0.013	0.23	0.133	5.98	1.04	<0.000	0.11	0.74	1.16
B11	09/05/2012	1.88	23.79	7.18	17.59	22.29	0.465	0.062	106.6	5.03	6.23	0.017	0.003	0.051	0.25	103	12.26	0.004	0.001	0.32	0.008	0.10	0.013	5.22	1.04	0.002	0.09	0.69	0.23
B11	21/05/2012	1.76	34.56	7.86	18.20	28.12	0.446	0.035	114.1	6.73	7.01	0.007	0.001	0.051	0.07	<100	11.90	0.003	<0.000	0.24	0.007	0.24	0.029	5.71	0.89	<0.000	0.12	0.71	0.23
B11	04/06/2012	1.95	28.79	8.28	20.86	23.01	0.132	0.042	99.1	3.23	6.15	0.001	0.002	0.048	0.07	<100	6.73	0.002	<0.000	0.24	0.005	0.03	0.006	4.85	0.94	<0.000	0.08	0.69	0.38
B11	18/06/2012	2.04	32.48	19.54	35.83	23.54	0.209	0.059	113.7	3.49	7.03	0.005	<0.000	0.047	0.07	<100	7.86	0.003	<0.000	0.30	0.007	<0.000	<0.000	5.35	1.06	0.065	0.11	0.88	1.16
B11	02/07/2012	1.78	37.83	9.83	33.92	26.65	0.503	0.067	126.6	3.09	7.91	<0.000	<0.000	0.063	0.07	<100	17.61	0.004	0.006	0.28	0.005	0.18	0.183	6.24	0.95	<0.000	0.17	0.77	1.34
B11	16/07/2012	1.92	33.82	9.57	42.37	23.40	2.273	0.067	129.1	3.73	8.58	<0.000	<0.000	0.056	0.09	<100	15.27	0.003	0.006	0.31	0.007	0.34	0.032	6.28	1.05	0.019	0.16	0.74	2.43
B11	30/07/2012	1.79	41.38	20.25	55.02	28.17	1.209	0.083	131.6	2.02	8.29	0.008	0.003	0.074	0.07	<100	9.61	0.003	0.007	0.32	0.005	<0.000	0.085	6.34	0.87	0.032	0.19	0.72	0.58
B11	13/08/2012	1.65	38.84	13.44	35.19	24.99	0.704	0.065	132.9	2.06	8.46	0.005	0.003	0.065	0.07	<100	7.87	0.003	0.004	0.30	0.006	<0.000	0.010	6.46	0.89	<0.000	0.19	0.69	0.95
B11	27/08/2012	1.58	43.06	17.95	112.44	30.28	1.758	0.050	131.8	2.18	8.50	<0.000	0.002	0.065	0.02	<100	11.37	0.003	<0.000	0.30	0.004	0.05	0.010	6.39	0.88	0.000	0.18	0.66	0.98
B11	10/09/2012	1.59	34.64	16.67	46.46	22.28	1.896	0.055	134.2	3.04	8.83	<0.000	<0.000	0.065	0.08	101	9.45	0.003	<0.000	0.31	0.006	0.15	0.006	6.56	0.96	0.014	0.19	0.68	0.36
B11	24/09/2012	1.49	37.18	8.88	194.43	23.97	1.452	0.066	124.5	1.43	8.34	<0.000	0.002	0.064	0.03	<100	12.34	0.002	<0.000	0.27	0.004	0.15	0.003	6.12	0.88	<0.000	0.15	0.69	0.08
B11	08/10/2012	2.03	40.17	16.69	79.02	25.67	1.872	0.045	123.4	15.12	8.68	0.002	0.003	0.056	0.05	104	40.06	0.005	0.006	0.24	0.016	0.11	0.093	6.36	1.14	0.015	0.11	0.82	1.82
B11	22/10/2012	2.35	38.12	18.55	150.86	25.87	3.667	0.063	116.4	4.71	7.88	0.010	0.003	0.233	0.03	<100	697.3	0.002	<0.000	0.35	0.008	0.10	0.019	6.18	1.07	0.163	0.11	0.93	0.80
B11	05/11/2012	2.50	40.68	17.72	154.08	27.00	14.608	0.075	116.2	7.07	8.40	<0.000	<0.000	0.119	0.03	<100	676.1	0.004	0.009	0.31	0.010	0.06	0.080	6.28	1.15	0.032	0.12	0.96	1.76

Sample ID	Date	As	B	Br	Cu	Li	Mn	Se	Sr	Al	Ba	Be	Cd	Co	Cr	F	Fe	Gd	Hg	Mo	Nd	Ni	Pb	Rb	Sb	Sn	U	V	Zn
B18	14/02/2011	1.58	35.97	25.60	0.83	25.81	1.296	0.035	134.4	4.35	8.58	0.004	0.001	0.085	0.09	<100	4.79	0.003	0.004	0.25	0.006	0.18	0.061	6.57	0.70	<0.000	0.23	0.83	1.57
B18	28/02/2011	1.54	34.25	23.95	0.73	25.05	0.466	0.043	133.8	3.07	8.38	0.003	0.000	0.078	0.09	<100	2.87	0.002	0.116	0.24	0.005	0.16	0.027	6.53	0.68	<0.000	0.23	0.83	0.48
B18	14/03/2011	1.54	34.37	22.91	1.29	25.17	0.245	0.039	134.1	3.19	8.23	0.003	0.001	0.074	0.32	<100	3.57	0.002	0.003	0.32	0.004	0.29	0.027	6.48	0.67	<0.000	0.22	0.77	0.57
B18	28/03/2011	1.54	36.28	24.04	0.87	25.81	0.254	0.038	132.6	3.71	8.24	0.000	0.003	0.080	0.07	<100	2.51	0.004	0.155	0.25	0.005	0.06	0.039	6.32	0.70	0.006	0.22	0.82	1.44
B18	11/04/2011	1.57	34.17	23.68	0.83	26.31	0.325	0.034	132.0	2.32	8.25	0.001	0.002	0.080	0.07	<100	2.82	0.003	0.004	0.19	0.004	0.02	0.026	6.29	0.69	0.005	0.17	0.78	0.08
B18	26/04/2011	1.59	30.61	25.64	1.83	22.68	3.707	0.040	130.3	3.72	7.96	0.004	0.012	0.087	0.34	<100	5.84	0.002	0.021	0.38	0.003	0.30	0.067	6.45	0.66	0.039	0.22	0.86	0.38
B18	09/05/2011	1.53	34.52	24.18	0.89	27.58	6.412	0.032	129.3	3.68	8.30	0.004	0.002	0.103	0.10	<100	139.85	0.002	0.003	0.25	0.004	0.17	0.026	6.18	0.64	0.003	0.21	0.83	0.31
B18	23/05/2011	0.36	30.42	21.62	0.11	N.A	1.778	0.001	N.A	3.56	0.25	0.004	<0.000	0.012	0.06	<100	85.15	0.001	0.006	0.00	0.004	0.03	0.021	0.09	0.17	<0.000	0.03	0.33	0.07
B18	06/06/2011	0.32	32.04	20.99	0.55	N.A	3.556	<0.000	N.A	4.89	4.61	0.009	0.001	0.017	2.88	<100	43.68	0.002	0.027	1.13	0.005	1.37	0.082	0.24	0.23	<0.000	0.07	0.24	0.89
B18	20/06/2011	1.69	33.96	25.05	1.30	27.37	2.371	0.063	128.1	5.16	8.20	0.006	0.002	0.068	0.10	104	19.77	0.004	<0.000	0.24	0.008	0.18	0.247	6.38	0.84	0.014	0.17	0.79	8.46
B18	04/07/2011	1.51	35.93	22.32	0.81	25.91	9.356	0.052	132.4	3.20	11.13	0.004	0.002	0.096	0.08	110	80.14	0.002	<0.000	0.25	0.005	0.16	0.015	6.36	0.71	<0.000	0.22	0.74	0.25
B18	18/07/2011	1.36	36.34	23.32	0.76	26.39	12.531	0.032	129.9	2.85	9.96	0.002	0.003	0.117	0.07	<100	84.80	0.002	0.001	0.24	0.005	0.21	0.022	6.50	0.65	<0.000	0.21	0.70	1.04
B18	16/08/2011	0.95	35.90	23.74	0.81	24.86	43.021	0.048	131.0	2.56	10.11	0.011	0.002	0.171	0.06	104	89.89	0.001	0.011	0.26	0.003	0.34	0.015	6.48	0.57	<0.000	0.20	0.51	0.53
B18	29/08/2011	1.02	35.78	25.02	4.32	26.13	45.745	0.026	135.4	2.18	10.45	0.067	0.004	0.183	0.06	116	157.61	0.002	0.077	0.26	0.002	0.34	0.014	6.97	0.56	<0.000	0.24	0.54	0.39
B18	12/09/2011	0.86	30.52	23.49	1.16	20.62	25.421	0.032	135.3	1.92	10.38	0.013	0.003	0.141	0.02	102	109.17	0.000	<0.000	0.24	0.002	0.29	0.005	6.79	0.47	<0.000	0.22	0.43	0.39
B18	26/09/2011	1.03	37.82	17.47	0.79	27.98	22.477	0.032	136.2	2.34	11.10	0.002	0.002	0.128	0.05	<100	85.34	0.002	<0.000	0.26	0.003	0.22	0.019	6.83	0.66	0.003	0.24	0.51	0.82
B18	10/10/2011	0.95	37.24	20.58	0.88	25.88	19.788	0.035	132.3	3.36	11.43	0.005	0.002	0.140	0.04	<100	126.07	0.002	0.002	0.25	0.004	0.76	0.025	6.74	0.62	0.006	0.22	0.48	0.70
B18	24/10/2011	1.21	37.63	18.52	0.96	25.30	9.102	0.045	132.9	2.27	10.40	0.006	0.001	0.106	0.06	<100	59.72	0.002	0.006	0.27	0.004	0.22	0.029	6.82	0.68	0.026	0.22	0.59	1.07
B18	07/11/2011	1.31	38.14	18.84	1.52	25.92	4.763	0.039	137.9	5.22	10.41	0.009	0.002	0.092	0.10	<100	44.40	0.002	0.001	0.27	0.005	0.24	0.045	7.14	0.70	0.008	0.22	0.64	5.48
B18	21/11/2011	1.40	38.38	16.37	0.75	26.12	2.827	0.028	132.0	2.69	8.85	0.006	0.001	0.091	0.07	<100	44.68	0.001	0.005	0.27	0.003	0.10	0.023	6.90	0.68	0.052	0.22	0.70	0.22
B18	05/12/2011	1.59	38.52	21.05	0.83	26.51	2.970	0.045	138.8	1.81	9.95	0.007	0.002	0.085	0.07	<100	13.59	0.003	<0.000	0.28	0.005	0.12	0.005	6.86	0.75	<0.000	0.23	0.78	2.07
B18	19/12/2011	1.49	34.55	24.73	0.96	24.32	0.359	0.044	132.0	1.54	9.09	0.010	0.002	0.069	0.12	<100	1.63	0.002	0.003	0.27	0.004	0.12	0.005	6.46	0.72	0.005	0.22	0.79	0.10
B18	03/01/2012	1.53	31.68	13.82	1.03	24.19	0.506	0.061	134.2	1.78	9.29	0.006	0.002	0.084	0.08	101	3.27	0.002	<0.000	0.27	0.005	0.27	0.011	6.90	0.81	0.024	0.22	0.83	0.70
B18	16/01/2012	1.61	33.47	19.22	0.81	27.33	0.004	0.048	130.1	<0.000	8.16	0.005	0.000	0.060	0.07	103	0.43	0.001	<0.000	0.30	0.001	0.06	0.007	6.52	0.76	<0.000	0.02	0.59	<0.000
B18	30/01/2012	1.73	33.05	24.90	1.46	24.65	0.409	0.045	132.0	3.20	9.04	0.005	0.001	0.086	0.08	<100	4.01	0.003	0.006	0.28	0.005	0.23	0.052	6.87	0.84	0.024	0.22	0.85	0.75
B18	13/02/2012	1.66	27.75	22.35	1.44	22.78	7.751	0.050	130.5	16.98	8.92	0.006	0.000	0.102	0.10	<100	24.99	0.005	0.000	0.27	0.016	0.44	0.168	6.66	0.80	0.009	0.20	0.85	2.15
B18	27/02/2012	1.47	35.56	23.45	0.79	28.86	0.696	0.046	125.6	8.65	7.90	0.009	<0.000	0.075	0.09	<100	6.69	0.003	0.002	0.26	0.008	0.09	0.082	6.25	0.70	0.029	0.21	0.79	0.34
B18	12/03/2012	1.56	38.56	19.09	0.87	28.13	0.478	0.036	134.6	2.14	8.80	0.013	0.003	0.074	0.05	<100	2.72	0.003	0.002	0.27	0.004	<0.000	0.019	6.73	0.73	0.014	0.23	0.80	0.64
B18	26/03/2012	1.56	35.09	14.31	0.98	24.42	0.813	0.075	138.9	1.89	8.77	<0.000	<0.000	0.085	0.02	<100	6.89	0.002	0.001	0.29	0.005	0.31	0.008	6.98	0.78	0.019	0.23	0.85	2.23
B18	10/04/2012	1.49	32.28	13.07	2.13	24.64	0.089	0.056	133.3	2.42	8.28	<0.000	0.001	0.074	0.07	<100	3.30	0.002	0.001	0.26	0.004	0.13	0.024	6.66	0.74	<0.000	0.21	0.75	0.37
B18	23/04/2012	1.47	29.70	10.37	1.37	22.09	0.423	0.056	129.0	1.81	8.05	0.002	0.001	0.093	0.10	<100	6.36	0.003	0.001	0.31	0.004	0.25	0.054	6.47	0.72	0.319	0.22	0.71	2.25
B18	09/05/2012	1.39	28.69	14.50	1.19	23.57	0.500	0.054	123.4	2.00	7.93	0.007	0.003	0.073	0.27	<100	4.22	0.002	0.000	0.32	0.005	0.17	0.042	6.20	0.72	0.002	0.19	0.69	1.09
B18	21/05/2012	1.41	39.71	14.29	2.30	29.88	0.098	0.029	126.9	1.65	8.43	0.017	0.001	0.072	0.08	<100	1.63	0.003	<0.000	0.24	0.004	0.22	0.053	6.31	0.63	0.001	0.20	0.75	0.24
B18	04/06/2012	1.56	34.53	16.60	0.75	25.87	0.180	0.028	121.6	1.09	8.33	0.002	0.001	0.068	0.09	<100	2.27	0.001	<0.000	0.23	0.002	0.02	0.004	5.88	0.61	<0.000	0.19	0.79	0.50
B18	18/06/2012	1.58	38.22	26.58	1.48	27.41	0.426	0.053	134.5	2.06	9.58	0.000	<0.000	0.067	0.15	<100	4.09	0.003	<0.000	0.29	0.005	<0.000	<0.000	6.27	0.77	0.021	0.22	0.80	5.67
B18	02/07/2012	1.69	40.78	11.81	0.92	22.79	2.792	0.052	147.4	4.51	18.14	<0.000	<0.000	0.082	0.11	<100	13.55	0.003	0.005	0.32	0.007	0.25	0.168	5.95	0.95	<0.000	0.29	0.77	1.55
B18	16/07/2012	1.90	36.07	11.11	0.88	20.87	4.366	0.053	146.4	5.43	18.33	<0.000	<0.000	0.091	0.12	<100	15.93	0.003	0.004	0.33	0.006	0.44	0.041	6.06	0.92	0.001	0.30	0.87	4.58
B18	30/07/2012	1.79	43.16	19.34	0.68	23.43	4.726	0.045	144.7	7.16	19.08	0.009	0.005	0.087	0.10	103	17.84	0.004	0.004	0.35	0.008	<0.000	0.022	5.79	0.88	0.014	0.30	0.73	0.65
B18	13/08/2012	1.70	39.61	13.46	0.82	19.69	5.331	0.043	143.5	5.89	19.26	0.009	0.006	0.083	0.11	<100	11.65	0.004	0.003	0.45	0.006	<0.000	0.031	5.79	0.89	0.107	0.28	0.76	1.40
B18	27/08/2012	1.85	43.57	15.75	0.92	23.55	5.873	0.052	149.6	4.64	19.56	0.005	0.002	0.092	0.13	<100	11.34	0.002	0.012	0.43	0.007	0.28	0.024	6.11	0.99	0.290	0.28	0.78	1.57
B18	10/09/2012	1.80	36.81	15.80	1.28	19.41	5.609	0.037	146.5	3.81	18.50	<0.000	0.001	0.084	0.09	102	14.03	0.004	<0.000	0.35	0.006	0.22	0.010	6.18	0.97	0.006	0.27	0.80	0.29
B18	24/09/2012	1.63	42.13	11.57	5.62	22.58	4.562	0.030	146.6	3.26	16.03	<0.000	0.003	0.085	0.11	<100	11.65	0.003	<0.000	0.29	0.006	0.14	0.007	6.50	0.81	<0.000	0.26	0.86	0.07
B18	08/10/2012	2.32	42.97	12.34	0.73	22.96	18.661	0.037	138.3	3.88	13.95	<0.000	0.003	0.090	0.09	<100	132.22	0.004	0.007	0.30	0.008	0.09	0.052	6.20	0.76	0.003	0.23	0.79	0.81
B18	22/10/2012	1.62	43.04	14.77	0.79	25.05	4.921	0.043	131.9	3.92	10.97	0.007	0.003	0.083	0.09	<100	32.48	0.004	0.001	0.32	0.006	0.14	0.031	6.44	0.73	0.058	0.22	0.77	0.61
B18	05/11/2012	1.58	45.68	15.40	0.64	26.41	2.572	0.031	133.4	4.14	10.91	<0.000	<0.000	0.076	0.07	<100	36.64	0.002	0.007	0.33	0.006	0.04	0.015	6.67	0.81	0.023	0.23	0.77	0.62

Sample ID	Date	As	B	Br	Cu	Li	Mn	Se	Sr	Al	Ba	Be	Cd	Co	Cr	F	Fe	Gd	Hg	Mo	Nd	Ni	Pb	Rb	Sb	Sn	U	V	Zn
B20	14/02/2011	1.99	32.20	17.46	1.45	27.25	0.285	0.073	141.6	4.21	10.79	0.004	0.002	0.053	0.07	<100	4.20	0.002	0.000	0.27	0.006	0.17	0.081	4.65	1.30	<0.000	0.11	0.92	2.27
B20	28/02/2011	1.98	31.33	17.44	1.53	27.15	0.316	0.078	144.0	4.56	11.57	0.003	0.003	0.053	0.09	<100	2.49	0.003	0.011	0.25	0.006	0.22	0.068	4.75	1.29	<0.000	0.12	0.89	3.96
B20	14/03/2011	1.91	30.22	16.09	0.99	26.82	0.202	0.072	141.0	3.46	10.52	0.003	0.001	0.046	0.30	100	3.51	0.002	0.002	0.34	0.006	0.27	0.025	4.61	1.25	<0.000	0.12	0.84	0.58
B20	28/03/2011	1.95	31.37	13.03	1.15	28.04	0.060	0.057	142.0	2.94	10.61	<0.000	0.002	0.046	0.04	100	1.77	0.003	0.084	0.26	0.005	0.04	0.014	4.50	1.26	0.001	0.09	0.88	0.36
B20	11/04/2011	1.90	28.79	16.56	1.53	27.40	0.145	0.064	140.0	2.83	11.33	0.000	0.002	0.045	0.05	101	1.86	0.003	0.001	0.19	0.003	0.01	0.012	4.38	1.26	0.012	0.08	0.82	<0.000
B20	26/04/2011	1.88	25.35	17.06	1.90	24.94	0.068	0.058	142.6	3.21	10.07	0.003	0.002	0.045	0.31	106	2.40	0.003	0.023	0.38	0.004	0.28	0.013	4.64	1.24	<0.000	0.11	0.86	0.02
B20	09/05/2011	1.90	28.92	18.36	2.12	29.32	0.121	0.068	139.5	3.20	10.21	0.004	0.001	0.045	0.06	<100	2.48	0.003	0.003	0.26	0.004	0.14	0.016	4.38	1.21	0.002	0.11	0.88	0.41
B20	23/05/2011	1.82	27.97	16.36	1.76	30.03	0.264	0.063	138.8	1.83	9.75	0.006	0.002	0.043	0.07	<100	2.53	0.002	0.031	0.26	0.005	0.14	0.027	4.37	1.16	<0.000	0.10	0.83	2.27
B20	06/06/2011	1.74	29.38	21.74	1.41	27.78	0.893	0.049	138.5	8.08	9.41	0.004	0.007	0.052	3.64	116	8.81	0.002	0.004	2.89	0.005	2.23	0.058	4.21	1.16	<0.000	0.10	0.81	1.44
B20	20/06/2011	1.85	31.49	26.92	1.65	30.07	0.420	0.053	146.9	1.45	10.91	0.014	0.002	0.043	0.05	100	2.04	0.002	<0.000	0.25	0.005	0.12	0.030	4.71	1.19	0.004	0.13	0.82	0.31
B20	04/07/2011	1.84	32.23	28.06	1.20	30.36	0.201	0.038	145.7	2.36	11.20	0.004	0.004	0.047	0.07	109	3.03	0.003	0.025	0.25	0.005	0.14	0.020	4.67	1.19	0.082	0.12	0.85	0.38
B20	18/07/2011	1.77	32.64	30.40	2.29	30.50	0.146	0.043	151.8	1.75	11.68	0.004	0.003	0.059	0.07	<100	2.72	0.003	0.001	0.25	0.004	0.18	0.019	4.72	1.13	0.008	0.13	0.86	0.27
B20	16/08/2011	1.87	39.12	34.36	1.48	29.75	0.205	0.042	160.2	1.57	12.70	0.009	0.004	0.052	0.04	122	3.06	0.003	0.004	0.24	0.006	0.20	0.042	4.94	1.10	<0.000	0.13	0.87	0.59
B20	29/08/2011	1.95	39.62	33.44	1.52	29.11	0.099	0.045	166.2	1.31	14.41	0.026	0.004	0.050	0.08	105	2.56	0.003	0.029	0.24	0.005	0.18	0.009	5.24	1.22	<0.000	0.14	0.90	0.19
B20	12/09/2011	1.88	31.63	37.07	1.21	24.34	0.148	0.045	173.9	1.51	13.36	0.008	0.004	0.046	0.05	<100	2.44	0.003	<0.000	0.23	0.005	0.21	0.016	5.23	1.08	<0.000	0.16	0.85	0.56
B20	26/09/2011	2.02	37.93	20.22	1.67	34.32	0.225	0.046	175.1	3.81	14.25	0.004	0.006	0.052	0.23	<100	4.16	0.003	<0.000	0.25	0.006	0.26	0.047	5.41	1.28	0.001	0.19	0.90	3.58
B20	10/10/2011	1.97	37.93	34.51	1.54	32.79	0.385	0.044	182.5	2.00	14.92	0.006	0.005	0.054	0.06	<100	4.96	0.003	0.002	0.24	0.006	0.22	0.021	5.52	1.29	0.002	0.21	0.91	0.39
B20	24/10/2011	2.03	40.31	35.40	1.22	34.39	0.114	0.055	194.6	5.47	15.83	0.008	0.004	0.059	0.06	<100	6.60	0.004	0.008	0.29	0.009	0.22	0.019	5.83	1.39	0.047	0.23	0.86	0.21
B20	07/11/2011	1.97	41.97	29.98	1.86	31.20	0.063	0.061	176.7	1.37	16.05	0.010	0.004	0.068	0.11	<100	1.64	0.003	0.001	0.27	0.006	0.28	0.007	5.48	1.35	0.002	0.18	0.87	0.13
B20	21/11/2011	2.13	48.48	23.89	1.84	32.71	0.079	0.062	159.3	1.81	13.91	0.006	0.003	0.078	0.05	<100	1.89	0.005	0.003	0.27	0.005	0.14	0.010	5.49	1.37	0.028	0.12	0.95	0.17
B20	05/12/2011	2.06	45.56	20.84	1.69	31.33	0.132	0.053	157.8	2.20	12.34	0.010	0.003	0.074	0.05	<100	2.90	0.004	0.002	0.27	0.006	0.15	0.004	5.42	1.33	0.001	0.12	0.95	1.37
B20	19/12/2011	2.15	42.03	21.14	2.45	28.49	0.087	0.051	141.1	1.62	11.96	0.008	0.003	0.069	0.05	113	1.33	0.004	0.001	0.27	0.005	0.16	0.006	4.95	1.35	0.002	0.10	0.98	0.18
B20	03/01/2012	2.04	38.10	10.86	1.84	28.63	0.090	0.066	149.7	1.86	12.94	0.008	0.004	0.079	0.05	112	2.87	0.005	<0.000	0.28	0.007	0.30	0.017	5.40	1.47	0.015	0.12	0.97	2.73
B20	16/01/2012	2.08	41.05	12.98	1.42	32.80	<0.000	0.067	148.8	0.18	11.62	0.005	0.001	0.073	0.04	<100	0.51	0.002	<0.000	0.30	0.001	0.07	0.011	5.21	1.42	<0.000	0.02	0.94	0.43
B20	30/01/2012	2.17	37.47	17.88	1.72	28.07	0.074	0.066	145.6	2.23	11.77	0.006	0.001	0.072	0.06	103	1.75	0.004	0.004	0.30	0.006	0.25	0.008	5.27	1.54	0.012	0.12	1.02	0.19
B20	13/02/2012	2.20	32.76	13.42	2.87	24.67	0.377	0.058	129.4	2.15	10.52	0.008	0.000	0.067	0.18	<100	5.71	0.004	0.001	0.32	0.005	0.28	0.058	4.97	1.54	0.005	0.09	0.99	0.39
B20	27/02/2012	1.89	38.55	13.15	1.59	31.86	0.068	0.048	118.2	1.38	9.05	0.011	<0.000	0.058	0.05	108	1.31	0.004	0.001	0.31	0.005	0.03	0.005	4.51	1.36	<0.000	0.08	0.92	0.27
B20	12/03/2012	1.96	38.72	8.26	2.17	29.85	0.459	0.045	125.8	2.17	9.56	0.009	0.004	0.072	0.02	110	5.43	0.003	0.001	0.33	0.005	<0.000	0.011	4.73	1.41	0.006	0.09	0.91	2.54
B20	26/03/2012	1.98	35.81	3.80	1.74	26.13	0.332	0.080	134.7	1.51	10.05	<0.000	<0.000	0.066	<0.000	116	3.97	0.003	0.000	0.32	0.004	0.28	0.007	5.02	1.53	0.011	0.09	0.93	2.19
B20	10/04/2012	1.96	32.60	2.15	1.71	26.77	0.358	0.054	132.1	2.35	10.16	<0.000	0.001	0.062	0.05	<100	6.60	0.003	0.000	0.31	0.004	0.17	0.045	4.76	1.42	<0.000	0.09	0.90	2.58
B20	23/04/2012	1.91	28.95	2.46	2.06	24.11	0.066	0.061	129.7	1.89	9.90	0.003	0.002	0.058	0.05	<100	2.37	0.003	0.001	0.32	0.005	0.21	0.031	4.64	1.35	0.118	0.09	0.83	0.35
B20	09/05/2012	1.86	28.22	9.57	1.25	26.78	0.413	0.068	128.2	2.69	9.77	0.014	0.004	0.067	0.25	111	6.52	0.004	0.001	0.37	0.006	0.22	0.027	4.43	1.29	0.089	0.10	0.83	3.29
B20	21/05/2012	1.78	35.21	4.70	2.40	31.49	0.200	0.035	126.2	6.70	9.89	0.008	0.001	0.050	0.04	<100	5.72	0.004	<0.000	0.25	0.007	0.25	0.009	4.41	1.20	<0.000	0.08	0.80	0.15
B20	04/06/2012	1.79	31.00	8.75	1.64	26.90	0.014	0.043	121.4	1.03	9.58	0.002	0.002	0.049	0.07	105	2.35	0.002	<0.000	0.26	0.003	0.68	0.011	4.02	1.09	<0.000	0.09	0.84	0.47
B20	18/06/2012	1.85	35.35	19.34	1.80	30.60	0.102	0.054	135.4	2.30	10.40	0.003	<0.000	0.040	0.08	<100	3.15	0.004	0.000	0.34	0.005	<0.000	0.002	4.41	1.36	0.032	0.10	0.89	1.61
B20	02/07/2012	2.06	35.63	3.72	1.11	28.01	0.233	0.044	127.0	4.27	9.74	<0.000	<0.000	0.051	0.10	<100	5.03	0.003	0.003	0.30	0.006	0.12	0.035	4.40	1.35	<0.000	0.10	0.84	0.62
B20	16/07/2012	1.97	30.51	3.89	1.37	23.88	0.129	0.046	126.4	1.40	10.14	<0.000	<0.000	0.041	0.07	<100	2.50	0.003	0.003	0.28	0.005	0.27	0.015	4.27	1.34	<0.000	0.10	0.85	1.08
B20	30/07/2012	2.04	38.70	15.31	2.42	29.92	0.281	0.060	129.9	3.93	10.56	0.009	0.004	0.053	0.08	<100	7.54	0.003	0.003	0.31	0.005	<0.000	0.070	4.45	1.30	0.021	0.11	0.83	2.02
B20	13/08/2012	1.97	36.00	11.22	1.77	26.43	0.137	0.052	135.3	1.86	10.97	0.011	0.003	0.047	0.07	106	1.77	0.003	0.002	0.31	0.005	<0.000	0.016	4.50	1.23	0.041	0.12	0.81	0.59
B20	27/08/2012	2.12	40.93	16.93	2.07	28.58	0.175	0.058	141.6	2.30	13.95	0.004	0.001	0.051	0.09	106	2.12	0.004	0.006	0.31	0.007	0.16	0.019	4.91	1.42	0.095	0.12	0.85	4.63
B20	10/09/2012	2.25	34.85	21.58	1.94	23.67	0.181	0.055	138.6	2.41	13.67	<0.000	0.000	0.056	0.06	<100	3.16	0.003	<0.000	0.28	0.007	0.19	0.034	4.88	1.43	0.002	0.11	0.86	1.16
B20	24/09/2012	1.91	39.18	13.89	0.93	28.05	0.085	0.029	139.5	0.17	11.51	<0.000	0.003	0.048	0.05	102	1.30	0.003	<0.000	0.24	0.006	0.07	0.007	4.78	1.32	<0.000	0.10	0.93	<0.000
B20	08/10/2012	1.99	42.88	19.38	1.87	29.58	0.090	0.032	142.6	0.81	11.50	<0.000	0.003	0.048	0.04	104	1.79	0.004	0.004	0.25	0.004	0.08	0.013	4.88	1.31	<0.000	0.10	0.86	0.66
B20	22/10/2012	2.07	44.70	23.13	1.23	29.10	0.390	0.023	133.9	1.64	14.24	0.004	0.002	0.051	0.05	<100	2.54	0.005	<0.000	0.26	0.005	0.08	0.003	4.89	1.32	<0.000	0.10	0.96	<0.000
B20	05/11/2012	1.97	47.51	21.66	2.99	29.80	0.353	0.027	135.4	2.61	15.03	<0.000	<0.000	0.044	0.07	<100	3.80	0.005	0.004	0.29	0.007	0.06	0.012	4.96	1.42	0.014	0.10	0.88	0.56

Sample ID	Date	As	B	Br	Cu	Li	Mn	Se	Sr	Al	Ba	Be	Cd	Co	Cr	F	Fe	Gd	Hg	Mo	Nd	Ni	Pb	Rb	Sb	Sn	U	V	Zn
B23	14/02/2011	5.11	91.38	55.07	1.22	179.38	0.138	1.224	1166.5	3.57	108.12	0.002	0.006	0.087	0.20	359	1.97	0.007	<0.000	2.57	0.015	0.68	0.018	14.80	0.84	<0.000	9.91	1.69	0.32
B23	28/02/2011	5.05	88.52	55.30	1.17	170.43	0.152	1.216	1157.0	3.29	106.66	0.001	0.005	0.083	0.22	379	1.32	0.006	0.259	2.42	0.013	0.64	0.014	14.66	0.85	<0.000	9.84	1.64	0.43
B23	14/03/2011	4.97	87.46	54.36	1.16	176.19	0.166	1.244	1148.1	3.55	104.74	0.004	0.006	0.082	0.46	353	2.00	0.006	0.011	2.45	0.013	0.76	0.025	14.75	0.74	<0.000	9.76	1.63	0.49
B23	28/03/2011	4.86	91.48	53.54	1.46	184.57	0.220	1.053	1110.9	6.96	99.62	<0.000	0.009	0.082	0.23	336	6.17	0.007	0.007	2.51	0.014	0.56	0.038	13.96	0.90	0.002	9.17	1.58	0.39
B23	11/04/2011	5.21	89.67	54.33	0.73	179.41	<0.000	1.302	1110.2	1.04	98.72	<0.000	0.003	0.074	0.15	336	<0.000	0.002	0.002	2.60	0.000	0.45	<0.000	14.05	0.80	0.013	9.50	1.57	<0.000
B23	26/04/2011	6.44	83.39	59.14	0.14	160.77	4.917	1.175	1200.8	69.28	107.71	0.013	7.130	0.142	0.63	342	121.2	0.024	0.068	2.73	0.099	0.94	0.255	15.20	0.84	<0.000	9.87	1.88	1.74
B23	09/05/2011	4.69	82.61	52.91	0.78	127.02	0.145	1.026	913.5	2.95	90.49	0.003	0.005	0.007	0.08	346	2.35	0.005	0.003	0.16	0.014	0.16	0.034	0.34	0.31	0.004	4.75	0.34	0.90
B23	23/05/2011	4.62	86.01	45.21	1.50	176.53	0.226	1.143	1021.6	2.21	92.84	0.007	0.007	0.079	0.22	320	2.55	0.006	0.006	2.25	0.013	0.61	0.043	13.57	0.86	<0.000	7.82	1.52	1.02
B23	06/06/2011	4.44	85.52	40.70	1.41	153.15	0.487	0.913	876.5	3.90	78.44	0.004	0.007	0.087	1.79	316	7.63	0.005	0.004	2.97	0.012	1.39	0.070	12.52	0.91	<0.000	6.22	1.46	0.66
B23	20/06/2011	4.94	89.74	49.40	1.25	168.25	0.068	1.141	979.4	1.65	93.29	0.006	0.007	0.082	0.19	339	0.88	0.008	<0.000	2.50	0.013	0.58	0.010	13.53	0.92	<0.000	7.76	1.62	1.33
B23	04/07/2011	5.06	95.24	53.15	1.34	174.29	0.153	1.366	1109.1	2.63	107.99	0.003	0.009	0.090	0.26	369	2.66	0.008	0.034	2.55	0.015	0.72	0.025	14.36	0.84	0.034	9.20	1.73	0.63
B23	18/07/2011	4.91	93.62	53.12	1.41	174.05	0.097	1.291	1091.2	1.83	104.01	0.003	0.010	0.085	0.20	348	1.26	0.004	0.001	2.44	0.012	0.67	0.046	14.64	0.86	0.004	8.52	1.67	1.83
B23	16/08/2011	5.29	92.05	59.62	1.33	160.31	0.096	1.206	1148.8	1.44	117.49	0.006	0.010	0.087	0.19	379	0.73	0.007	0.005	2.75	0.012	0.74	0.016	13.89	0.78	<0.000	9.33	1.83	0.36
B23	29/08/2011	5.35	90.58	60.54	1.72	156.95	0.098	1.314	1165.0	1.85	123.31	0.007	0.010	0.093	0.21	384	1.84	0.006	0.142	2.75	0.013	0.77	0.051	14.98	0.83	<0.000	9.87	1.86	0.81
B23	12/09/2011	5.07	79.89	59.60	1.71	135.25	0.050	1.395	1183.9	1.08	118.67	0.022	0.009	0.088	0.19	386	1.67	0.006	<0.000	2.76	0.017	0.69	0.050	14.46	0.78	<0.000	9.29	1.69	0.34
B23	26/09/2011	4.90	95.28	32.12	1.47	170.68	0.137	1.175	948.4	1.99	92.91	0.005	0.009	0.077	0.19	340	1.46	0.006	<0.000	2.51	0.012	0.52	0.027	14.11	1.04	0.001	7.31	1.69	1.31
B23	10/10/2011	5.39	86.51	43.89	0.84	150.37	0.034	1.360	892.9	0.09	89.74	0.001	0.006	0.076	0.14	352	<0.000	0.003	0.001	2.62	0.002	0.49	0.007	13.50	1.10	<0.000	6.65	1.61	0.14
B23	24/10/2011	4.90	87.23	40.74	2.02	146.21	0.295	0.904	752.3	4.39	74.80	0.006	0.009	0.071	0.15	435	10.64	0.005	0.006	2.46	0.013	0.49	0.071	12.41	1.23	0.058	4.86	1.64	1.37
B23	07/11/2011	4.50	65.85	28.21	1.81	93.85	0.296	0.342	369.0	11.78	35.79	0.010	0.017	0.086	0.22	381	9.33	0.012	0.020	2.05	0.018	0.38	0.044	7.79	1.49	0.126	1.77	1.53	0.17
B23	21/11/2011	4.85	88.59	36.80	1.46	152.93	<0.000	0.846	786.9	1.72	77.73	0.004	0.008	0.074	0.16	352	1.02	0.006	0.004	2.41	0.010	0.42	0.011	12.40	1.12	0.023	5.40	1.63	0.49
B23	05/12/2011	4.74	86.63	34.36	1.62	149.47	0.059	0.848	774.5	1.67	76.97	0.008	0.007	0.073	0.13	386	1.19	0.004	0.002	2.37	0.010	0.40	0.006	12.34	1.14	0.001	5.09	1.60	1.01
B23	19/12/2011	4.71	74.43	32.36	1.61	119.83	0.193	0.520	556.1	2.91	50.64	0.007	0.007	0.063	0.12	363	3.51	0.005	0.003	2.13	0.009	0.37	0.018	9.29	1.27	<0.000	2.99	1.46	1.49
B23	03/01/2012	4.72	59.17	16.03	1.62	99.14	0.231	0.436	446.5	2.40	41.69	0.005	0.005	0.058	0.14	342	1.69	0.004	<0.000	1.97	0.007	0.45	0.015	8.75	1.40	0.021	2.29	1.53	2.70
B23	16/01/2012	5.26	75.96	28.19	1.08	142.19	0.006	0.851	626.9	0.56	63.19	0.001	0.003	0.058	0.09	379	<0.000	0.002	<0.000	2.23	0.001	0.30	0.008	10.64	1.28	0.009	4.11	1.57	0.54
B23	30/01/2012	4.99	66.16	29.89	1.62	116.15	0.168	0.793	579.6	2.75	59.49	0.005	0.003	0.064	0.14	372	4.17	0.005	0.004	2.09	0.008	0.46	0.015	9.99	1.40	0.007	3.56	1.65	0.96
B23	13/02/2012	5.10	63.98	32.61	1.49	119.29	0.139	0.783	675.2	1.61	68.64	0.004	0.003	0.060	0.32	330	3.08	0.005	0.001	2.08	0.009	0.58	0.009	10.72	1.25	0.006	4.29	1.64	1.22
B23	27/02/2012	4.18	71.31	27.95	1.41	135.77	0.119	0.591	513.6	1.80	46.07	0.009	0.004	0.054	0.14	351	1.43	0.004	0.002	1.84	0.007	0.24	0.010	8.66	1.20	<0.000	2.97	1.44	0.31
B23	12/03/2012	4.62	76.45	29.22	1.47	140.01	0.157	0.782	660.9	2.57	62.07	0.008	0.008	0.062	0.11	339	1.12	0.005	0.001	2.10	0.009	0.21	0.014	10.10	1.18	0.006	4.40	1.40	0.25
B23	26/03/2012	4.89	83.51	31.93	1.58	140.31	0.386	1.110	883.4	2.28	84.96	<0.000	0.003	0.070	0.10	368	4.59	0.005	0.002	2.44	0.010	0.72	0.010	12.64	1.16	0.012	6.06	1.56	2.26
B23	10/04/2012	4.65	75.21	30.12	1.79	142.93	0.306	1.095	865.7	2.20	82.44	<0.000	0.006	0.069	0.16	361	4.82	0.006	0.001	2.29	0.011	0.52	0.017	12.28	1.07	<0.000	5.91	1.45	8.14
B23	23/04/2012	4.35	58.96	20.23	1.87	103.10	0.087	0.745	624.4	2.16	57.66	<0.000	0.005	0.062	0.10	280	1.65	0.005	0.001	2.04	0.008	0.44	0.053	9.60	1.15	0.063	3.80	1.32	0.64
B23	09/05/2012	4.49	63.36	27.97	2.50	122.42	0.326	0.836	692.4	2.86	68.26	0.016	0.008	0.064	0.31	289	2.40	0.004	0.001	2.23	0.011	0.42	0.066	10.00	1.09	<0.000	4.43	1.37	1.25
B23	21/05/2012	4.54	92.40	35.46	1.28	188.03	0.026	0.873	908.0	2.45	92.83	0.003	0.010	0.063	0.16	337	0.97	0.006	<0.000	2.34	0.012	0.65	0.017	12.11	0.91	<0.000	6.54	1.49	0.88
B23	04/06/2012	4.49	77.41	35.01	1.19	156.95	0.180	0.798	811.1	1.12	76.82	0.001	0.007	0.068	0.16	295	2.47	0.005	<0.000	2.30	0.008	0.35	0.007	10.73	0.88	<0.000	5.57	1.48	0.42
B23	18/06/2012	5.21	87.40	54.65	1.42	176.59	0.049	1.015	1061.1	1.93	100.67	<0.000	0.005	0.064	0.19	370	2.24	0.007	0.000	2.58	0.013	0.28	0.002	12.99	0.96	0.025	7.48	1.76	2.82
B23	02/07/2012	5.44	94.20	41.15	1.27	170.64	0.074	1.065	1095.9	2.12	108.25	<0.000	0.002	0.086	0.29	305	1.76	0.008	0.003	2.86	0.014	0.72	0.029	14.51	0.98	<0.000	8.69	1.72	0.65
B23	16/07/2012	5.39	83.13	38.97	1.69	152.06	0.165	1.110	1095.4	3.79	115.14	<0.000	0.002	0.087	0.22	389	3.98	0.008	0.006	2.92	0.019	1.03	0.041	13.97	1.01	<0.000	8.76	1.76	2.11
B23	30/07/2012	5.48	98.40	46.69	1.51	183.88	0.731	1.085	1061.0	1.69	110.96	0.006	0.010	0.093	0.20	339	1.71	0.007	0.004	3.07	0.015	0.40	0.036	14.01	0.91	0.013	8.65	1.71	0.84
B23	13/08/2012	5.12	89.26	38.58	1.80	151.67	0.165	1.164	1046.9	2.89	108.67	0.007	0.008	0.088	0.20	432	2.37	0.008	0.004	2.84	0.015	0.30	0.046	13.84	0.98	0.032	8.67	1.63	1.74
B23	27/08/2012	5.54	94.30	47.06	1.32	155.58	0.121	1.111	1088.3	3.40	118.81	<0.000	0.006	0.093	0.21	371	2.17	0.007	0.004	3.30	0.016	0.66	0.018	13.97	1.00	0.023	8.89	1.76	1.87
B23	10/09/2012	5.27	101.56	46.14	1.73	175.34	0.086	1.055	1035.5	1.97	109.09	0.008	0.009	0.099	0.17	381	1.75	0.008	<0.000	3.19	0.013	0.65	0.015	13.42	0.87	0.032	8.50	1.82	0.94
B23	24/09/2012	5.39	99.88	37.94	1.24	177.19	0.008	1.219	1110.3	1.97	113.33	<0.000	0.007	0.092	0.17	362	0.08	0.008	<0.000	3.07	0.014	0.55	<0.000	14.68	0.88	<0.000	8.63	1.81	<0.000
B23	08/10/2012	5.01	99.89	39.49	1.43	189.68	0.077	1.156	1070.0	1.20	106.20	0.000	0.009	0.077	0.18	360	2.10	0.007	0.007	2.53	0.014	0.46	0.014	14.53	0.96	<0.000	7.81	1.72	1.05
B23	22/10/2012	4.97	99.76	38.85	1.34	187.79	0.159	1.211	994.2	2.59	96.68	0.002	0.008	0.088	0.19	364	1.73	0.006	0.002	2.84	0.014	0.50	0.006	13.57	0.92	<0.000	7.73	1.73	0.15
B23	05/11/2012	4.98	101.64	38.71	1.61	186.46	0.154	1.102	945.7	1.83	92.66	<0.000	0.004	0.074	0.17	359	2.30	0.006	0.008	2.76	0.013	0.44	0.020	13.47	1.05	0.016	7.45	1.68	1.42

Sample ID	Date	As	B	Br	Cu	Li	Mn	Se	Sr	Al	Ba	Be	Cd	Co	Cr	F	Fe	Gd	Hg	Mo	Nd	Ni	Pb	Rb	Sb	Sn	U	V	Zn
B26	14/02/2011	4.11	22.90	16.08	1.19	23.69	0.095	0.046	131.8	4.83	8.61	0.003	0.001	0.045	0.06	<100	3.43	0.003	0.001	0.25	0.005	0.15	0.013	4.22	1.12	<0.000	0.20	0.91	0.22
B26	28/02/2011	4.04	21.00	18.36	1.31	23.77	0.776	0.052	134.1	12.42	8.80	0.004	0.004	0.041	0.10	<100	15.05	0.004	0.016	0.22	0.011	0.20	0.161	4.20	1.04	<0.000	0.18	0.88	2.79
B26	14/03/2011	3.89	21.11	18.74	1.16	24.90	0.206	0.050	142.0	3.59	8.79	0.005	0.004	0.040	0.29	101	2.60	0.003	0.004	0.30	0.006	0.26	0.018	4.23	1.03	0.029	0.18	0.83	0.30
B26	28/03/2011	3.90	22.42	18.06	1.21	24.34	0.109	0.037	135.1	3.79	8.50	<0.000	0.005	0.042	0.08	<100	3.62	0.003	0.022	0.21	0.006	0.04	0.012	3.92	1.03	0.000	0.19	0.82	0.30
B26	11/04/2011	4.08	20.36	17.19	1.15	22.88	0.051	0.036	126.5	0.77	8.22	0.000	0.001	0.039	0.04	<100	0.50	0.002	0.083	0.26	0.002	0.15	0.039	3.79	1.08	<0.000	0.05	0.71	0.47
B26	26/04/2011	3.92	20.14	18.11	1.84	20.64	0.881	0.042	129.8	4.06	8.16	0.004	0.003	0.053	0.32	104	15.68	0.002	0.001	0.34	0.006	0.32	0.011	4.10	1.05	<0.000	0.18	0.84	0.16
B26	09/05/2011	3.88	25.26	22.67	1.37	25.93	0.263	0.044	137.0	3.72	8.63	0.003	0.003	0.041	0.07	<100	2.73	0.002	0.004	0.22	0.005	0.17	0.035	4.08	1.03	<0.000	0.18	0.84	0.49
B26	23/05/2011	4.38	33.49	32.23	5.40	29.68	2.370	0.043	158.0	17.17	11.54	0.011	0.015	0.081	0.18	<100	222.47	0.008	0.059	0.20	0.025	0.34	N.A	4.98	1.13	0.096	0.22	1.08	13.91
B26	06/06/2011	4.70	54.51	37.52	3.32	34.49	1.568	0.047	178.3	7.14	14.32	0.008	0.017	0.085	2.88	<100	27.03	0.008	0.010	1.40	0.013	1.67	0.148	6.67	1.36	0.020	0.25	1.18	5.66
B26	20/06/2011	4.77	54.10	36.61	3.41	34.83	0.499	0.049	173.4	12.02	13.75	0.047	0.008	0.069	0.04	119	20.10	0.032	<0.000	0.24	0.229	0.24	0.158	7.18	1.39	0.001	0.21	1.25	1.02
B26	04/07/2011	4.64	55.31	36.53	2.51	35.54	1.671	0.047	176.7	7.48	14.70	0.009	0.009	0.061	0.04	106	16.09	0.007	0.008	0.25	0.013	0.29	0.037	7.19	1.38	0.019	0.22	1.23	0.42
B26	18/07/2011	4.58	55.31	37.37	2.73	34.10	1.691	0.036	172.0	2.65	14.56	0.004	0.010	0.079	0.05	<100	36.88	0.005	0.000	0.26	0.009	0.32	0.120	7.15	1.37	0.000	0.21	1.26	2.70
B26	16/08/2011	4.55	55.12	35.48	2.44	31.33	0.928	0.043	160.9	3.81	14.06	0.007	0.010	0.062	0.03	115	32.59	0.004	0.007	0.31	0.011	0.32	0.066	7.12	1.36	<0.000	0.18	1.24	3.71
B26	29/08/2011	4.55	54.81	37.00	3.08	30.63	1.932	0.047	158.4	3.12	13.66	0.077	0.010	0.082	0.03	145	55.07	0.004	0.008	0.33	0.010	0.29	0.062	7.25	1.34	<0.000	0.17	1.31	0.69
B26	12/09/2011	4.95	47.68	37.74	5.39	24.99	0.533	0.050	154.9	1.87	12.85	0.055	0.011	0.070	0.01	128	5.44	0.005	<0.000	0.36	0.011	0.26	0.036	7.31	1.41	<0.000	0.15	1.36	0.46
B26	26/09/2011	5.20	62.67	19.02	2.66	37.78	0.602	0.048	161.2	2.67	14.29	0.004	0.013	0.067	0.02	102	8.44	0.006	<0.000	0.41	0.010	0.24	0.019	7.90	1.75	<0.000	0.17	1.48	0.71
B26	10/10/2011	5.25	59.87	32.01	3.27	34.29	0.795	0.046	152.4	3.47	13.50	0.006	0.011	0.064	0.02	110	4.45	0.005	0.002	0.45	0.008	0.25	0.047	7.69	1.80	0.094	0.14	1.54	0.70
B26	24/10/2011	5.33	56.02	28.95	2.77	34.10	0.980	0.055	154.3	6.73	13.78	0.008	0.010	0.061	0.03	118	8.99	0.007	0.005	0.44	0.013	0.26	0.158	7.62	1.78	0.033	0.14	1.47	0.66
B26	07/11/2011	4.64	51.02	22.24	1.98	32.55	0.052	0.041	151.4	2.43	12.86	0.005	0.012	0.056	0.05	121	3.02	0.006	0.010	0.38	0.008	0.17	0.017	6.85	1.60	0.044	0.14	1.28	0.68
B26	21/11/2011	5.02	45.10	13.72	2.02	29.98	0.235	0.049	130.1	4.79	10.27	0.006	0.006	0.057	0.05	117	7.20	0.005	0.001	0.37	0.009	0.16	0.018	5.90	1.54	0.010	0.11	1.29	0.58
B26	05/12/2011	4.71	37.70	12.61	1.71	26.75	0.290	0.036	115.0	4.51	8.72	0.008	0.005	0.055	0.05	<100	4.04	0.005	0.002	0.36	0.009	0.19	0.010	5.26	1.43	<0.000	0.09	1.20	1.61
B26	19/12/2011	4.51	31.62	15.58	1.49	24.33	0.077	0.031	112.5	3.30	8.18	0.006	0.007	0.040	0.07	112	1.80	0.004	0.002	0.30	0.006	0.13	0.011	4.59	1.24	<0.000	0.09	1.07	0.46
B26	03/01/2012	4.78	26.01	<0.000	2.02	22.55	0.263	0.049	101.7	5.87	7.27	0.006	0.005	0.055	0.08	126	7.90	0.004	<0.000	0.33	0.009	0.27	0.033	4.33	1.31	0.009	0.10	1.07	5.08
B26	16/01/2012	4.53	26.22	3.54	1.64	25.42	0.107	0.050	93.8	1.21	6.60	0.008	0.002	0.039	0.05	122	0.46	0.002	<0.000	0.24	0.003	0.04	0.001	3.81	1.22	<0.000	0.02	0.75	<0.000
B26	30/01/2012	4.17	19.88	9.68	2.36	19.37	0.155	0.036	95.8	5.59	6.89	0.006	0.003	0.051	0.10	<100	3.41	0.005	0.003	0.29	0.009	0.28	0.036	3.85	1.25	0.041	0.08	0.95	1.40
B26	27/02/2012	3.75	21.42	6.80	1.59	21.58	0.306	0.057	134.5	2.01	8.30	0.000	0.010	0.044	0.01	<100	3.17	0.005	0.001	0.23	0.007	0.30	0.007	4.08	0.98	0.003	0.14	0.72	4.78
B26	12/03/2012	3.76	25.18	8.81	1.55	23.83	0.721	0.036	120.7	5.98	7.52	0.009	0.012	0.054	0.09	<100	8.98	0.006	0.000	0.23	0.009	<0.000	0.013	3.55	0.90	0.016	0.14	0.67	2.52
B26	26/03/2012	3.90	25.79	5.10	1.77	21.38	0.371	0.062	128.2	2.08	7.89	<0.000	0.005	0.054	0.02	<100	4.59	0.005	0.001	0.25	0.005	0.31	0.004	3.85	1.02	0.012	0.15	0.75	2.32
B26	10/04/2012	3.83	26.69	5.15	2.03	22.18	0.092	0.051	128.7	3.74	8.23	<0.000	0.007	0.041	0.07	102	6.81	0.005	0.001	0.23	0.007	0.15	0.048	3.91	0.98	<0.000	0.17	0.71	0.43
B26	23/04/2012	3.88	30.72	4.25	2.04	21.06	0.435	0.043	133.5	2.29	8.64	<0.000	0.007	0.053	0.09	100	6.37	0.004	0.001	0.23	0.006	0.31	0.016	4.27	1.03	0.035	0.18	0.76	2.18
B26	09/05/2012	4.23	29.77	5.27	1.79	21.84	0.540	0.067	113.9	3.63	7.90	0.005	0.006	0.054	0.45	102	8.99	0.004	0.000	0.37	0.006	0.36	0.026	4.07	1.12	0.008	0.14	0.84	3.00
B26	04/06/2012	4.30	38.00	9.25	2.09	25.01	0.470	0.048	124.1	6.94	8.66	0.007	0.006	0.055	0.10	<100	12.59	0.005	0.000	0.27	0.011	0.22	0.081	4.25	1.16	0.005	0.16	0.80	5.57
B26	18/06/2012	4.23	35.07	18.56	2.38	25.83	0.652	0.060	133.2	3.62	9.38	<0.000	<0.000	0.049	0.07	<100	22.05	0.005	<0.000	0.26	0.008	<0.000	0.012	4.41	1.17	0.060	0.18	0.93	0.93
B26	02/07/2012	4.36	35.54	4.68	1.85	25.97	0.119	0.090	134.0	4.23	9.71	<0.000	<0.000	0.047	0.09	103	4.09	0.005	0.002	0.26	0.007	0.22	0.033	4.76	1.23	<0.000	0.21	0.84	0.79
B26	16/07/2012	4.10	31.28	7.01	2.66	21.70	0.227	0.079	134.7	4.40	10.19	<0.000	<0.000	0.045	0.06	<100	6.96	0.003	0.004	0.25	0.009	0.44	0.085	4.86	1.26	<0.000	0.23	0.89	1.97
B26	30/07/2012	4.35	40.01	19.37	1.74	27.82	0.231	0.069	135.1	2.73	10.56	0.008	0.005	0.043	0.05	<100	6.79	0.005	0.001	0.26	0.008	<0.000	0.021	4.91	1.21	0.005	0.22	0.88	0.50
B26	13/08/2012	4.10	36.77	13.73	1.90	23.63	0.177	0.079	146.3	3.11	11.54	0.006	0.004	0.043	0.05	106	3.39	0.005	0.002	0.25	0.007	<0.000	0.045	5.26	1.17	0.000	0.22	0.84	1.31
B26	27/08/2012	4.47	43.36	19.36	1.84	27.70	0.967	0.051	154.6	2.16	11.94	<0.000	0.002	0.059	0.05	<100	40.44	0.005	<0.000	0.27	0.008	0.16	<0.000	5.87	1.40	<0.000	0.21	1.02	0.69
B26	10/09/2012	4.33	46.04	21.83	1.59	31.12	0.185	0.073	143.6	2.57	11.43	0.010	0.005	0.041	0.02	102	5.83	0.005	<0.000	0.26	0.007	0.15	0.011	5.40	1.22	0.013	0.21	1.04	0.80
B26	24/09/2012	3.74	42.66	13.52	1.39	29.42	0.138	0.093	166.0	0.83	12.82	<0.000	0.005	0.035	0.05	115	8.88	0.004	<0.000	0.23	0.008	0.08	0.007	5.72	1.23	<0.000	0.27	0.92	<0.000
B26	08/10/2012	4.51	54.84	21.63	2.60	32.80	0.693	0.025	137.1	5.56	12.01	0.004	0.008	0.046	0.05	111	4.51	0.005	0.002	0.29	0.012	0.15	0.018	6.37	1.49	<0.000	0.14	1.19	0.96
B26	22/10/2012	4.44	54.27	20.05	1.65	34.87	0.155	0.033	142.5	3.94	13.08	0.005	0.007	0.041	0.07	111	3.32	0.005	<0.000	0.27	0.008	0.09	0.016	6.51	1.45	<0.000	0.14	1.26	0.37
B26	05/11/2012	4.39	55.30	20.01	1.46	33.71	0.227	0.024	143.4	3.65	12.06	<0.000	0.002	0.039	0.06	<100	5.02	0.004	0.002	0.29	0.008	0.06	0.008	6.42	1.47	<0.000	0.15	1.13	0.42

Sample ID	Date	As	B	Br	Cu	Li	Mn	Se	Sr	Al	Ba	Be	Cd	Co	Cr	F	Fe	Gd	Hg	Mo	Nd	Ni	Pb	Rb	Sb	Sn	U	V	Zn
B27	14/02/2011	1.97	58.67	46.31	0.90	35.57	0.266	0.555	362.6	3.92	26.16	0.003	0.003	0.051	0.16	<100	4.14	0.003	<0.000	0.69	0.006	0.25	0.014	9.45	0.90	<0.000	2.70	1.00	0.68
B27	28/02/2011	1.94	55.52	47.58	1.10	34.79	0.161	0.549	375.8	2.91	26.67	0.005	0.002	0.049	0.15	<100	28.14	0.003	0.101	0.62	0.006	0.25	0.018	9.20	0.86	0.017	2.91	0.95	0.46
B27	14/03/2011	1.91	55.29	43.94	0.85	34.64	0.230	0.555	386.2	3.47	26.77	0.005	0.003	0.047	0.37	119	23.71	0.003	0.004	0.67	0.007	0.35	0.022	9.22	0.71	0.009	2.92	0.93	0.33
B27	28/03/2011	1.93	59.09	51.94	1.04	36.52	0.099	0.453	387.6	3.66	27.42	<0.000	0.004	0.049	0.12	108	2.98	0.003	0.032	0.65	0.006	0.14	0.008	9.10	0.85	0.001	3.03	0.97	0.46
B27	11/04/2011	1.05	51.37	56.91	0.85	34.91	0.041	0.616	379.1	0.69	33.12	0.000	0.004	0.045	0.12	108	0.26	0.001	0.031	0.64	0.001	0.21	0.010	9.05	1.02	<0.000	2.24	0.91	0.33
B27	26/04/2011	0.71	56.11	56.24	1.23	3.81	0.177	0.679	354.8	3.29	21.59	0.003	0.006	0.011	0.42	109	4.17	0.003	0.013	0.20	0.006	0.21	0.009	0.92	0.37	<0.000	1.76	0.40	0.23
B27	09/05/2011	1.93	59.03	57.02	1.55	39.06	0.192	0.692	420.0	4.61	28.96	0.004	0.007	0.048	0.17	113	9.64	0.003	0.006	0.62	0.007	0.31	0.055	9.67	0.81	0.003	3.54	0.99	3.03
B27	23/05/2011	1.79	58.87	60.39	1.65	40.31	0.501	0.762	428.1	3.47	29.71	0.005	0.007	0.047	0.17	102	3.51	0.004	0.324	0.58	0.008	0.28	0.055	9.86	0.81	0.001	3.59	0.93	4.57
B27	06/06/2011	0.90	52.37	57.77	0.72	12.92	0.428	0.236	453.3	3.03	19.46	0.007	0.004	0.026	2.83	104	6.79	0.003	0.073	1.38	0.007	1.53	0.008	2.74	0.51	<0.000	2.13	0.58	0.46
B27	20/06/2011	1.96	62.26	64.78	2.86	41.81	0.745	0.794	449.1	5.37	32.28	0.006	0.007	0.053	0.20	122	13.25	0.005	<0.000	0.61	0.013	0.35	0.248	10.70	0.86	0.009	4.03	1.03	5.47
B27	04/07/2011	1.81	61.86	56.59	1.08	39.71	0.552	0.748	422.3	3.71	30.63	0.003	0.008	0.052	0.18	109	14.05	0.003	0.005	0.59	0.009	0.29	0.055	10.02	0.82	0.009	3.83	0.98	0.56
B27	18/07/2011	1.89	58.67	54.52	2.13	38.26	0.934	0.585	404.9	1.96	31.48	0.003	0.007	0.054	0.15	122	25.20	0.003	0.000	0.58	0.007	0.29	0.040	9.50	0.86	<0.000	3.59	0.98	1.02
B27	16/08/2011	2.06	56.66	48.79	1.34	30.84	0.709	0.580	359.8	2.16	31.75	0.006	0.005	0.053	0.12	123	12.99	0.003	<0.000	0.64	0.007	0.28	0.027	8.59	0.87	<0.000	2.83	1.00	0.53
B27	29/08/2011	2.17	57.06	51.30	1.49	31.46	0.722	0.648	381.2	4.67	34.14	0.010	0.007	0.055	0.13	133	10.84	0.004	0.021	0.66	0.010	0.31	0.095	8.98	0.86	<0.000	3.16	1.11	8.28
B27	12/09/2011	2.17	54.10	64.66	1.11	29.00	0.184	0.837	479.3	1.42	42.03	0.005	0.007	0.046	0.13	141	6.73	0.003	<0.000	0.68	0.007	0.30	0.020	10.25	0.78	<0.000	4.53	1.09	0.29
B27	26/09/2011	2.19	69.13	49.49	2.11	40.85	0.270	0.864	490.8	3.63	46.68	0.005	0.006	0.048	0.15	127	3.92	0.004	<0.000	0.65	0.009	0.30	0.058	10.87	0.96	<0.000	5.23	1.09	1.37
B27	10/10/2011	2.33	65.41	60.78	0.54	39.30	0.024	1.031	528.3	0.17	49.64	0.001	0.004	0.046	0.11	<100	<0.000	0.001	<0.000	0.66	0.002	0.31	<0.000	11.28	0.95	<0.000	6.13	1.00	0.05
B27	24/10/2011	2.17	71.28	67.09	1.21	42.50	0.085	0.882	578.9	1.57	57.33	0.006	0.006	0.050	0.15	<100	2.18	0.004	0.005	0.68	0.011	0.35	0.016	11.96	1.02	0.024	6.84	1.08	0.20
B27	07/11/2011	2.26	68.19	57.66	1.37	39.76	0.242	0.766	479.2	1.88	44.03	0.008	0.007	0.059	0.19	112	4.21	0.005	0.008	0.64	0.009	0.27	0.026	10.77	1.01	0.031	5.02	1.08	0.45
B27	21/11/2011	2.06	67.61	58.48	1.06	40.36	0.085	0.788	497.9	1.31	46.18	0.006	0.007	0.046	0.15	109	10.80	0.004	0.003	0.59	0.008	0.22	0.008	10.95	0.95	0.010	5.09	1.04	0.12
B27	05/12/2011	2.05	65.27	46.76	1.56	36.74	0.010	0.663	447.6	1.44	39.76	0.007	0.005	0.044	0.14	108	0.47	0.003	0.002	0.60	0.009	0.19	0.006	9.84	0.95	<0.000	4.26	0.98	0.10
B27	19/12/2011	2.05	56.08	37.39	1.65	31.52	0.200	0.430	335.5	1.97	28.92	0.009	0.004	0.044	0.15	116	2.58	0.004	0.002	0.63	0.005	0.24	0.010	8.42	0.99	<0.000	2.48	1.01	0.16
B27	03/01/2012	2.20	53.92	26.92	2.48	31.41	0.281	0.497	352.5	4.19	32.13	0.007	0.006	0.053	0.14	107	6.27	0.003	<0.000	0.66	0.006	0.39	0.023	8.97	1.08	0.003	2.85	1.06	1.66
B27	16/01/2012	2.15	61.25	31.56	0.70	35.94	<0.000	0.536	335.1	0.18	28.76	0.002	0.003	0.040	0.11	130	0.17	0.001	<0.000	0.67	0.001	0.19	<0.000	8.58	1.01	<0.000	3.65	1.01	0.74
B27	30/01/2012	2.38	55.77	39.88	1.43	30.80	0.048	0.515	350.8	1.29	31.42	0.006	0.002	0.051	0.13	128	1.44	0.004	0.003	0.68	0.005	0.34	0.012	8.88	1.07	0.033	2.94	1.11	0.40
B27	13/02/2012	2.18	41.98	34.64	1.30	25.65	0.083	0.339	279.4	1.78	22.95	0.007	0.002	0.052	0.21	<100	2.08	0.003	0.008	0.70	0.005	0.41	0.020	7.97	1.13	0.383	1.76	1.02	0.18
B27	27/02/2012	2.04	53.10	19.55	1.35	26.09	0.132	0.318	260.8	1.45	20.01	<0.000	0.001	0.043	0.07	118	0.94	0.002	0.002	0.75	0.005	0.32	0.013	7.92	1.12	<0.000	1.47	1.00	0.62
B27	12/03/2012	2.04	57.90	22.16	1.86	31.76	0.197	0.224	234.5	2.56	17.19	0.013	0.005	0.053	0.09	113	1.28	0.002	0.001	0.72	0.005	0.01	0.038	7.54	1.05	0.004	1.20	0.99	1.99
B27	26/03/2012	2.09	55.29	16.94	1.23	28.92	0.070	0.307	254.9	2.10	17.67	<0.000	0.000	0.051	0.05	100	2.87	0.003	0.001	0.79	0.005	0.32	0.040	8.13	1.10	0.006	1.37	1.05	0.20
B27	10/04/2012	2.01	51.59	14.43	1.86	28.32	0.076	0.267	232.2	1.45	15.78	0.007	0.016	0.065	0.12	141	1.59	0.002	0.001	0.78	0.004	0.18	0.021	7.62	1.04	0.319	1.18	1.00	0.22
B27	23/04/2012	1.94	46.79	9.78	2.18	24.62	0.322	0.193	209.8	2.83	14.40	<0.000	0.002	0.050	0.11	147	25.46	0.003	0.002	0.76	0.004	0.23	0.072	7.28	1.06	0.028	0.93	0.94	1.10
B27	09/05/2012	2.01	46.44	12.94	2.52	26.23	0.072	0.159	182.3	2.57	12.71	0.029	0.005	0.055	0.33	128	3.02	0.002	0.001	0.85	0.005	0.27	0.015	6.57	1.06	0.055	0.73	1.01	0.55
B27	21/05/2012	1.92	57.93	8.81	1.51	31.06	0.144	0.135	176.3	3.39	13.31	0.006	0.003	0.049	0.11	154	2.38	0.003	<0.000	0.77	0.004	0.28	0.028	6.62	1.00	<0.000	0.67	1.01	0.40
B27	04/06/2012	2.02	52.74	12.46	0.81	28.15	0.050	0.114	162.0	1.65	11.99	<0.000	0.003	0.046	0.11	155	2.71	0.001	<0.000	0.79	0.002	0.02	0.023	6.02	0.91	<0.000	0.57	1.00	0.50
B27	18/06/2012	2.15	53.34	22.40	1.11	27.03	0.267	0.111	178.1	6.61	12.57	0.001	<0.000	0.064	0.12	142	10.24	0.004	<0.000	0.83	0.006	<0.000	<0.000	6.30	1.07	0.013	0.59	1.04	0.94
B27	02/07/2012	2.17	56.19	10.54	0.98	27.80	0.475	0.129	189.5	4.88	14.46	<0.000	<0.000	0.050	0.14	142	11.40	0.003	0.001	0.86	0.005	0.18	0.207	6.91	1.14	<0.000	0.72	1.05	0.32
B27	16/07/2012	2.19	46.06	11.44	1.25	22.07	0.293	0.156	191.0	2.12	16.36	<0.000	<0.000	0.050	0.12	145	2.93	0.004	0.005	0.82	0.006	0.39	0.027	6.69	1.12	<0.000	0.75	0.99	1.46
B27	30/07/2012	2.30	58.84	28.88	1.33	27.33	1.527	0.207	208.9	3.95	20.53	0.009	0.007	0.066	0.14	126	33.97	0.004	0.002	0.87	0.006	<0.000	0.052	6.89	1.11	0.030	0.83	1.02	0.88
B27	13/08/2012	2.26	54.49	18.29	1.10	24.44	0.928	0.219	226.7	3.24	22.59	0.007	0.005	0.058	0.14	144	20.76	0.002	0.004	0.75	0.004	<0.000	0.017	7.03	1.08	0.015	0.88	0.99	0.86
B27	27/08/2012	2.42	57.73	20.90	1.28	27.33	0.947	0.216	225.3	2.14	22.43	<0.000	0.002	0.064	0.12	138	34.47	0.004	0.003	0.77	0.005	0.17	0.010	7.37	1.23	0.037	0.83	1.05	0.53
B27	10/09/2012	2.13	58.69	25.81	1.02	28.62	1.466	0.180	212.4	3.23	20.95	0.008	0.005	0.067	0.09	136	38.13	0.003	<0.000	0.72	0.005	0.14	0.004	6.91	1.05	0.006	0.79	1.01	0.18
B27	24/09/2012	2.30	56.07	15.98	0.95	26.96	1.316	0.198	219.2	0.93	22.33	0.001	0.005	0.068	0.11	148	20.65	0.002	<0.000	0.71	0.005	0.11	0.015	7.31	1.12	<0.000	0.81	1.10	<0.000
B27	08/10/2012	2.29	57.75	17.22	1.20	27.09	0.109	0.193	215.4	1.13	20.12	0.000	0.005	0.047	0.11	141	2.41	0.002	0.004	0.73	0.005	0.08	0.016	7.22	1.14	<0.000	0.78	1.16	1.04
B27	22/10/2012	2.27	55.75	19.14	1.06	27.57	0.811	0.158	198.7	1.32	18.28	0.002	0.004	0.047	0.11	137	1.56	0.003	0.001	0.69	0.004	0.06	0.006	6.74	1.10	<0.000	0.70	1.13	<0.000
B27	05/11/2012	2.44	57.25	19.13	1.56	28.38	0.118	0.169	194.4	1.58	18.79	<0.000	0.001	0.045	0.10	146	3.11	0.001	0.006	0.72	0.004	0.09	0.001	6.79	1.19	0.005	0.69	1.20	0.24

Sample ID	Date	As	B	Br	Cu	Li	Mn	Se	Sr	Al	Ba	Be	Cd	Co	Cr	F	Fe	Gd	Hg	Mo	Nd	Ni	Pb	Rb	Sb	Sn	U	V	Zn
B29	14/02/2011	4.11	114.73	64.82	1.17	96.08	0.250	0.598	911.5	5.81	87.06	0.003	0.006	0.087	0.19	316	4.78	0.005	0.004	3.48	0.013	0.57	0.056	17.34	0.48	<0.000	9.88	1.56	0.92
B29	28/02/2011	4.17	113.46	65.31	1.30	94.93	0.301	0.642	932.5	4.34	87.60	0.003	0.006	0.087	0.21	344	2.68	0.005	0.055	3.37	0.013	0.85	0.061	17.75	0.47	0.006	9.92	1.54	0.93
B29	14/03/2011	4.02	112.16	61.16	1.04	92.88	0.104	0.657	922.2	3.56	87.92	0.002	0.005	0.083	0.41	393	2.21	0.005	0.032	3.26	0.012	0.64	0.016	17.52	0.39	0.008	9.97	1.46	0.39
B29	28/03/2011	4.48	120.49	59.78	0.72	N.A	0.148	0.809	915.9	4.06	64.74	0.000	0.004	0.018	0.08	432	2.06	0.005	0.125	0.56	0.013	0.04	0.022	2.03	0.19	0.003	4.53	0.48	0.30
B29	11/04/2011	4.45	92.25	52.70	0.37	77.26	<0.000	0.511	944.4	0.34	4.63	<0.000	0.003	0.062	0.05	439	0.23	0.001	0.003	2.90	<0.000	0.27	<0.000	14.44	0.33	<0.000	1.25	1.26	<0.000
B29	26/04/2011	5.65	100.58	64.04	0.60	84.48	0.320	0.641	922.4	30.77	87.18	0.009	4.461	0.115	0.51	431	62.32	0.013	0.058	3.52	0.052	0.74	0.145	17.36	0.40	<0.000	10.03	1.64	1.61
B29	09/05/2011	4.07	110.00	60.87	1.22	101.60	0.259	0.783	912.4	4.18	87.44	0.003	0.006	0.089	0.18	453	5.81	0.005	0.012	3.36	0.012	0.58	0.034	16.37	0.46	<0.000	9.94	1.48	0.20
B29	23/05/2011	3.96	109.64	62.18	1.40	102.66	0.217	0.700	914.4	3.03	85.87	0.003	0.006	0.081	0.17	400	3.07	0.005	0.073	3.20	0.011	0.51	0.063	17.17	0.44	0.000	9.82	1.47	0.84
B29	06/06/2011	3.86	114.81	59.84	1.81	96.19	0.565	0.681	895.9	3.54	85.56	0.018	0.008	0.096	2.96	387	7.42	0.005	0.007	4.28	0.012	1.98	0.033	16.54	0.44	<0.000	9.99	1.52	0.67
B29	20/06/2011	4.19	118.67	68.46	2.00	105.56	0.295	0.751	955.3	2.73	91.84	0.014	0.008	0.085	0.17	416	4.41	0.007	0.000	3.52	0.014	0.56	0.203	17.94	0.48	0.173	10.68	1.56	1.17
B29	04/07/2011	4.05	122.03	64.79	1.01	101.25	0.169	0.671	923.9	3.01	88.16	0.002	0.008	0.084	0.17	470	3.85	0.005	0.017	3.45	0.012	0.56	0.035	17.69	0.44	0.005	10.13	1.57	3.42
B29	18/07/2011	4.36	118.67	64.92	1.06	N.A	0.531	0.526	904.0	12.85	97.10	0.005	0.009	0.017	0.14	483	10.74	0.007	0.001	0.23	0.021	0.21	0.276	0.96	0.15	0.011	5.69	0.23	11.18
B29	16/08/2011	4.16	117.68	70.04	1.22	94.91	0.211	0.556	900.9	1.62	95.38	0.007	0.010	0.077	0.16	474	2.20	0.004	0.017	3.47	0.012	0.58	0.037	16.66	0.44	<0.000	9.00	1.60	0.41
B29	29/08/2011	4.03	114.78	67.38	1.54	92.28	0.092	0.613	916.3	1.95	90.52	0.013	0.009	0.083	0.19	433	2.42	0.005	0.041	3.56	0.012	0.58	0.039	16.78	0.43	<0.000	9.08	1.57	1.17
B29	12/09/2011	4.11	116.12	66.30	1.34	101.62	0.103	0.693	917.6	1.68	92.31	0.008	0.009	0.094	0.11	586	4.61	0.005	0.019	3.84	0.012	0.59	0.021	16.40	0.45	0.015	9.18	1.59	0.35
B29	26/09/2011	4.17	121.39	48.51	1.30	112.04	0.129	0.744	963.2	1.87	101.13	0.003	0.011	0.080	0.13	483	1.53	0.007	<0.000	3.64	0.012	0.47	0.023	18.42	0.52	<0.000	10.87	1.62	0.79
B29	10/10/2011	4.27	118.29	61.00	0.39	110.30	<0.000	0.940	829.8	0.17	79.68	<0.000	0.004	0.082	0.16	423	<0.000	0.001	<0.000	3.86	0.000	0.42	0.002	17.99	0.54	0.017	11.01	1.61	0.01
B29	24/10/2011	4.41	126.16	64.56	1.32	114.34	0.086	0.810	1036.8	2.61	110.87	0.005	0.009	0.087	0.16	430	3.63	0.006	0.005	3.94	0.014	0.57	0.037	19.65	0.57	0.027	11.51	1.67	0.74
B29	07/11/2011	4.52	126.51	60.15	1.37	108.00	0.060	0.606	938.2	1.52	101.53	0.006	0.010	0.091	0.19	462	1.01	0.007	0.007	3.66	0.013	0.53	0.065	18.23	0.52	0.030	10.70	1.70	0.55
B29	21/11/2011	4.38	129.54	61.00	1.05	107.67	0.062	0.560	924.1	1.94	100.57	0.004	0.009	0.075	0.14	492	3.09	0.006	0.002	3.56	0.011	0.46	0.013	18.39	0.51	0.002	10.15	1.60	0.15
B29	05/12/2011	4.34	126.24	65.48	1.26	108.62	<0.000	0.625	922.1	1.41	98.23	0.009	0.009	0.076	0.17	457	0.04	0.006	0.016	3.63	0.013	0.48	0.012	17.85	0.50	0.115	9.21	1.62	0.12
B29	19/12/2011	4.15	117.58	64.31	1.55	100.56	0.074	0.610	884.5	6.64	95.88	0.009	0.008	0.074	0.18	461	4.76	0.006	0.002	3.51	0.011	0.49	0.014	17.43	0.48	<0.000	9.02	1.52	0.13
B29	03/01/2012	4.35	113.34	54.00	1.64	102.28	0.086	0.644	927.2	2.61	98.35	0.007	0.008	0.085	0.18	451	3.98	0.005	0.001	3.71	0.012	0.74	0.052	18.58	0.53	0.018	10.09	1.68	0.71
B29	16/01/2012	4.79	126.96	58.90	0.61	122.71	<0.000	0.780	900.6	0.41	94.35	0.001	0.005	0.078	0.16	437	0.11	0.002	<0.000	3.84	0.001	0.44	<0.000	17.97	0.53	<0.000	10.53	1.61	0.07
B29	30/01/2012	4.59	105.18	65.19	1.37	99.99	0.196	0.663	929.7	1.99	95.88	0.006	0.005	0.088	0.16	459	2.98	0.005	0.006	3.82	0.012	0.71	0.020	18.25	0.53	0.285	10.56	1.65	1.42
B29	13/02/2012	4.65	94.81	67.28	1.62	90.88	0.370	0.619	907.8	2.08	98.05	0.007	0.003	0.083	0.31	451	5.59	0.006	0.007	3.67	0.014	0.76	0.033	17.78	0.52	0.146	10.18	1.62	1.60
B29	27/02/2012	4.02	120.36	57.76	1.50	95.07	0.068	0.690	966.7	1.76	94.11	0.001	0.004	0.073	0.10	403	0.32	0.006	0.004	3.83	0.012	0.71	0.010	18.85	0.51	0.028	10.15	1.54	2.09
B29	12/03/2012	4.20	137.49	65.60	1.53	110.91	0.290	0.666	922.4	1.91	91.25	0.008	0.009	0.081	0.13	412	3.94	0.005	0.003	3.66	0.012	0.37	0.027	18.18	0.48	0.007	9.89	1.59	2.37
B29	26/03/2012	4.22	127.29	60.59	1.82	96.68	0.039	0.695	960.2	3.40	96.07	0.005	0.004	0.072	0.09	430	0.54	0.005	0.003	3.94	0.013	0.69	0.018	18.70	0.52	0.008	10.25	1.60	0.39
B29	10/04/2012	4.09	108.52	60.32	1.28	95.12	0.474	0.660	930.7	2.85	95.83	0.000	0.007	0.091	0.15	525	5.79	0.007	0.003	3.79	0.013	0.54	0.047	18.37	0.51	0.123	10.22	1.49	2.29
B29	23/04/2012	3.83	102.99	56.46	1.28	81.83	0.062	0.620	889.2	2.06	87.56	<0.000	0.007	0.076	0.14	454	1.92	0.005	0.003	3.54	0.010	0.51	0.026	17.45	0.47	0.014	9.44	1.36	0.39
B29	09/05/2012	3.99	108.28	62.80	0.89	95.10	0.129	0.648	870.1	2.24	85.99	0.008	0.009	0.072	0.34	442	1.51	0.005	0.002	3.68	0.012	0.50	0.019	17.30	0.47	0.034	9.11	1.46	0.54
B29	21/05/2012	3.90	141.73	61.89	0.96	116.61	0.252	0.456	875.3	1.73	91.70	0.002	0.006	0.070	0.15	492	3.50	0.005	<0.000	3.60	0.010	0.64	0.001	17.71	0.36	<0.000	9.28	1.49	1.62
B29	04/06/2012	3.84	127.73	64.50	0.84	105.43	0.051	0.504	860.6	1.10	87.56	0.000	0.008	0.068	0.16	451	0.90	0.004	<0.000	3.69	0.008	0.35	0.007	17.02	0.37	<0.000	8.88	1.50	1.89
B29	18/06/2012	4.04	118.42	73.43	1.28	105.22	0.081	0.563	902.2	1.88	83.89	<0.000	0.003	0.067	0.19	420	1.25	0.006	0.001	3.62	0.011	0.17	<0.000	16.31	0.49	0.011	8.63	1.53	3.50
B29	02/07/2012	4.43	123.07	59.05	1.01	104.96	0.087	0.548	918.8	1.59	94.77	<0.000	0.001	0.080	0.20	467	1.63	0.007	0.003	3.89	0.013	0.66	0.018	18.34	0.52	<0.000	9.77	1.63	0.60
B29	16/07/2012	4.26	105.37	57.16	1.25	89.91	0.306	0.541	897.0	1.80	100.65	<0.000	0.002	0.076	0.17	405	1.50	0.005	0.009	3.91	0.012	0.82	0.033	17.59	0.53	<0.000	9.72	1.58	0.82
B29	30/07/2012	4.34	135.49	71.19	1.52	109.49	0.190	0.524	890.7	2.63	100.75	0.008	0.009	0.079	0.20	473	2.96	0.006	0.003	3.84	0.012	0.30	0.043	17.75	0.51	0.020	9.46	1.56	1.24
B29	13/08/2012	4.11	124.92	67.22	1.29	95.63	0.144	0.495	893.8	10.18	100.48	0.009	0.010	0.069	0.19	491	1.43	0.006	0.003	3.76	0.012	0.13	0.030	17.81	0.50	0.019	9.18	1.48	1.74
B29	27/08/2012	4.16	124.05	65.54	0.99	94.71	0.409	0.571	939.8	1.57	96.33	<0.000	0.006	0.068	0.16	492	6.89	0.006	<0.000	3.80	0.013	0.55	0.005	17.71	0.54	<0.000	9.33	1.54	0.87
B29	10/09/2012	3.96	140.27	76.99	1.22	111.79	0.435	0.491	918.0	1.95	100.67	0.008	0.012	0.065	0.17	444	13.47	0.007	<0.000	3.75	0.010	0.49	0.114	17.81	0.50	0.011	9.20	1.54	0.47
B29	24/09/2012	4.23	138.11	67.36	0.91	107.14	0.038	0.502	951.5	0.44	99.24	<0.000	0.007	0.067	0.17	460	1.18	0.006	0.001	3.56	0.012	0.44	0.011	18.04	0.39	<0.000	9.37	1.57	<0.000
B29	08/10/2012	4.08	133.74	57.88	1.80	111.14	0.324	0.686	928.3	20.46	93.24	0.001	0.007	0.075	0.17	495	7.94	0.006	0.011	3.68	0.014	0.42	0.016	17.59	0.39	<0.000	9.23	1.56	0.26
B29	22/10/2012	4.08	135.92	64.48	1.15	115.53	0.093	0.575	881.9	1.31	90.63	0.007	0.008	0.069	0.18	441	0.94	0.005	0.006	3.70	0.009	0.41	0.004	16.85	0.43	<0.000	8.95	1.61	0.27
B29	05/11/2012	4.01	145.58	73.55	1.45	120.18	0.084	0.522	902.3	2.85	95.77	<0.000	0.004	0.060	0.18	443	1.88	0.007	0.010	3.85	0.015	0.39	0.003	17.37	0.54	0.011	9.42	1.59	0.48

Sample ID	Date	As	B	Br	Cu	Li	Mn	Se	Sr	Al	Ba	Be	Cd	Co	Cr	F	Fe	Gd	Hg	Mo	Nd	Ni	Pb	Rb	Sb	Sn	U	V	Zn
B33	14/02/2011	2.66	25.10	17.51	1.08	22.91	1.808	0.042	110.7	7.27	5.56	0.003	0.000	0.045	0.06	<100	5.11	0.003	<0.000	0.29	0.008	0.14	0.040	5.50	1.07	<0.000	0.09	0.79	0.39
B33	28/02/2011	2.55	23.09	18.70	1.00	22.69	1.271	0.051	114.7	5.23	5.69	0.004	0.001	0.042	0.07	<100	3.90	0.003	0.023	0.26	0.007	0.13	0.039	5.42	1.01	<0.000	0.09	0.72	0.66
B33	14/03/2011	2.48	22.64	18.02	1.09	22.61	0.208	0.042	116.8	21.17	5.90	0.005	0.002	0.082	0.33	<100	5.90	0.003	0.004	0.35	0.007	0.26	0.034	5.30	1.06	0.009	0.09	0.71	0.63
B33	28/03/2011	2.49	25.43	21.19	1.24	23.70	1.008	0.048	118.5	4.84	5.85	0.003	0.003	0.051	0.09	<100	11.69	0.004	0.021	0.26	0.008	0.08	0.041	5.21	1.00	0.038	0.09	0.71	0.22
B33	11/04/2011	2.47	23.81	18.03	1.08	22.88	0.587	0.038	110.1	4.60	5.37	0.002	0.002	0.040	0.07	<100	9.99	0.003	0.004	0.21	0.008	0.02	0.094	4.94	1.01	0.005	0.07	0.64	0.34
B33	26/04/2011	2.59	22.39	21.77	2.16	20.89	1.162	0.036	116.9	5.46	5.91	0.005	0.004	0.048	0.35	<100	5.94	0.003	0.009	0.40	0.009	0.28	0.019	5.35	1.01	0.020	0.09	0.72	0.05
B33	09/05/2011	2.57	22.58	24.65	1.67	19.77	1.027	0.044	122.0	4.76	6.75	0.004	0.002	0.040	0.08	102	3.78	0.003	0.000	0.25	0.008	0.19	0.059	5.59	1.03	<0.000	0.10	0.70	0.87
B33	23/05/2011	2.81	37.16	32.04	1.38	27.29	1.934	0.045	140.4	4.35	10.40	0.008	0.003	0.049	0.09	<100	11.09	0.005	0.013	0.22	0.010	0.26	0.110	6.28	1.13	0.021	0.11	0.80	1.89
B33	06/06/2011	3.17	54.52	38.70	1.98	31.33	1.220	0.037	159.5	7.10	13.64	0.011	0.004	0.065	2.60	<100	12.96	0.006	0.005	1.32	0.011	1.39	0.128	7.96	1.32	0.014	0.10	0.99	0.74
B33	20/06/2011	3.34	58.66	37.63	2.76	30.25	5.002	0.053	156.1	3.06	14.18	0.014	0.002	0.055	0.04	<100	12.99	0.006	<0.000	0.28	0.012	0.23	0.208	8.61	1.41	<0.000	0.11	1.05	1.77
B33	04/07/2011	3.34	59.16	39.76	1.70	31.66	0.549	0.043	159.5	3.71	14.22	0.006	0.003	0.053	0.05	115	6.63	0.006	<0.000	0.27	0.011	0.18	0.023	8.89	1.27	<0.000	0.12	1.04	2.16
B33	18/07/2011	3.46	64.64	37.57	1.76	30.94	0.613	0.036	148.0	2.30	14.10	0.006	0.004	0.047	0.04	117	6.84	0.005	<0.000	0.27	0.010	0.20	0.028	8.77	1.44	<0.000	0.10	1.07	2.04
B33	16/08/2011	3.65	59.05	41.02	1.82	29.76	4.078	0.042	152.7	2.39	13.43	0.009	0.004	0.053	0.03	105	5.38	0.006	0.024	0.31	0.010	0.17	0.018	9.45	1.55	<0.000	0.10	1.17	0.20
B33	29/08/2011	3.73	58.34	39.84	1.88	29.69	2.780	0.051	144.2	2.37	13.64	0.011	0.004	0.057	0.03	113	10.15	0.006	0.737	0.34	0.010	0.22	0.025	9.27	1.57	0.005	0.10	1.24	0.24
B33	12/09/2011	3.57	52.46	37.60	2.49	25.61	1.947	0.049	142.1	2.47	12.89	0.098	0.004	0.062	0.03	140	8.75	0.005	<0.000	0.33	0.011	0.20	0.015	8.97	1.44	<0.000	0.09	1.17	0.35
B33	26/09/2011	3.69	59.82	33.61	2.24	32.17	2.173	0.046	140.5	4.82	13.81	0.006	0.012	0.057	0.04	131	7.25	0.006	<0.000	0.35	0.012	0.14	0.038	9.42	1.70	0.017	0.10	1.31	8.57
B33	10/10/2011	3.94	56.69	68.38	1.41	30.87	0.082	0.072	137.5	0.25	13.44	0.009	0.005	0.056	0.08	103	1.44	0.004	0.002	0.40	0.003	0.19	0.029	11.82	1.85	0.005	0.02	1.13	0.12
B33	24/10/2011	3.69	59.13	33.16	1.64	31.57	3.653	0.068	138.2	2.74	13.53	0.009	0.003	0.051	0.07	103	5.55	0.005	0.012	0.38	0.009	0.18	0.019	9.56	1.82	0.037	0.08	1.25	0.34
B33	07/11/2011	3.55	52.07	24.05	1.60	30.35	2.360	0.055	137.2	3.29	11.30	0.010	0.004	0.048	0.14	114	4.05	0.006	0.003	0.38	0.009	0.23	0.012	9.09	1.64	0.003	0.09	1.16	0.04
B33	21/11/2011	3.44	47.60	17.16	2.26	29.74	0.258	0.061	120.8	5.53	7.42	0.023	0.002	0.057	0.06	111	3.47	0.004	0.002	0.39	0.009	0.10	0.012	7.64	1.51	0.001	0.09	1.14	0.13
B33	05/12/2011	3.23	39.85	13.74	1.45	27.37	0.614	0.051	113.7	4.95	6.67	0.007	0.002	0.052	0.06	110	5.03	0.004	0.000	0.36	0.008	0.15	0.037	7.01	1.38	<0.000	0.09	1.04	2.37
B33	19/12/2011	3.05	34.74	17.57	1.59	25.64	0.690	0.033	108.3	6.35	6.15	0.009	0.004	0.050	0.11	105	7.73	0.004	0.001	0.35	0.010	0.20	0.064	6.14	1.22	<0.000	0.08	0.92	3.88
B33	03/01/2012	3.00	29.55	2.83	1.61	23.79	0.902	0.054	101.0	6.98	5.75	0.009	0.002	0.057	0.12	110	7.83	0.005	<0.000	0.37	0.010	0.27	0.019	6.09	1.36	0.002	0.08	0.92	1.45
B33	16/01/2012	2.87	23.71	<0.000	1.35	22.23	0.655	0.055	90.9	0.77	4.91	0.007	0.000	0.044	0.04	102	0.67	0.002	<0.000	0.27	0.003	0.21	0.007	5.42	1.29	<0.000	0.03	0.70	1.45
B33	30/01/2012	2.88	23.88	11.13	1.62	22.24	0.274	0.047	96.1	8.85	5.17	0.008	<0.000	0.048	0.09	131	4.46	0.005	0.005	0.36	0.009	0.20	0.041	5.51	1.35	0.010	0.08	0.85	0.63
B33	13/02/2012	2.85	19.11	14.16	1.40	19.32	0.809	0.043	99.4	5.75	5.36	0.006	0.001	0.048	0.13	<100	6.21	0.005	0.005	0.33	0.009	0.36	0.084	5.25	1.18	0.070	0.08	0.76	0.25
B33	27/02/2012	2.20	25.53	17.04	1.78	26.04	2.601	0.055	107.9	3.92	5.60	0.010	0.004	0.045	0.09	<100	8.38	0.007	0.003	0.28	0.008	0.10	0.029	4.90	0.94	0.010	0.09	0.67	1.66
B33	12/03/2012	2.31	22.36	5.68	1.37	19.72	0.866	0.054	113.0	2.71	6.00	0.001	0.001	0.040	0.01	<100	3.85	0.005	0.002	0.28	0.008	0.30	0.016	5.00	0.98	0.102	0.09	0.59	0.65
B33	26/03/2012	2.46	25.49	5.78	2.34	21.20	0.501	0.068	116.9	3.84	5.88	0.008	<0.000	0.049	0.01	<100	3.45	0.004	0.000	0.29	0.008	0.42	0.015	5.08	1.05	0.015	0.10	0.66	0.40
B33	10/04/2012	2.37	24.71	5.22	1.79	21.60	0.924	0.052	114.1	3.67	6.11	<0.000	0.001	0.046	0.08	100	8.83	0.003	0.001	0.28	0.006	0.17	0.069	4.97	1.00	0.009	0.11	0.64	3.29
B33	23/04/2012	2.65	31.07	3.04	2.15	19.48	0.577	0.071	114.2	4.01	7.49	<0.000	0.002	0.050	0.07	105	8.74	0.005	0.000	0.25	0.009	0.20	0.015	5.19	1.08	<0.000	0.10	0.63	3.01
B33	09/05/2012	2.93	27.66	4.44	1.54	18.72	0.121	0.053	86.3	6.28	6.06	0.010	0.003	0.049	0.26	<100	3.76	0.004	0.001	0.34	0.012	0.10	0.006	4.64	1.20	0.023	0.07	0.77	0.11
B33	21/05/2012	3.01	34.02	3.93	1.66	23.50	0.377	0.049	89.2	8.57	6.53	0.007	0.000	0.047	0.08	122	6.84	0.004	<0.000	0.24	0.011	0.27	0.013	4.89	1.17	<0.000	0.07	0.82	1.95
B33	04/06/2012	3.25	29.81	8.83	1.69	21.71	0.153	0.062	96.3	7.00	9.40	0.003	0.001	0.054	0.09	112	4.64	0.004	<0.000	0.22	0.011	0.24	0.006	5.27	1.14	<0.000	0.07	0.90	0.31
B33	18/06/2012	3.39	30.56	21.84	1.89	22.49	0.532	0.052	104.4	5.84	7.97	0.002	<0.000	0.050	0.06	101	6.47	0.006	<0.000	0.25	0.012	<0.000	0.000	5.61	1.32	0.009	0.08	0.94	4.95
B33	02/07/2012	3.29	31.96	8.62	1.83	22.77	0.279	0.058	104.6	6.19	8.70	<0.000	<0.000	0.043	0.05	105	10.54	0.005	0.001	0.25	0.014	0.27	0.271	6.15	1.43	<0.000	0.08	0.90	0.32
B33	16/07/2012	3.33	31.71	12.86	1.70	22.02	3.471	0.043	115.9	4.54	9.38	<0.000	<0.000	0.047	0.05	<100	6.40	0.004	0.003	0.25	0.012	0.34	0.030	6.66	1.43	<0.000	0.08	0.94	1.82
B33	30/07/2012	3.43	47.61	29.02	1.50	31.15	0.857	0.047	126.1	3.57	10.68	0.005	0.001	0.048	0.01	<100	7.73	0.008	<0.000	0.25	0.012	0.14	0.014	7.35	1.47	0.012	0.09	1.05	0.30
B33	13/08/2012	3.50	44.26	23.36	1.39	25.06	2.700	0.063	133.3	5.76	11.54	0.010	0.003	0.044	0.03	<100	7.43	0.006	0.002	0.26	0.013	<0.000	0.014	7.79	1.40	0.014	0.09	0.99	0.58
B33	27/08/2012	3.76	54.95	24.05	1.68	29.13	3.509	0.033	131.7	4.42	12.44	0.004	0.000	0.050	0.03	106	6.60	0.006	0.001	0.30	0.013	0.18	0.011	8.53	1.75	0.008	0.08	1.22	1.55
B33	10/09/2012	4.11	45.78	20.74	2.00	24.21	2.160	0.066	119.7	7.13	12.18	0.003	0.000	0.043	0.04	109	13.65	0.009	<0.000	0.33	0.013	0.48	0.020	8.60	1.89	<0.000	0.07	1.30	0.39
B33	24/09/2012	3.74	50.61	26.23	1.95	30.44	0.303	0.028	124.3	6.03	12.23	0.004	0.005	0.037	0.05	118	5.31	0.006	<0.000	0.31	0.010	0.20	0.030	8.85	1.79	<0.000	0.07	1.33	1.13
B33	08/10/2012	3.41	53.59	19.50	1.23	32.33	2.643	0.033	131.0	3.97	12.36	0.001	0.003	0.034	0.05	113	7.57	0.006	0.003	0.31	0.011	0.06	0.029	8.94	1.67	<0.000	0.07	1.25	0.24
B33	22/10/2012	3.39	49.39	20.66	1.17	31.54	1.987	0.041	125.1	4.07	11.78	0.008	0.002	0.035	0.08	109	4.81	0.005	<0.000	0.29	0.009	0.06	0.014	8.16	1.48	0.023	0.07	1.17	<0.000
B33	05/11/2012	3.35	57.08	22.27	1.13	32.95	2.661	0.028	128.3	4.38	11.23	<0.000	<0.000	0.036	0.05	108	5.84	0.006	0.005	0.33	0.010	0.08	0.007	8.12	1.52	0.010	0.08	1.13	0.36

Sample ID	Date	As	B	Br	Cu	Li	Mn	Se	Sr	Al	Ba	Be	Cd	Co	Cr	F	Fe	Gd	Hg	Mo	Nd	Ni	Pb	Rb	Sb	Sn	U	V	Zn
B39	14/02/2011	11.72	23.94	15.37	0.46	17.08	341.67	0.033	90.5	5.91	20.64	0.003	0.000	0.481	5.63	141	989.2	0.00	0.01	2.46	0.01	3.29	0.27	0.55	0.15	0.01	0.01	0.13	1.45
B39	28/02/2011	14.15	31.29	18.78	0.35	25.86	493.23	0.028	137.3	4.44	27.76	0.003	<0.000	0.655	0.07	127	555.6	0.002	0.002	0.34	0.007	2.33	0.430	4.41	0.19	<0.000	0.04	0.16	1.32
B39	14/03/2011	10.96	30.13	17.94	0.25	26.10	188.21	0.030	135.6	3.03	22.66	0.002	<0.000	0.302	0.06	127	813.6	0.003	0.011	0.44	0.006	0.90	0.267	7.40	0.21	<0.000	0.04	0.16	0.87
B39	28/03/2011	7.74	27.07	16.56	0.30	25.75	254.49	0.015	136.6	5.60	12.94	0.002	0.002	0.323	0.27	117	432.1	0.002	0.003	0.46	0.005	0.84	0.053	7.33	0.18	<0.000	0.03	0.12	0.23
B39	11/04/2011	2.17	27.18	19.14	0.22	27.53	122.88	0.023	136.7	1.14	21.60	0.000	0.000	0.154	0.04	117	449.9	0.002	0.370	0.12	0.006	0.43	0.548	1.42	0.12	0.030	0.02	0.12	0.37
B39	26/04/2011	9.44	22.36	19.28	1.68	23.25	275.96	0.027	130.8	4.48	23.40	0.003	0.003	0.414	0.00	120	N.A	0.001	0.004	0.15	0.001	0.50	<0.000	6.95	0.15	0.001	0.01	0.02	<0.000
B39	09/05/2011	8.61	21.51	19.29	0.84	23.21	486.82	0.014	137.0	2.89	24.97	0.002	0.001	0.608	0.31	115	450.1	0.002	0.009	0.45	0.004	0.85	0.217	6.85	0.16	0.009	0.03	0.11	0.43
B39	23/05/2011	8.59	24.07	19.44	0.29	28.49	839.45	0.018	132.6	2.61	28.04	0.004	0.001	0.914	0.04	109	395.3	0.002	0.002	0.35	0.004	0.82	0.033	7.15	0.13	<0.000	0.03	0.13	4.30
B39	06/06/2011	10.27	23.31	29.58	0.82	19.84	712.00	0.00	124.3	7.42	15.92	0.01	0.00	1.05	0.05	116	407.9	0.002	0.398	0.26	0.004	0.84	0.059	6.66	0.16	0.010	0.03	0.12	0.84
B39	20/06/2011	10.96	26.58	26.65	0.37	29.61	1672.77	0.024	142.9	2.46	36.21	0.004	0.002	1.494	0.05	130	898.5	0.002	0.002	0.43	0.005	1.10	0.171	7.48	0.13	<0.000	0.03	0.14	0.68
B39	04/07/2011	5.20	24.44	27.02	0.18	24.51	326.53	0.011	125.2	3.49	8.75	0.003	0.028	0.249	0.05	104	339.4	0.001	0.017	0.09	0.004	0.26	0.080	1.20	0.06	0.086	0.02	0.10	0.57
B39	18/07/2011	7.10	27.18	26.96	0.71	30.21	1608.34	0.026	144.5	3.53	32.94	0.001	0.006	0.655	0.05	116	363.9	0.002	<0.000	0.04	0.005	1.14	0.204	7.54	0.11	<0.000	0.03	0.09	0.79
B39	16/08/2011	20.58	36.82	41.62	0.53	31.77	1826.36	0.022	180.4	2.81	54.68	0.032	0.005	2.459	0.03	101	2124.5	0.004	0.063	0.18	0.007	1.39	0.094	8.90	0.11	<0.000	0.03	0.19	0.44
B39	29/08/2011	9.50	34.37	36.93	1.24	31.78	1456.08	0.028	169.8	6.07	33.66	0.027	0.007	1.493	0.13	115	844.9	0.003	0.156	0.20	0.007	1.37	0.127	9.13	0.10	0.009	0.05	0.15	11.26
B39	12/09/2011	2.35	35.38	36.03	0.60	29.90	1324.21	0.026	170.5	<0.000	25.78	0.000	0.002	0.506	<0.000	137	N.A	0.001	<0.000	0.82	0.001	1.20	<0.000	8.91	0.09	<0.000	0.01	0.02	0.13
B39	26/09/2011	36.86	53.29	34.01	0.66	35.48	2401.40	0.031	164.1	4.35	84.05	0.008	0.026	3.557	0.04	126	2793.4	0.006	<0.000	0.80	0.014	1.88	0.066	9.40	0.15	0.016	0.03	0.31	3.97
B39	10/10/2011	4.59	57.29	34.35	0.12	36.70	976.01	0.032	162.7	<0.000	39.16	0.000	0.001	0.393	0.01	101	N.A	0.002	0.002	0.66	0.001	1.43	<0.000	9.98	0.15	<0.000	0.00	0.01	<0.000
B39	24/10/2011	33.22	59.19	42.61	0.21	36.93	1594.88	0.041	171.2	2.73	77.04	0.006	0.004	2.370	0.05	104	1832.2	0.004	0.018	0.06	0.009	1.72	0.020	10.64	0.15	0.140	0.02	0.23	0.74
B39	07/11/2011	39.26	57.01	32.05	0.34	36.17	1428.56	0.044	165.1	4.16	74.43	0.010	0.003	2.186	0.06	118	1970.6	0.006	0.003	0.13	0.017	1.56	0.183	10.92	0.22	0.001	0.02	0.31	0.65
B39	21/11/2011	31.92	58.12	23.79	0.24	36.41	275.93	0.030	153.1	3.04	38.34	0.006	0.002	0.486	0.08	114	1604.0	0.005	0.002	0.45	0.014	1.25	0.281	10.38	0.21	<0.000	0.02	0.27	0.22
B39	05/12/2011	25.80	51.12	20.91	0.77	35.01	297.13	0.033	144.7	2.53	37.23	0.012	0.001	0.589	0.03	115	1223.5	0.005	0.011	0.48	0.010	0.95	0.105	9.23	0.17	0.097	0.02	0.20	1.31
B39	19/12/2011	22.10	45.44	22.40	0.35	33.25	345.76	0.027	136.2	2.65	36.03	0.007	0.002	0.671	0.05	116	844.2	0.005	0.002	0.45	0.009	0.98	0.102	8.56	0.15	<0.000	0.01	0.19	1.62
B39	03/01/2012	18.09	40.12	9.50	0.45	31.15	330.43	0.038	132.8	2.76	34.79	0.007	0.001	0.679	0.04	119	733.6	0.004	<0.000	0.43	0.008	1.08	0.226	8.89	0.14	0.000	0.02	0.14	2.11
B39	16/01/2012	4.26	33.49	3.60	0.33	29.98	N.A	0.035	122.6	0.04	19.74	0.004	<0.000	0.061	0.01	113	N.A	0.002	<0.000	0.25	0.001	0.56	<0.000	8.07	0.14	<0.000	0.00	<0.000	<0.000
B39	30/01/2012	16.83	35.38	15.99	0.64	28.42	170.76	0.034	123.2	1.91	26.68	0.004	<0.000	0.372	0.04	161	691.9	0.004	0.005	0.39	0.007	0.73	0.099	8.10	0.17	0.008	0.02	0.11	0.10
B39	13/02/2012	17.08	26.51	14.61	0.60	23.90	181.65	0.027	117.8	2.13	23.75	0.006	<0.000	0.400	0.05	128	580.0	0.004	0.005	0.41	0.007	1.10	0.063	7.59	0.16	0.067	0.02	0.12	1.10
B39	27/02/2012	14.42	35.33	13.58	0.31	31.65	320.05	0.027	112.1	1.80	23.09	0.007	<0.000	0.464	0.07	<100	607.1	0.003	0.005	0.42	0.006	0.74	0.048	7.06	0.14	0.016	0.02	0.16	0.45
B39	12/03/2012	13.69	30.67	3.15	0.36	25.72	182.37	0.044	124.1	2.37	24.05	<0.000	<0.000	0.349	<0.000	116	500.1	0.001	0.003	0.40	0.006	0.88	0.042	7.72	0.14	0.045	0.03	0.10	2.80
B39	26/03/2012	12.96	30.73	3.19	0.39	26.72	200.62	0.042	124.5	2.67	23.80	<0.000	<0.000	0.399	<0.000	132	527.4	0.003	0.002	0.37	0.006	0.97	0.058	7.55	0.13	0.017	0.02	0.09	3.47
B39	10/04/2012	10.82	26.86	1.97	0.52	26.98	169.28	0.035	122.8	1.68	23.44	<0.000	<0.000	0.354	0.05	124	528.8	0.002	0.003	0.31	0.004	0.56	0.023	7.25	0.13	0.002	0.02	0.06	0.15
B39	23/04/2012	9.57	23.77	2.54	0.79	24.61	176.12	0.036	122.5	1.89	24.61	<0.000	<0.000	0.369	0.01	107	578.4	0.002	0.002	0.30	0.003	0.66	0.069	6.93	0.11	<0.000	0.02	0.05	1.66
B39	09/05/2012	4.02	23.10	9.15	0.41	24.85	309.03	0.018	120.6	1.17	27.48	0.006	0.002	0.441	0.02	117	134.9	0.002	0.003	0.25	0.003	0.64	0.031	6.26	0.18	0.025	0.02	0.04	0.50
B39	21/05/2012	5.69	31.68	7.10	0.68	27.77	N.A	0.014	119.9	2.17	20.31	0.003	<0.000	0.318	0.02	<100	224.5	0.002	<0.000	0.18	0.003	0.69	0.202	6.08	0.22	<0.000	0.04	0.14	2.92
B39	04/06/2012	6.83	33.13	8.45	0.89	27.65	100.33	0.016	124.2	56.37	18.26	0.005	0.005	0.235	0.16	116	288.6	0.003	<0.000	0.26	0.007	0.46	1.346	7.41	0.25	0.019	0.04	0.18	0.79
B39	18/06/2012	8.35	31.02	19.30	0.67	23.28	372.51	0.043	125.0	3.23	20.31	<0.000	<0.000	0.309	0.04	<100	458.1	0.003	0.001	0.25	0.006	0.35	0.438	5.94	0.36	0.003	0.08	0.30	9.35
B39	02/07/2012	5.97	32.56	5.29	0.62	22.80	209.12	0.029	128.2	1.55	15.45	<0.000	<0.000	0.094	0.04	108	188.8	0.003	0.001	0.20	0.004	0.50	0.599	6.37	0.43	<0.000	0.08	0.19	0.22
B39	16/07/2012	6.28	28.99	5.42	0.75	21.64	123.94	0.036	127.9	2.65	17.90	<0.000	<0.000	0.172	0.04	102	213.7	0.002	0.003	0.23	0.005	0.81	0.457	6.55	0.31	<0.000	0.08	0.13	1.64
B39	30/07/2012	5.43	37.04	14.05	0.47	28.29	164.85	0.037	126.6	1.92	16.55	<0.000	0.001	0.088	0.04	<100	201.1	0.002	<0.000	0.22	0.004	0.49	0.173	6.49	0.23	0.010	0.07	0.10	1.74
B39	13/08/2012	6.33	31.38	9.71	0.51	22.76	616.86	0.011	131.3	2.28	21.41	0.005	0.004	0.196	0.04	107	217.5	0.002	0.003	0.39	0.004	0.46	0.146	6.96	0.18	0.004	0.05	0.02	2.39
B39	27/08/2012	8.22	35.00	14.30	0.27	27.43	1090.33	0.022	139.1	1.40	28.37	<0.000	<0.000	1.154	0.03	108	440.7	0.003	0.002	0.43	0.005	1.02	0.089	7.68	0.21	0.002	0.04	0.08	0.49
B39	10/09/2012	5.83	29.34	13.31	0.33	22.22	724.99	0.027	135.5	1.48	21.64	<0.000	0.001	0.371	0.04	110	131.8	0.002	<0.000	0.41	0.002	0.81	0.080	7.69	0.17	<0.000	0.04	0.08	0.37
B39	24/09/2012	15.57	40.55	19.94	0.28	30.51	1368.34	0.021	151.2	1.04	39.69	0.002	0.003	1.928	0.04	119	1009.3	0.003	0.001	0.57	0.008	1.21	0.056	8.55	<0.000	0.017	0.04	0.13	0.76
B39	08/10/2012	20.90	45.16	26.86	0.20	32.65	1638.46	0.027	148.8	2.75	47.07	0.006	0.007	2.250	0.03	109	1382.1	0.004	0.021	0.67	0.011	1.31	0.036	8.52	0.09	0.062	0.03	0.20	1.22
B39	22/10/2012	33.59	53.25	26.35	0.52	35.05	1902.41	0.019	149.6	4.22	67.69	0.018	0.005	2.823	0.04	106	2521.3	0.005	0.008	0.66	0.019	1.47	0.065	8.82	0.10	0.004	0.02	0.33	1.84
B39	05/11/2012	36.47	57.43	25.62	0.11	38.34	1512.66	0.019	152.0	3.84	62.61	<0.000	0.000	2.579	0.04	112	2530.0	0.004	0.009	0.61	0.016	1.40	0.028	9.10	0.18	0.005	0.02	0.31	1.75

Sample ID	Date	As	B	Br	Cu	Li	Mn	Se	Sr	Al	Ba	Be	Cd	Co	Cr	F	Fe	Gd	Hg	Mo	Nd	Ni	Pb	Rb	Sb	Sn	U	V	Zn
B50	14/02/2011	5.47	78.58	55.12	1.14	58.21	0.133	0.063	86.7	5.94	34.08	0.01	0.01	0.08	3.01	140	14.53	0.01	0.00	1.51	0.01	1.70	0.13	6.38	1.32	0.02	1.57	1.17	2.19
B50	14/03/2011	2.81	27.73	19.74	1.36	24.83	0.113	0.058	146.3	5.74	110.93	0.005	0.006	0.065	0.69	<100	3.42	0.004	<0.000	1.44	0.010	0.49	0.406	10.85	0.87	0.029	8.31	1.85	4.94
B50	28/03/2011	0.83	6.20	15.46	0.52	57.56	0.027	0.018	132.7	4.44	14.61	0.004	0.006	0.037	0.34	100	2.96	0.004	0.000	0.32	0.008	0.31	0.191	3.94	1.00	0.002	0.28	0.73	0.26
B50	11/04/2011	1.29	12.01	19.88	0.72	31.52	0.087	0.024	168.2	2.29	3.56	<0.000	0.001	0.014	0.03	103	1.17	0.002	0.030	0.11	0.005	<0.000	0.028	0.87	0.38	<0.000	0.13	0.26	<0.000
B50	26/04/2011	3.82	28.06	27.97	1.61	22.51	3.801	0.054	151.4	2.50	8.11	<0.000	0.002	0.020	0.04	108	1.87	0.002	0.001	0.09	0.004	0.02	0.049	1.91	0.29	<0.000	0.11	0.34	0.83
B50	09/05/2011	4.71	72.20	51.40	1.20	36.41	1.327	0.420	N.A	57.57	18.06	0.010	0.277	0.088	0.51	182	128.99	0.019	0.002	0.37	0.087	0.53	1.488	5.27	1.25	<0.000	0.28	1.05	6.28
B50	23/05/2011	3.39	48.95	35.70	1.44	33.32	7.897	0.076	200.9	20.19	69.14	0.005	0.006	0.067	0.56	102	33.38	0.006	0.003	0.96	0.018	0.44	0.344	8.11	0.99	<0.000	4.73	1.75	0.69
B50	06/06/2011	3.30	61.32	46.44	2.65	53.02	0.64	0.17	299.0	50.71	24.39	0.010	0.011	0.083	0.20	102	85.37	0.013	0.019	0.29	0.042	0.46	8.913	5.55	1.23	0.039	0.61	1.04	5.44
B50	20/06/2011	0.88	61.83	29.47	0.57	34.47	0.228	0.017	180.6	3.41	19.31	0.012	0.003	0.006	0.17	136	3.93	0.003	<0.000	0.02	0.008	0.05	0.065	0.18	0.25	<0.000	0.77	0.24	1.45
B50	04/07/2011	3.87	76.50	49.05	1.63	81.87	0.130	0.238	427.6	3.74	47.72	0.006	0.010	0.070	0.33	131	3.69	0.006	0.003	0.48	0.010	0.45	0.066	7.83	1.20	0.001	2.82	1.45	0.22
B50	18/07/2011	3.24	54.21	39.10	1.85	59.18	0.352	0.187	321.8	4.60	39.46	0.007	0.009	0.063	0.30	140	6.84	0.006	0.001	0.41	0.012	0.48	0.112	6.24	1.08	<0.000	1.98	1.20	1.62
B50	16/08/2011	4.02	67.10	49.94	2.03	71.87	0.270	0.192	442.9	4.28	48.30	0.025	0.011	0.067	0.27	128	4.29	0.007	0.000	0.55	0.012	0.50	0.057	8.14	1.13	<0.000	2.90	1.54	0.80
B50	29/08/2011	3.90	62.88	50.73	2.38	60.76	0.302	0.138	380.5	2.81	42.04	0.063	0.012	0.081	0.26	135	3.74	0.006	0.127	0.55	0.013	0.45	0.069	7.86	1.17	<0.000	2.47	1.39	0.70
B50	12/09/2011	3.93	68.48	52.06	1.83	80.50	0.336	0.287	446.6	3.23	49.29	0.012	0.013	0.079	0.29	155	2.44	0.005	0.010	0.61	0.010	0.50	0.049	8.09	1.13	<0.000	3.00	1.53	0.46
B50	26/09/2011	4.18	78.88	35.07	1.58	91.94	0.528	0.312	466.5	3.11	52.79	0.004	0.011	0.074	0.33	147	1.97	0.006	<0.000	0.61	0.010	0.40	0.091	8.98	1.31	<0.000	3.22	1.54	0.85
B50	10/10/2011	3.51	76.07	44.41	0.90	86.07	0.014	0.316	439.7	0.05	49.42	0.002	0.007	0.068	0.27	115	0.35	0.003	<0.000	0.63	0.001	0.36	0.022	8.61	1.33	0.004	1.22	1.28	1.45
B50	24/10/2011	4.19	76.45	42.99	1.62	83.68	1.372	0.317	446.9	10.10	52.02	0.005	0.010	0.083	0.31	119	9.58	0.007	0.003	0.61	0.015	0.41	0.200	8.61	1.31	0.012	3.05	1.56	0.93
B50	07/11/2011	3.94	45.62	28.70	2.78	36.06	1.028	0.141	182.3	8.12	23.33	0.007	0.016	0.106	7.32	120	21.58	0.007	0.006	2.41	0.017	3.12	0.070	7.16	1.91	0.020	0.23	1.45	1.02
B50	21/11/2011	3.80	52.53	25.74	1.45	55.74	0.173	0.207	277.7	3.78	31.14	0.004	0.006	0.074	0.18	133	7.44	0.004	0.001	0.51	0.009	0.31	0.017	6.69	1.34	<0.000	1.30	1.34	0.60
B50	05/12/2011	4.15	62.57	35.73	1.66	75.29	0.231	0.300	403.9	2.67	42.47	0.023	0.007	0.080	0.35	127	4.00	0.004	0.012	0.57	0.009	0.65	0.040	7.25	1.19	0.052	2.54	1.52	1.62
B50	19/12/2011	2.98	33.51	16.97	2.05	25.22	0.229	0.068	145.5	4.09	18.76	0.009	0.005	0.060	0.09	<100	4.07	0.006	0.001	0.33	0.010	0.35	0.070	4.84	1.28	<0.000	0.30	0.93	1.75
B50	03/01/2012	2.97	25.16	0.60	1.82	22.15	0.412	0.070	125.3	3.81	16.44	0.008	0.005	0.071	0.09	112	6.27	0.005	<0.000	0.33	0.013	0.49	0.037	4.56	1.42	0.003	0.21	0.88	2.41
B50	16/01/2012	3.75	35.82	8.95	0.86	54.49	0.006	0.105	211.4	0.25	24.20	0.003	0.001	0.055	0.11	139	0.30	0.001	<0.000	0.48	0.002	0.16	0.005	5.25	1.30	<0.000	0.25	1.08	<0.000
B50	30/01/2012	3.62	33.46	22.42	2.06	46.43	0.409	0.205	289.5	3.69	32.72	0.013	0.003	0.071	0.22	120	5.91	0.005	0.002	0.40	0.009	0.48	0.037	5.65	1.21	0.026	1.61	1.14	2.66
B50	27/02/2012	2.99	38.15	10.91	1.40	36.71	0.111	0.153	218.4	2.91	24.47	<0.000	0.007	0.052	0.09	<100	3.40	0.006	0.002	0.32	0.010	0.42	0.025	4.96	1.08	0.007	0.98	0.90	1.42
B50	12/03/2012	3.39	51.71	22.09	1.20	66.07	0.190	0.209	338.8	3.13	36.39	0.008	0.008	0.056	0.24	<100	1.72	0.004	0.001	0.44	0.010	0.10	0.027	5.73	1.08	0.001	2.27	1.09	0.69
B50	26/03/2012	3.20	44.66	13.02	1.35	46.25	0.321	0.188	280.8	2.74	31.14	<0.000	0.005	0.062	0.12	<100	4.82	0.005	<0.000	0.40	0.009	0.51	0.022	5.42	1.22	0.012	1.60	1.03	2.23
B50	23/04/2012	2.78	30.57	1.61	1.94	19.82	0.167	0.068	128.4	3.43	16.35	<0.000	0.004	0.053	0.09	111	3.82	0.006	0.001	0.25	0.011	0.39	0.033	4.14	1.30	0.002	0.27	0.76	1.04
B50	21/05/2012	3.09	22.68	4.98	1.43	25.00	0.214	0.097	128.3	3.72	15.67	0.019	0.004	0.069	0.30	113	4.45	0.004	0.000	0.45	0.011	0.33	0.030	4.02	1.40	0.314	0.33	0.89	0.87
B50	04/06/2012	3.15	32.86	10.19	1.93	34.58	0.308	0.099	180.1	5.98	22.06	0.008	0.004	0.069	0.15	115	6.67	0.006	<0.000	0.34	0.014	0.37	0.078	4.73	1.41	<0.000	0.46	0.91	1.77
B50	18/06/2012	3.50	40.44	25.80	1.56	56.89	0.397	0.156	277.3	3.31	31.18	0.001	0.000	0.062	0.17	118	4.78	0.003	<0.000	0.43	0.009	0.13	0.010	5.75	1.35	0.018	1.02	1.25	1.31
B50	02/07/2012	3.64	54.24	24.45	1.67	67.83	0.273	0.222	393.3	5.92	42.64	<0.000	0.001	0.071	0.33	103	6.06	0.006	0.002	0.45	0.014	0.54	0.048	6.75	1.31	<0.000	2.47	1.24	1.45
B50	16/07/2012	3.72	52.98	29.86	1.54	61.57	0.277	0.274	432.6	6.45	47.41	<0.000	0.001	0.064	0.30	113	7.87	0.005	0.004	0.51	0.016	0.69	0.054	7.47	1.38	<0.000	2.77	1.30	4.03
B50	30/07/2012	3.77	70.55	45.40	1.30	82.94	0.262	0.243	449.6	2.78	49.44	0.010	0.007	0.067	0.36	109	1.88	0.006	0.001	0.53	0.012	0.13	0.027	7.50	1.21	0.002	3.02	1.34	0.83
B50	13/08/2012	3.76	63.04	37.99	1.53	61.09	0.312	0.196	374.2	4.01	39.85	0.008	0.007	0.066	0.28	120	2.21	0.006	0.001	0.52	0.009	<0.000	0.025	7.01	1.27	<0.000	2.30	1.29	1.72
B50	27/08/2012	4.21	69.05	37.75	1.51	76.42	0.212	0.264	456.4	2.83	50.78	<0.000	0.004	0.063	0.35	126	1.80	0.006	<0.000	0.60	0.011	0.41	0.017	8.12	1.44	<0.000	2.96	1.47	0.49
B50	10/09/2012	4.03	74.01	41.75	1.34	86.32	0.327	0.226	400.9	3.79	44.60	0.011	0.007	0.061	0.30	127	2.35	0.006	<0.000	0.61	0.008	0.41	0.024	7.55	1.24	0.001	2.65	1.59	0.94
B50	24/09/2012	4.01	76.82	32.95	1.43	82.10	0.168	0.194	397.8	2.26	43.39	<0.000	0.008	0.063	0.25	137	2.62	0.006	<0.000	0.54	0.009	0.26	0.018	8.18	1.32	<0.000	2.46	1.59	<0.000
B50	08/10/2012	3.96	78.07	38.03	1.12	91.93	0.395	0.175	406.4	3.73	44.57	0.006	0.008	0.064	0.30	133	2.83	0.006	0.005	0.56	0.010	0.30	0.025	7.70	1.22	<0.000	2.66	1.58	0.64
B50	22/10/2012	3.86	78.45	37.05	1.21	88.65	0.515	0.181	375.3	3.02	40.75	0.005	0.007	0.061	0.29	129	1.77	0.006	0.002	0.53	0.008	0.25	0.017	7.36	1.17	<0.000	2.38	1.54	0.16
B50	05/11/2012	3.92	77.95	34.27	1.49	85.51	0.388	0.195	363.0	3.86	42.03	<0.000	0.004	0.056	0.30	131	3.09	0.005	0.005	0.75	0.010	0.29	0.021	7.61	1.24	0.397	2.42	1.51	1.44

Sample ID	Date	As	B	Br	Cu	Li	Mn	Se	Sr	Al	Ba	Be	Cd	Co	Cr	F	Fe	Gd	Hg	Mo	Nd	Ni	Pb	Rb	Sb	Sn	U	V	Zn
B56	14/02/2011	3.01	33.58	60.04	1.46	54.59	0.360	0.283	368.9	6.94	25.55	0.005	0.004	0.092	0.13	130	3.74	0.005	<0.000	0.98	0.011	0.38	0.042	10.73	0.66	<0.000	2.47	1.00	0.89
B56	28/02/2011	2.84	33.69	58.46	1.48	55.08	0.543	0.402	397.2	6.35	26.57	0.004	0.005	0.083	0.12	160	3.83	0.005	0.062	0.96	0.014	0.40	0.078	10.94	0.65	<0.000	2.88	0.93	1.83
B56	14/03/2011	1.12	13.97	59.09	1.15	24.19	0.912	0.108	138.4	6.54	7.90	0.006	0.002	0.048	0.38	137	4.60	0.004	0.007	0.43	0.009	0.43	0.077	4.66	0.37	<0.000	0.74	0.48	2.50
B56	28/03/2011	2.83	29.46	31.67	1.51	44.23	0.471	0.197	238.6	8.36	15.65	0.005	0.005	0.081	0.08	149	3.53	0.005	0.734	0.91	0.009	0.25	0.020	7.77	0.73	0.006	1.24	0.88	0.24
B56	11/04/2011	3.03	31.55	55.36	0.99	55.60	0.043	0.409	367.3	0.71	29.99	0.001	0.004	0.076	0.10	160	0.17	0.001	0.041	1.14	0.002	0.40	0.006	10.20	0.65	0.003	3.06	0.85	1.33
B56	26/04/2011	2.89	26.33	41.78	2.42	39.52	0.312	0.276	289.1	5.76	19.12	0.004	0.006	0.077	0.35	142	3.43	0.005	0.005	0.91	0.011	0.45	0.011	8.54	0.72	0.000	2.00	0.84	0.94
B56	09/05/2011	0.05	N.A	36.64	0.34	51.30	0.132	0.098	N.A	3.45	0.83	0.003	<0.000	0.003	0.04	119	1.85	0.003	0.004	0.01	0.005	0.05	0.011	0.13	0.09	0.028	0.12	0.13	0.57
B56	23/05/2011	2.99	39.27	61.93	1.34	67.23	0.536	0.687	484.0	4.04	31.90	0.004	0.006	0.088	0.16	169	2.06	0.005	0.043	1.08	0.010	0.42	0.022	11.84	0.60	0.004	4.22	1.00	0.80
B56	06/06/2011	2.75	34.52	48.76	2.26	57.37	0.926	0.444	361.7	4.91	23.53	0.019	0.007	0.099	2.66	155	6.53	0.005	0.005	2.00	0.013	1.56	0.029	10.28	0.64	0.002	2.59	0.94	0.70
B56	20/06/2011	1.22	36.23	25.06	1.40	24.15	0.473	0.111	125.8	7.71	8.89	0.005	0.005	0.060	0.06	162	8.22	0.006	<0.000	0.37	0.011	0.25	0.058	4.31	0.39	0.002	0.71	0.57	2.02
B56	04/07/2011	2.98	42.51	57.22	1.88	59.38	0.929	0.458	362.9	3.63	24.58	0.007	0.010	0.128	0.09	184	4.79	0.008	0.019	1.09	0.015	0.40	0.030	11.41	0.66	0.038	2.58	0.97	2.27
B56	18/07/2011	2.94	42.58	47.06	2.35	54.97	0.884	0.328	295.5	2.50	20.74	0.008	0.010	0.133	0.07	179	2.28	0.007	<0.000	1.02	0.011	0.41	0.035	10.00	0.67	<0.000	1.77	1.05	1.26
B56	16/08/2011	3.08	44.88	56.66	2.39	48.56	0.939	0.189	281.3	2.13	19.15	0.008	0.015	0.169	0.05	156	1.48	0.009	0.022	0.96	0.011	0.39	0.014	10.65	0.75	<0.000	1.16	0.99	0.66
B56	29/08/2011	3.56	46.27	47.13	3.22	40.99	1.868	0.057	204.0	2.75	16.28	0.025	0.020	0.209	0.07	147	4.57	0.008	0.081	0.92	0.016	0.83	0.044	9.94	0.85	<0.000	0.50	1.05	5.92
B56	12/09/2011	3.17	42.24	53.87	2.86	41.87	2.236	0.148	258.4	3.47	18.20	0.020	0.019	0.182	0.08	188	2.78	0.008	0.020	1.01	0.015	0.53	0.045	10.40	0.72	0.064	1.02	1.04	0.88
B56	26/09/2011	3.48	51.26	46.67	2.46	61.00	3.439	0.273	335.9	2.82	25.04	0.007	0.018	0.183	0.07	193	5.89	0.008	<0.000	1.14	0.013	3.09	0.031	12.01	0.79	0.017	1.98	1.18	0.97
B56	10/10/2011	3.49	54.99	50.51	2.91	53.78	3.557	0.180	267.0	2.58	20.30	0.009	0.021	0.205	0.05	149	1.56	0.008	0.014	1.15	0.013	0.53	0.023	11.64	0.86	0.011	1.15	1.14	0.95
B56	24/10/2011	3.37	53.44	53.22	2.46	56.76	5.154	0.243	307.6	2.13	23.05	0.007	0.017	0.181	0.07	158	1.48	0.007	0.011	1.22	0.013	0.53	0.064	12.09	0.89	0.026	1.58	1.15	0.52
B56	07/11/2011	3.49	40.40	20.08	2.95	38.57	0.807	0.071	135.8	53.42	12.34	0.014	0.014	0.148	0.09	166	24.70	0.013	0.007	0.89	0.037	0.49	0.162	8.79	1.16	0.065	0.11	1.21	0.49
B56	21/11/2011	3.75	33.01	13.60	2.37	33.00	0.305	0.044	114.9	16.93	9.50	0.010	0.008	0.129	0.05	145	5.06	0.007	0.001	0.71	0.018	0.31	0.038	7.44	1.10	<0.000	0.07	1.06	2.69
B56	05/12/2011	3.19	39.97	28.07	2.21	46.70	1.462	0.120	210.6	3.99	14.52	0.012	0.010	0.151	0.04	164	2.49	0.007	0.003	1.00	0.011	0.42	0.007	9.30	0.70	0.045	0.68	1.06	1.86
B56	19/12/2011	3.26	33.50	18.62	2.17	33.59	0.419	0.036	131.0	6.97	9.85	0.012	0.011	0.139	0.05	140	3.65	0.006	0.009	0.79	0.012	0.38	0.010	7.21	0.88	0.073	0.13	0.96	2.12
B56	03/01/2012	3.16	27.83	3.65	2.13	33.84	0.279	0.041	122.1	25.74	9.59	0.010	0.007	0.127	0.06	181	12.35	0.007	<0.000	0.88	0.017	0.40	0.023	7.19	0.97	<0.000	0.11	1.02	0.19
B56	16/01/2012	3.42	30.13	4.72	1.47	44.68	0.042	0.078	167.5	0.28	11.64	0.003	0.002	0.106	0.02	230	0.18	0.002	<0.000	1.29	0.003	0.29	0.002	8.58	0.91	<0.000	0.08	1.02	<0.000
B56	30/01/2012	3.29	30.71	24.89	2.28	43.11	0.308	0.118	187.1	14.21	14.26	0.008	0.003	0.121	0.07	214	4.94	0.006	0.005	1.06	0.011	0.50	0.022	8.39	0.88	0.013	0.54	1.08	1.06
B56	13/02/2012	3.22	25.11	28.78	2.18	39.28	0.557	0.136	206.8	9.84	14.50	0.009	0.004	0.121	0.08	175	5.12	0.006	0.001	1.06	0.012	0.73	0.040	8.48	0.85	0.007	0.74	0.95	0.55
B56	27/02/2012	2.69	26.96	15.71	1.65	38.25	0.157	0.061	131.9	8.68	9.31	0.009	0.001	0.097	0.07	133	2.98	0.004	0.002	0.72	0.011	0.17	0.008	6.23	0.78	0.003	0.24	0.82	7.48
B56	12/03/2012	3.03	34.26	24.78	1.67	47.48	1.072	0.240	270.9	5.24	18.49	<0.000	0.003	0.112	0.01	174	5.45	0.006	0.002	1.38	0.012	0.53	0.004	9.95	0.72	0.015	1.23	1.02	3.22
B56	26/03/2012	3.01	35.41	24.73	2.04	46.82	0.396	0.214	259.3	5.26	17.42	0.004	0.004	0.112	0.01	167	1.71	0.006	0.001	1.28	0.011	0.43	0.003	9.48	0.78	0.000	1.20	0.96	0.67
B56	10/04/2012	2.81	27.26	10.06	2.31	35.17	0.385	0.079	162.7	7.64	11.54	<0.000	0.007	0.113	0.05	134	5.79	0.007	0.001	0.89	0.014	0.45	0.041	6.99	0.78	0.008	0.39	0.78	5.45
B56	23/04/2012	2.81	28.20	12.55	2.15	37.92	0.354	0.115	189.6	5.06	12.67	<0.000	0.007	0.104	0.04	189	2.33	0.005	0.001	1.13	0.009	0.34	0.004	7.75	0.73	<0.000	0.71	0.84	0.47
B56	09/05/2012	3.09	21.24	4.93	2.58	30.33	0.435	0.057	113.3	36.04	7.99	0.032	0.006	0.092	0.30	174	13.18	0.005	0.001	1.02	0.020	0.34	0.042	6.01	0.84	0.132	0.21	0.84	2.68
B56	21/05/2012	2.93	33.15	8.66	2.03	45.83	0.679	0.032	147.1	15.37	10.41	0.004	0.005	0.102	0.04	218	6.98	0.006	<0.000	1.27	0.011	0.45	0.009	7.13	0.68	<0.000	0.37	0.99	2.77
B56	04/06/2012	3.23	25.87	5.24	1.95	30.03	0.303	0.036	101.4	44.93	7.70	0.010	0.004	0.075	0.07	172	14.37	0.007	<0.000	0.56	0.020	0.23	0.021	5.88	0.97	<0.000	0.06	0.87	0.50
B56	18/06/2012	3.23	28.69	19.49	2.80	36.54	0.366	0.042	126.2	13.49	8.76	<0.000	0.001	0.081	0.03	149	5.18	0.006	<0.000	0.91	0.014	<0.000	<0.000	6.65	0.87	0.005	0.12	0.98	0.47
B56	02/07/2012	3.36	32.26	29.77	2.09	41.67	0.457	0.059	165.5	7.88	11.08	<0.000	0.002	0.079	0.06	168	4.48	0.006	0.000	0.96	0.015	0.25	<0.000	7.64	0.82	<0.000	0.31	1.01	1.56
B56	16/07/2012	3.13	31.85	21.17	1.95	40.79	0.438	0.117	202.7	5.50	13.89	<0.000	0.000	0.100	0.06	160	3.01	0.005	0.003	1.04	0.011	0.88	0.027	8.57	0.82	<0.000	0.60	0.95	2.85
B56	30/07/2012	3.11	44.41	50.83	1.67	59.85	0.502	0.156	261.8	3.89	18.03	0.003	0.007	0.107	0.04	154	3.42	0.005	<0.000	1.20	0.012	0.31	0.000	9.54	0.75	0.007	1.23	0.99	0.76
B56	13/08/2012	3.26	36.79	33.26	1.73	43.49	0.310	0.146	247.9	3.85	17.73	0.008	0.009	0.110	0.05	145	1.84	0.006	0.002	0.96	0.013	<0.000	0.008	9.20	0.75	<0.000	1.16	0.86	0.82
B56	27/08/2012	3.74	42.53	22.58	2.41	33.43	0.287	0.044	148.2	4.03	11.80	0.004	0.006	0.134	0.04	133	1.81	0.007	<0.000	0.75	0.015	0.36	0.004	8.27	0.94	<0.000	0.17	0.95	2.03
B56	10/09/2012	3.83	38.12	28.28	2.48	31.87	0.263	0.094	175.3	3.27	13.87	<0.000	0.006	0.132	0.03	140	1.68	0.008	<0.000	0.77	0.014	0.40	0.000	8.92	0.94	<0.000	0.44	0.98	0.59
B56	24/09/2012	3.63	47.04	28.70	2.33	42.63	0.524	0.117	206.3	2.63	15.58	0.002	0.012	0.129	0.03	160	1.57	0.007	<0.000	0.87	0.015	0.45	0.011	9.64	0.80	0.007	0.72	1.06	0.71
B56	08/10/2012	3.37	48.62	37.63	2.13	53.15	0.684	0.143	247.9	3.90	17.69	0.017	0.008	0.130	0.05	178	2.04	0.006	0.011	1.01	0.012	0.37	0.008	9.70	0.78	0.022	1.24	1.05	1.15
B56	22/10/2012	3.65	47.55	33.29	2.13	44.27	0.535	0.078	179.7	3.75	13.76	0.008	0.011	0.142	0.03	146	2.28	0.007	<0.000	1.10	0.013	0.31	0.011	9.38	0.79	<0.000	0.47	1.05	0.21
B56	05/11/2012	3.59	52.64	26.32	2.09	49.76	0.727	0.085	188.0	5.34	14.41	<0.000	0.007	0.133	0.17	163	11.19	0.008	0.006	0.96	0.012	0.37	0.008	9.39	0.89	0.012	0.58	1.09	1.41

Sample ID	Date	As	B	Br	Cu	Li	Mn	Se	Sr	Al	Ba	Be	Cd	Co	Cr	F	Fe	Gd	Hg	Mo	Nd	Ni	Pb	Rb	Sb	Sn	U	V	Zn
B65	14/02/2011	2.89	23.80	34.37	0.36	34.29	0.107	0.093	238.6	4.47	26.05	0.003	0.001	0.009	0.09	220	3.09	0.001	0.002	0.75	0.005	0.15	0.049	5.21	0.65	0.002	1.65	0.87	1.52
B65	28/02/2011	3.66	41.99	64.81	0.44	59.62	0.108	0.149	318.6	4.15	28.67	0.003	0.001	0.012	0.12	219	2.55	0.002	0.499	1.27	0.005	0.19	0.034	11.22	0.83	<0.000	2.04	1.14	1.32
B65	14/03/2011	3.50	43.02	63.36	0.36	61.57	0.176	0.138	326.7	3.10	26.10	0.003	0.001	0.013	0.36	206	1.45	0.001	0.011	1.23	0.004	0.29	0.032	11.52	0.60	<0.000	1.92	1.09	0.95
B65	28/03/2011	3.85	44.75	64.42	1.40	64.21	0.166	0.115	316.6	5.69	29.10	0.002	0.003	0.046	0.14	220	4.31	0.002	0.041	1.34	0.006	0.16	0.110	10.53	0.90	0.014	2.08	1.19	1.46
B65	11/04/2011	1.70	18.64	62.81	0.13	68.50	<0.000	0.058	340.5	0.04	13.31	<0.000	0.000	0.005	0.05	213	<0.000	0.001	0.005	0.61	0.000	<0.000	<0.000	4.22	0.54	<0.000	0.21	0.52	3.63
B65	09/05/2011	3.70	47.44	69.07	0.85	69.09	0.220	0.161	326.6	4.53	26.76	0.006	0.003	0.023	0.16	218	1.72	0.003	0.016	1.25	0.005	0.22	0.039	11.32	0.83	0.019	2.00	1.26	1.73
B65	23/05/2011	3.38	46.50	67.51	0.49	68.02	0.105	0.124	320.5	1.83	24.96	0.006	0.002	0.013	0.14	217	1.43	0.001	0.047	1.14	0.005	0.17	0.015	11.32	0.77	0.004	1.77	1.12	1.59
B65	06/06/2011	2.64	31.71	49.20	0.62	50.98	0.564	0.100	265.2	2.91	20.19	0.006	0.002	0.020	2.77	198	8.84	0.002	0.008	1.92	0.004	1.37	0.013	8.24	0.66	0.004	1.48	0.96	1.80
B65	20/06/2011	3.55	47.77	73.20	1.61	67.95	0.278	0.136	328.4	3.07	26.66	0.006	0.003	0.020	0.15	185	5.17	0.002	0.012	1.15	0.009	0.62	0.150	11.75	0.83	0.088	1.97	1.17	3.20
B65	04/07/2011	3.48	46.33	71.33	0.48	65.80	0.290	0.142	331.9	3.27	24.09	0.011	0.016	0.015	0.15	159	3.08	0.001	0.011	1.11	0.006	0.18	0.055	12.02	0.81	0.026	1.91	1.21	1.09
B65	18/07/2011	3.49	46.80	69.10	0.42	67.32	0.112	0.129	323.9	2.34	25.61	0.005	0.004	0.012	0.14	204	1.70	0.001	0.019	1.15	0.005	0.20	0.028	11.80	0.81	0.075	1.93	1.20	0.82
B65	16/08/2011	4.47	45.57	86.12	0.47	66.98	0.068	0.108	362.9	2.01	45.71	0.009	0.004	0.012	0.12	206	1.09	0.002	0.019	1.57	0.004	0.21	0.012	11.23	0.97	<0.000	2.31	1.20	0.47
B65	29/08/2011	4.38	45.37	78.72	0.74	64.93	0.098	0.084	339.5	1.56	43.26	0.030	0.005	0.014	0.13	283	0.85	0.001	1.054	1.45	0.004	0.24	0.016	10.86	0.99	<0.000	2.27	1.26	0.96
B65	12/09/2011	3.13	27.44	51.62	0.47	68.60	0.109	0.063	256.5	1.76	33.81	0.006	0.004	0.006	0.07	260	2.87	0.001	0.011	0.96	0.006	0.15	0.029	7.07	0.67	0.014	1.56	0.81	0.51
B65	26/09/2011	4.48	47.08	60.17	0.39	72.16	0.658	0.103	340.5	1.91	42.78	0.006	0.003	0.014	0.12	334	1.64	0.002	<0.000	1.53	0.005	0.19	0.010	11.34	1.09	0.007	2.33	1.24	0.64
B65	10/10/2011	4.76	44.57	69.75	0.28	69.38	0.136	0.109	339.3	0.56	44.71	0.001	0.002	0.010	0.11	286	<0.000	0.001	0.001	1.66	0.001	0.20	<0.000	11.36	1.13	<0.000	2.52	1.16	0.07
B65	24/10/2011	4.45	48.09	72.03	0.91	68.39	0.218	0.107	349.9	3.20	44.17	0.008	0.008	0.013	0.17	257	9.97	0.003	0.010	1.65	0.008	0.26	0.048	11.58	1.17	0.025	2.32	1.15	4.44
B65	07/11/2011	4.50	40.99	43.33	1.02	61.17	0.228	0.208	276.3	3.34	37.95	0.006	0.012	0.046	0.26	250	3.04	0.003	0.006	1.52	0.006	0.34	0.017	10.38	1.49	0.043	1.37	1.16	0.67
B65	21/11/2011	4.01	45.82	51.98	0.51	65.05	0.016	0.180	300.3	3.81	32.57	0.004	0.004	0.017	0.11	299	1.72	0.002	0.002	1.49	0.005	0.11	0.022	10.65	1.07	<0.000	1.60	1.10	0.30
B65	05/12/2011	4.46	45.68	53.02	0.60	66.84	0.187	0.149	310.0	2.40	38.52	0.008	0.004	0.021	0.11	272	2.47	0.002	0.005	1.73	0.007	0.22	0.009	10.14	1.11	0.027	1.92	1.08	1.68
B65	19/12/2011	4.42	40.38	46.15	0.66	60.15	0.039	0.186	271.3	2.68	32.68	0.008	0.004	0.016	0.14	283	1.94	0.002	0.008	1.55	0.005	0.31	0.043	9.06	1.12	0.039	1.58	1.09	3.31
B65	03/01/2012	4.64	35.06	20.48	0.81	55.87	0.172	0.183	228.4	2.85	30.33	0.007	0.002	0.032	0.16	285	2.48	0.003	0.000	1.68	0.005	0.27	0.025	8.75	1.33	<0.000	1.18	1.14	0.28
B65	16/01/2012	4.83	32.84	19.16	0.57	58.57	0.027	0.189	241.1	0.22	31.00	0.004	0.002	0.021	0.09	304	<0.000	0.001	<0.000	1.80	0.001	0.26	0.003	8.88	1.23	<0.000	0.52	1.11	0.38
B65	30/01/2012	4.31	38.13	49.23	0.74	57.26	0.092	0.141	279.5	1.30	29.21	0.006	0.000	0.016	0.12	283	0.37	0.002	0.007	1.59	0.004	0.24	0.008	10.17	1.16	0.006	1.72	1.23	0.95
B65	27/02/2012	3.63	43.48	49.14	0.81	74.16	0.067	0.132	283.9	5.85	29.59	0.010	0.000	0.016	0.14	285	0.68	0.002	0.003	1.64	0.004	0.15	0.015	10.47	0.96	<0.000	1.80	1.20	13.29
B65	12/03/2012	3.42	42.40	46.18	0.63	56.01	0.067	0.162	318.7	1.35	23.37	0.001	<0.000	0.016	0.11	262	0.30	0.002	0.003	1.23	0.004	0.36	0.005	11.64	0.92	0.015	1.76	1.19	1.76
B65	26/03/2012	3.53	45.45	47.74	0.63	61.22	0.310	0.140	325.9	1.56	24.96	<0.000	<0.000	0.029	0.08	258	3.48	0.002	0.002	1.33	0.004	0.82	0.009	12.04	0.95	0.012	1.89	1.20	3.34
B65	10/04/2012	3.48	41.67	49.94	0.69	62.91	0.178	0.127	322.9	3.11	25.61	<0.000	0.001	0.015	0.13	180	2.96	0.002	0.002	1.29	0.006	0.17	0.037	11.55	0.91	<0.000	1.96	1.13	3.94
B65	23/04/2012	3.46	38.66	42.99	0.75	54.78	0.027	0.147	305.5	1.41	26.58	<0.000	0.001	0.015	0.13	195	0.58	0.001	0.002	1.24	0.004	0.22	0.011	10.73	0.90	<0.000	1.75	1.04	0.63
B65	09/05/2012	3.60	34.99	32.52	1.10	55.69	0.573	0.159	260.3	1.71	24.67	0.099	0.004	0.044	0.30	216	9.09	0.001	0.001	1.49	0.004	0.28	0.017	9.64	1.01	0.088	1.33	1.03	5.62
B65	21/05/2012	3.28	49.61	40.39	0.61	73.10	0.273	0.097	287.3	1.88	23.38	0.002	0.001	0.022	0.11	225	3.58	0.002	<0.000	1.19	0.003	0.32	0.009	10.77	0.78	<0.000	1.59	1.14	2.91
B65	04/06/2012	3.82	45.88	34.27	0.63	64.55	0.047	0.190	255.0	1.55	22.70	0.014	0.004	0.023	0.15	238	1.07	0.002	0.004	1.45	0.004	0.20	0.010	8.96	0.99	0.024	1.21	1.06	1.03
B65	18/06/2012	3.59	45.84	50.79	0.42	65.01	0.057	0.100	285.8	1.54	21.02	<0.000	<0.000	0.016	0.14	223	1.19	0.001	0.001	1.23	0.004	<0.000	<0.000	10.22	0.88	0.005	1.41	1.22	1.11
B65	02/07/2012	3.40	45.20	59.14	0.42	64.46	0.044	0.125	301.6	1.65	23.33	<0.000	<0.000	0.012	0.13	259	1.94	0.002	0.001	1.16	0.004	<0.000	<0.000	10.37	0.83	<0.000	1.53	1.21	0.57
B65	16/07/2012	3.62	42.29	46.50	0.60	61.74	0.078	0.099	311.3	1.77	27.75	<0.000	<0.000	0.012	0.13	203	1.24	0.002	0.007	1.30	0.005	0.48	0.019	10.94	0.92	<0.000	1.87	1.11	2.76
B65	30/07/2012	3.60	55.50	67.51	0.30	76.58	0.048	0.092	317.6	1.43	26.79	<0.000	0.003	0.013	0.09	199	0.80	0.002	<0.000	1.28	0.005	0.41	<0.000	11.22	0.87	0.006	1.96	1.13	3.12
B65	13/08/2012	4.28	46.76	56.46	0.87	64.98	0.115	0.126	337.3	2.45	42.41	0.005	0.004	0.016	0.12	197	5.10	0.003	0.007	1.56	0.006	<0.000	0.013	10.53	0.99	0.001	2.24	1.09	1.50
B65	27/08/2012	3.89	48.30	55.69	0.69	62.79	0.059	0.109	335.1	1.51	29.67	<0.000	0.001	0.013	0.13	186	0.50	0.003	0.000	1.47	0.004	0.23	0.010	11.17	1.01	<0.000	2.09	1.17	1.44
B65	10/09/2012	4.50	40.71	59.39	0.43	53.98	0.044	0.105	334.2	1.31	43.54	<0.000	0.002	0.010	0.13	242	0.41	0.001	<0.000	1.56	0.005	0.36	<0.000	10.59	1.14	<0.000	2.26	1.06	0.60
B65	24/09/2012	4.26	48.42	57.32	0.49	63.50	0.029	0.078	334.2	0.22	38.94	<0.000	0.003	0.015	0.11	218	0.31	0.002	0.001	1.50	0.006	0.26	0.001	10.56	1.03	<0.000	2.30	1.17	0.47
B65	08/10/2012	4.44	50.57	64.31	0.44	72.33	0.359	0.077	330.4	4.09	42.08	0.006	0.005	0.011	0.13	252	2.44	0.002	0.017	1.62	0.005	0.24	0.017	10.42	1.03	0.013	2.19	1.11	2.76
B65	22/10/2012	4.40	52.15	65.14	0.41	75.33	0.100	0.069	331.1	2.01	40.29	0.005	0.004	0.011	0.14	262	1.12	0.002	0.004	1.61	0.004	0.19	0.005	10.46	1.03	<0.000	2.24	1.17	0.42
B65	05/11/2012	4.37	54.71	67.61	0.35	78.13	0.103	0.073	329.4	1.58	43.18	<0.000	0.000	0.008	0.11	283	1.46	0.002	0.009	1.79	0.006	0.11	0.002	10.60	1.10	0.003	2.29	1.14	0.90

Sample ID	Date	As	B	Br	Cu	Li	Mn	Se	Sr	Al	Ba	Be	Cd	Co	Cr	F	Fe	Gd	Hg	Mo	Nd	Ni	Pb	Rb	Sb	Sn	U	V	Zn
B66	14/02/2011	3.83	31.54	20.13	1.52	37.49	4.087	0.080	198.3	5.01	8.55	0.002	0.001	0.053	0.06	253	2.48	0.003	0.001	0.48	0.003	0.18	0.025	5.98	0.92	0.008	0.71	1.11	0.63
B66	28/02/2011	3.66	30.04	21.64	1.40	37.60	4.481	0.078	204.4	4.63	8.62	0.003	0.002	0.046	0.04	296	3.45	0.002	0.056	0.46	0.004	0.22	0.039	6.00	0.75	0.010	0.74	1.03	1.61
B66	14/03/2011	3.85	30.00	22.06	1.85	38.41	6.676	0.068	213.9	5.64	8.90	0.003	0.007	0.047	0.30	<100	3.87	0.002	0.002	0.52	0.006	0.36	0.094	6.04	0.86	0.006	0.82	1.05	4.52
B66	28/03/2011	3.69	31.64	23.44	1.32	40.14	11.941	0.082	212.9	4.26	9.49	<0.000	0.004	0.049	0.06	<100	3.22	0.002	0.027	0.47	0.005	0.11	0.046	5.87	0.88	0.006	0.83	1.04	6.53
B66	11/04/2011	3.96	31.28	24.34	0.98	43.08	0.047	0.107	230.8	0.39	10.42	<0.000	0.001	0.037	0.04	129	0.22	0.001	0.002	0.51	0.001	0.03	<0.000	6.18	0.87	<0.000	0.20	0.96	0.53
B66	26/04/2011	3.77	25.87	21.53	1.82	35.12	4.662	0.085	230.4	4.50	10.67	0.002	0.006	0.049	0.31	117	3.72	0.002	0.007	0.54	0.004	0.38	0.031	6.13	0.89	<0.000	0.92	1.00	0.52
B66	09/05/2011	4.38	28.71	23.24	1.45	49.29	23.112	0.091	230.1	4.17	11.88	0.003	0.005	0.074	0.08	159	4.80	0.003	0.005	0.48	0.004	0.31	0.040	5.36	0.81	<0.000	1.00	1.08	0.85
B66	23/05/2011	4.89	30.03	27.93	1.85	55.31	25.860	0.103	251.3	5.93	13.37	0.013	0.008	0.079	0.11	118	9.72	0.004	0.154	0.52	0.007	0.33	0.184	5.41	0.74	0.021	1.08	1.13	1.53
B66	06/06/2011	5.36	40.58	33.30	2.80	45.99	17.796	0.028	203.0	3.37	8.12	0.006	0.019	0.206	2.74	121	54.53	0.004	0.023	1.62	0.005	1.63	0.060	6.62	0.73	0.002	0.64	1.14	1.67
B66	20/06/2011	3.03	24.57	22.64	1.42	34.19	1.505	0.056	149.1	3.02	8.34	0.005	0.002	0.045	0.05	120	5.24	0.003	<0.000	0.28	0.006	0.26	0.067	3.67	0.53	<0.000	0.69	0.88	1.25
B66	04/07/2011	6.32	46.14	32.29	2.44	66.01	17.494	0.095	261.1	4.28	14.72	0.003	0.012	0.086	0.12	109	10.47	0.005	0.013	0.69	0.008	0.69	0.252	6.23	0.93	0.002	1.08	1.54	1.23
B66	18/07/2011	4.79	39.63	31.88	1.67	65.91	0.643	0.077	235.5	3.56	13.78	0.008	0.007	0.079	0.07	161	4.03	0.003	<0.000	0.61	0.005	0.37	0.079	5.73	0.73	0.003	0.68	1.32	2.82
B66	16/08/2011	6.07	56.46	39.28	2.90	38.53	0.773	0.044	181.7	2.52	0.08	0.010	0.017	0.339	0.04	158	3.43	N.A	0.415	0.44	1.148	0.35	0.008	7.79	0.10	0.113	0.03	1.50	1.52
B66	29/08/2011	5.72	53.01	40.19	3.09	35.05	0.735	0.025	179.1	2.23	11.81	0.034	0.017	0.094	0.01	144	1.86	0.007	<0.000	0.47	0.009	0.32	0.031	7.86	0.84	<0.000	0.23	1.56	1.68
B66	12/09/2011	5.95	56.79	42.37	3.13	35.37	0.958	0.052	175.5	2.91	12.02	0.013	0.023	0.107	0.00	132	3.69	0.009	0.008	0.52	0.011	0.32	0.039	7.86	0.96	<0.000	0.21	1.53	0.65
B66	26/09/2011	6.16	62.38	25.54	3.10	40.10	1.198	0.040	185.6	3.20	13.82	0.007	0.024	0.100	0.02	141	2.59	0.008	<0.000	0.60	0.010	0.34	0.049	8.95	1.14	<0.000	0.22	1.55	3.74
B66	10/10/2011	6.28	59.40	38.35	2.24	40.33	<0.000	0.039	188.7	0.08	13.01	0.004	0.014	0.076	0.01	164	0.26	0.003	<0.000	0.75	0.001	0.25	0.020	9.16	1.21	0.004	0.11	1.37	0.62
B66	24/10/2011	6.35	58.11	34.98	3.06	37.06	2.193	0.047	188.8	4.54	13.56	0.007	0.026	0.094	0.03	151	4.66	0.008	0.004	0.71	0.010	0.39	0.098	9.11	1.20	0.018	0.21	1.57	1.73
B66	07/11/2011	5.74	51.34	24.12	2.79	38.25	11.468	0.035	177.8	6.67	11.08	0.007	0.021	0.107	0.07	114	10.56	0.008	0.008	0.66	0.008	0.34	0.137	8.32	1.11	0.019	0.23	1.48	51.03
B66	21/11/2011	5.62	47.96	18.60	2.41	37.17	2.116	0.038	169.1	4.02	11.24	0.007	0.009	0.076	0.03	124	2.65	0.005	0.001	0.60	0.006	0.21	0.027	7.73	1.10	0.007	0.19	1.44	1.54
B66	05/12/2011	5.41	42.96	21.81	2.29	41.26	15.595	0.041	164.5	2.05	9.54	0.008	0.011	0.091	0.03	135	1.57	0.005	0.008	0.62	0.005	0.27	0.020	6.59	1.00	0.031	0.25	1.39	1.06
B66	19/12/2011	4.94	38.58	20.33	1.90	41.50	27.246	0.037	165.1	2.10	8.68	0.007	0.010	0.093	0.05	138	1.77	0.004	0.002	0.66	0.005	0.26	0.013	5.98	0.91	0.001	0.32	1.28	0.56
B66	03/01/2012	5.17	33.28	3.84	2.00	42.11	30.163	0.046	162.1	2.67	8.58	0.006	0.007	0.107	0.03	139	2.86	0.004	<0.000	0.67	0.005	0.37	0.019	6.06	1.01	0.004	0.32	1.38	0.67
B66	16/01/2012	5.28	37.30	10.90	1.40	52.66	0.504	0.052	159.6	0.02	7.71	0.003	0.002	0.080	0.00	139	0.42	0.001	<0.000	0.63	0.001	2.37	<0.000	5.69	0.93	<0.000	0.07	1.23	<0.000
B66	30/01/2012	5.19	30.75	14.03	1.91	41.17	32.449	0.064	159.1	2.36	8.57	0.005	0.004	0.102	0.02	138	4.96	0.004	0.003	0.67	0.006	0.38	0.031	5.65	1.00	0.049	0.35	1.31	1.94
B66	27/02/2012	4.73	31.17	2.75	2.53	39.02	24.356	0.072	165.7	2.85	8.02	0.015	0.003	0.084	<0.000	152	4.52	0.003	0.002	0.65	0.004	0.38	0.005	5.45	0.95	0.004	0.38	1.13	1.03
B66	12/03/2012	4.18	33.59	11.48	1.53	44.55	25.872	0.049	182.9	3.06	8.34	0.010	0.006	0.065	<0.000	153	4.12	0.003	0.001	0.56	0.005	0.00	0.044	5.38	0.94	0.005	0.59	1.08	0.84
B66	26/03/2012	5.02	31.65	5.06	2.06	45.50	36.444	0.102	187.4	3.84	9.65	<0.000	0.002	0.086	<0.000	129	7.78	0.005	0.000	0.67	0.005	0.85	0.062	5.33	0.92	0.003	0.45	1.23	3.96
B66	10/04/2012	4.33	27.53	5.24	1.99	40.03	45.045	0.094	176.0	1.76	8.07	<0.000	0.006	0.079	0.03	101	5.25	0.003	0.001	0.56	0.004	0.19	0.010	5.14	0.80	0.079	0.46	0.98	0.16
B66	23/04/2012	4.15	26.75	4.36	1.87	33.92	45.442	0.057	170.1	2.62	7.29	<0.000	0.006	0.083	0.03	136	8.20	0.003	0.001	0.49	0.004	0.39	0.059	5.14	0.79	<0.000	0.41	0.91	2.50
B66	09/05/2012	4.31	24.85	6.47	1.49	34.62	35.968	0.067	146.2	2.48	6.85	0.008	0.007	0.073	0.21	134	3.07	0.003	0.001	0.57	0.005	0.23	0.012	4.60	0.80	0.041	0.34	0.95	1.27
B66	21/05/2012	4.57	37.70	4.66	1.79	45.44	41.897	0.047	154.7	3.31	6.74	0.003	0.005	0.066	0.02	129	3.46	0.003	<0.000	0.46	0.004	0.34	0.004	5.00	0.79	<0.000	0.39	1.12	0.26
B66	18/06/2012	5.08	37.21	21.47	1.80	45.63	42.626	0.081	184.9	2.71	8.46	<0.000	0.001	0.070	0.05	124	10.01	0.003	<0.000	0.50	0.005	<0.000	<0.000	5.40	0.87	0.009	0.50	1.18	0.76
B66	02/07/2012	5.18	36.88	8.07	1.90	33.75	17.214	0.073	160.9	2.87	9.30	<0.000	<0.000	0.066	0.05	135	2.88	0.004	0.001	0.45	0.008	0.32	0.033	5.65	0.94	<0.000	0.32	1.10	0.51
B66	16/07/2012	5.05	35.02	14.01	2.24	31.21	30.360	0.049	175.5	4.71	9.47	<0.000	0.005	0.088	0.06	136	7.57	0.005	0.004	0.50	0.011	0.76	0.075	6.25	0.97	0.012	0.39	1.18	3.32
B66	30/07/2012	5.28	47.64	23.87	2.22	41.69	38.350	0.053	188.7	2.27	9.20	0.005	0.012	0.073	0.03	125	2.53	0.003	0.000	0.49	0.006	0.03	0.019	6.65	0.94	<0.000	0.48	1.23	0.75
B66	13/08/2012	5.23	45.21	21.86	1.86	36.99	42.683	0.020	193.8	2.49	8.40	0.005	0.011	0.066	0.02	124	3.10	0.004	0.002	0.49	0.004	<0.000	0.018	7.16	0.99	<0.000	0.48	1.30	0.84
B66	27/08/2012	6.20	49.63	28.68	2.56	28.35	7.313	0.042	173.5	2.12	12.67	<0.000	0.011	0.077	0.03	127	1.30	0.006	<0.000	0.46	0.009	0.29	0.011	7.82	1.10	<0.000	0.21	1.37	0.57
B66	10/09/2012	6.05	59.02	30.44	2.53	34.02	6.940	0.028	156.8	3.08	11.32	0.008	0.017	0.076	0.02	107	2.86	0.007	<0.000	0.53	0.010	0.38	0.024	7.82	1.00	0.001	0.16	1.45	1.16
B66	24/09/2012	6.42	52.65	21.11	2.34	30.68	6.630	0.026	157.1	1.31	11.74	0.003	0.016	0.083	0.01	128	0.69	0.007	<0.000	0.60	0.011	0.27	0.010	8.21	1.03	<0.000	0.13	1.65	0.05
B66	08/10/2012	5.99	51.64	24.62	2.28	34.35	10.815	0.023	157.1	3.14	10.83	0.008	0.016	0.070	0.04	124	1.90	0.007	0.009	0.61	0.009	0.27	0.033	7.91	0.99	0.000	0.15	1.61	1.31
B66	22/10/2012	5.81	53.37	23.05	2.08	38.97	18.513	0.003	162.7	2.23	10.52	0.002	0.016	0.072	0.01	129	1.14	0.005	0.001	0.62	0.006	0.22	0.009	7.68	0.90	<0.000	0.18	1.49	0.24
B66	05/11/2012	5.71	55.05	23.10	2.12	39.84	21.252	0.032	164.7	3.05	10.42	<0.000	0.010	0.064	0.02	144	2.47	0.005	0.004	0.68	0.007	0.21	0.023	7.60	0.99	0.145	0.19	1.44	0.96

Sample ID	Date	As	B	Br	Cu	Li	Mn	Se	Sr	Al	Ba	Be	Cd	Co	Cr	F	Fe	Gd	Hg	Mo	Nd	Ni	Pb	Rb	Sb	Sn	U	V	Zn
B71	28/02/2011	2.82	40.47	33.96	0.95	42.56	2.262	0.228	307.5	7.52	22.89	0.004	0.001	0.050	0.13	137	6.83	0.004	0.031	0.66	0.009	0.27	0.039	7.06	0.89	<0.000	1.66	0.91	0.38
B71	14/03/2011	3.05	42.62	36.78	0.93	47.95	4.407	0.219	355.1	18.90	25.89	0.005	0.004	0.060	0.41	165	20.52	0.005	0.004	0.80	0.018	0.41	0.329	8.26	0.66	<0.000	2.51	0.93	1.17
B71	28/03/2011	3.05	40.63	33.47	1.02	44.48	0.654	0.190	288.5	7.11	22.67	0.001	0.002	0.058	0.12	147	4.77	0.002	0.056	0.64	0.008	0.14	0.039	7.00	0.89	0.001	1.36	0.99	0.30
B71	11/04/2011	3.15	42.90	37.22	0.39	51.39	<0.000	0.275	343.7	0.45	28.28	<0.000	0.002	0.042	0.08	165	0.16	0.001	0.005	0.84	0.001	0.05	0.015	8.03	0.90	<0.000	0.61	0.99	0.20
B71	26/04/2011	3.07	38.68	43.38	1.49	46.14	2.745	0.220	362.1	23.82	26.75	0.005	0.016	0.063	0.47	159	23.92	0.007	0.020	0.88	0.024	0.43	0.091	9.05	0.95	<0.000	2.08	1.06	0.41
B71	09/05/2011	2.67	36.59	24.98	1.09	32.77	1.245	0.075	191.6	8.32	11.65	0.004	0.005	0.056	0.11	127	10.63	0.003	0.005	0.39	0.008	0.23	0.148	5.57	0.85	<0.000	0.60	1.05	1.36
B71	23/05/2011	0.86	34.88	24.23	1.54	37.23	4.698	0.009	126.3	39.32	2.93	0.018	0.010	0.064	0.28	<100	231.01	0.012	0.011	0.05	0.048	0.31	4.325	0.69	0.19	0.016	0.14	0.78	7.35
B71	06/06/2011	2.41	37.23	19.00	1.46	29.65	2.367	0.077	182.0	7.13	10.07	0.006	0.006	0.081	10.33	111	26.05	0.002	0.003	3.66	0.005	4.46	0.100	5.16	0.84	<0.000	0.58	0.98	1.50
B71	20/06/2011	3.04	48.02	41.78	1.20	52.60	1.050	0.300	338.0	2.17	22.59	0.006	0.002	0.058	0.11	167	4.06	0.003	<0.000	0.64	0.005	0.25	0.039	9.34	0.85	<0.000	1.97	1.12	0.52
B71	04/07/2011	2.61	41.24	22.25	1.17	34.45	0.841	0.075	193.3	4.05	11.38	0.003	0.003	0.057	0.12	129	4.92	0.002	0.002	0.38	0.005	0.31	0.050	5.87	0.81	<0.000	0.69	1.04	0.35
B71	18/07/2011	2.58	39.30	23.91	0.92	31.05	1.013	0.058	180.8	2.07	10.77	0.003	0.004	0.051	0.10	136	6.65	0.003	0.001	0.36	0.003	0.19	0.017	5.52	0.83	<0.000	0.54	1.04	0.37
B71	16/08/2011	2.61	40.00	22.40	2.31	29.99	0.694	0.080	182.8	2.10	10.57	0.033	0.004	0.054	0.10	118	2.29	0.002	0.066	0.36	0.003	0.20	0.021	5.50	0.86	0.039	0.53	1.10	0.33
B71	29/08/2011	2.48	37.21	24.27	2.84	26.83	1.495	0.041	178.9	2.63	10.15	0.053	0.003	0.055	0.06	124	2.75	0.001	<0.000	0.34	0.003	0.19	0.039	5.49	0.79	<0.000	0.43	0.92	1.00
B71	12/09/2011	2.59	39.13	19.78	1.16	29.41	0.909	0.063	170.3	3.94	9.73	0.035	0.003	0.052	0.03	143	5.64	0.003	0.005	0.35	0.005	0.19	0.269	5.21	0.73	<0.000	0.42	1.08	0.38
B71	26/09/2011	2.69	40.47	16.30	1.14	31.75	0.955	0.046	176.3	3.33	10.52	0.003	0.004	0.056	0.08	130	4.58	0.003	<0.000	0.36	0.005	0.19	0.054	5.60	0.90	<0.000	0.42	1.05	2.40
B71	10/10/2011	2.85	43.39	21.93	0.93	33.84	0.702	0.043	177.1	2.59	11.07	0.004	0.003	0.057	0.09	100	3.65	0.002	<0.000	0.36	0.003	0.18	0.033	5.86	0.97	0.023	0.40	1.11	0.99
B71	24/10/2011	2.91	40.73	21.00	1.12	30.39	1.209	0.055	175.3	6.86	10.59	0.005	0.002	0.068	0.10	104	9.33	0.002	0.004	0.38	0.008	0.24	0.472	5.58	0.96	0.015	0.44	1.18	0.50
B71	07/11/2011	4.73	51.35	30.26	2.42	49.13	16.280	0.047	196.8	4.26	10.49	0.006	0.011	0.117	0.09	145	9.75	0.005	0.004	0.70	0.007	0.35	0.087	7.49	1.04	0.027	0.48	1.38	1.22
B71	21/11/2011	3.98	49.83	23.70	2.03	49.21	12.345	0.039	190.3	3.72	10.37	0.006	0.006	0.102	0.03	142	92.54	0.003	0.004	0.61	0.004	0.27	0.035	7.12	0.99	0.007	0.40	1.17	0.78
B71	05/12/2011	2.72	38.94	20.89	1.33	29.90	0.996	0.054	168.9	2.70	9.84	0.007	0.003	0.053	0.10	114	2.36	0.003	0.008	0.36	0.003	0.23	0.009	5.23	0.91	0.024	0.40	1.05	0.33
B71	19/12/2011	2.62	37.31	18.93	1.12	29.37	0.413	0.067	178.3	9.00	10.42	0.004	0.003	0.047	0.09	115	2.69	0.002	0.003	0.40	0.004	0.16	0.130	5.49	0.97	<0.000	0.43	1.02	0.35
B71	03/01/2012	2.80	31.76	5.82	3.00	26.87	9.261	0.072	171.3	3.59	10.44	0.009	0.002	0.064	0.10	110	30.39	0.004	<0.000	0.38	0.006	0.33	0.045	5.49	1.04	<0.000	0.41	1.09	1.37
B71	16/01/2012	2.60	36.43	14.87	0.93	31.15	<0.000	0.083	168.8	<0.000	9.77	0.003	0.001	0.041	0.05	125	0.26	0.001	<0.000	0.34	0.000	0.12	0.001	5.14	0.97	<0.000	0.18	0.96	0.38
B71	30/01/2012	2.65	30.95	24.17	2.70	24.41	0.531	0.071	167.6	2.68	10.40	0.005	<0.000	0.054	0.09	119	6.18	0.003	0.003	0.36	0.003	0.32	0.039	5.21	1.03	0.106	0.40	1.03	1.62
B71	27/02/2012	2.73	33.75	7.22	1.36	27.26	0.924	0.084	174.9	2.45	10.12	0.004	0.004	0.060	0.03	108	2.31	0.003	0.002	0.40	0.004	0.51	0.033	5.35	0.95	<0.000	0.43	0.95	2.21
B71	12/03/2012	3.58	50.53	7.02	1.12	27.89	1.872	0.228	303.4	2.98	20.32	0.008	0.004	0.053	0.07	170	3.84	0.003	0.002	1.00	0.005	0.02	0.034	8.45	0.93	<0.000	1.83	1.08	0.51
B71	26/03/2012	2.64	36.72	12.56	1.22	26.67	0.438	0.100	182.4	1.97	10.79	0.001	<0.000	0.053	0.02	114	1.81	0.002	0.001	0.38	0.003	0.38	0.026	5.54	0.96	0.011	0.49	1.01	0.58
B71	10/04/2012	2.41	32.72	10.37	1.28	25.88	1.376	0.087	173.3	1.72	9.77	<0.000	0.000	0.058	0.07	115	5.98	0.002	0.001	0.35	0.002	0.22	0.017	5.24	0.87	0.043	0.46	0.88	2.25
B71	23/04/2012	2.47	31.11	9.68	1.39	23.80	0.555	0.079	172.6	2.34	9.89	<0.000	0.002	0.046	0.08	121	2.66	0.002	0.002	0.36	0.002	0.27	0.027	5.23	0.90	<0.000	0.43	0.88	0.49
B71	09/05/2012	2.90	27.03	9.76	1.08	27.78	2.696	0.068	155.0	2.55	8.55	0.007	0.004	0.055	0.42	113	3.61	0.002	0.000	0.46	0.004	0.21	0.033	4.88	0.89	0.038	0.38	0.88	1.13
B71	04/06/2012	2.64	41.24	17.97	1.11	30.06	0.865	0.070	189.1	4.05	10.86	0.009	0.003	0.058	0.13	114	7.82	0.003	0.001	0.38	0.006	0.25	0.037	5.10	0.99	0.015	0.57	0.99	4.57
B71	18/06/2012	2.60	39.25	26.08	0.91	30.07	0.462	0.071	187.7	1.47	11.00	<0.000	<0.000	0.044	0.09	112	3.20	0.003	<0.000	0.35	0.003	<0.000	<0.000	5.26	0.93	0.004	0.53	1.04	0.52
B71	02/07/2012	2.67	40.97	10.72	0.97	28.17	0.302	0.049	187.8	2.40	11.46	<0.000	<0.000	0.059	0.11	108	2.96	0.002	0.001	0.34	0.005	0.22	0.026	5.59	0.95	<0.000	0.53	1.08	0.32
B71	16/07/2012	2.55	34.93	10.57	1.05	23.86	1.418	0.055	183.1	2.64	11.39	<0.000	<0.000	0.049	0.08	112	8.04	0.002	0.004	0.33	0.004	0.45	0.045	5.50	0.97	<0.000	0.50	0.93	1.52
B71	30/07/2012	2.63	43.80	22.40	0.97	30.95	1.437	0.070	182.8	3.04	10.78	0.005	0.004	0.057	0.09	113	7.44	0.002	0.001	0.35	0.003	<0.000	0.081	5.48	0.87	0.012	0.53	0.93	2.76
B71	13/08/2012	4.44	41.22	18.62	1.97	37.70	3.151	0.031	180.3	2.30	9.34	0.020	0.007	0.074	0.05	125	4.04	0.004	0.002	0.55	0.004	<0.000	0.016	6.14	0.87	<0.000	0.45	1.08	0.78
B71	27/08/2012	2.95	42.28	16.53	1.24	31.04	1.151	0.075	199.3	2.13	11.84	<0.000	0.000	0.058	0.10	120	3.94	0.002	<0.000	0.40	0.004	0.25	0.030	6.09	1.00	<0.000	0.57	1.03	1.41
B71	10/09/2012	2.72	46.44	22.50	0.96	33.23	0.646	0.060	182.6	3.09	10.49	0.005	0.003	0.054	0.08	111	5.75	0.003	<0.000	0.37	0.003	0.31	0.043	5.59	0.85	0.006	0.48	1.07	1.97
B71	24/09/2012	2.73	41.81	12.31	0.80	29.70	0.603	0.049	183.5	0.82	10.54	<0.000	0.003	0.049	0.09	119	1.53	0.002	<0.000	0.33	0.003	0.17	0.016	5.57	0.84	<0.000	0.48	1.09	0.80
B71	08/10/2012	2.60	44.04	17.24	0.77	32.22	0.542	0.039	177.4	2.66	10.12	0.004	0.004	0.056	0.13	110	3.26	0.002	0.005	0.34	0.004	0.18	0.022	5.44	0.84	<0.000	0.46	1.05	1.67
B71	22/10/2012	2.56	47.99	18.05	0.84	35.87	0.579	0.036	181.6	1.70	10.34	0.004	0.003	0.049	0.09	112	1.74	0.003	0.000	0.34	0.003	0.12	0.008	5.57	0.85	<0.000	0.49	1.07	0.21
B71	05/11/2012	2.68	49.13	17.17	0.79	34.61	8.061	0.051	180.4	4.22	10.66	<0.000	0.000	0.072	0.09	115	42.89	0.002	0.003	0.39	0.007	0.09	0.036	5.64	0.94	0.098	0.49	1.13	0.86

Sample ID	Date	As	B	Br	Cu	Li	Mn	Se	Sr	Al	Ba	Be	Cd	Co	Cr	F	Fe	Gd	Hg	Mo	Nd	Ni	Pb	Rb	Sb	Sn	U	V	Zn
Allier	14/02/2011	2.65	39.15	26.38	1.74	28.06	3.223	0.060	134.9	11.83	29.84	0.018	0.006	0.057	0.12	<100	26.44	0.007	0.001	0.25	0.018	1.33	0.057	6.23	1.23	0.003	0.60	0.81	7.05
Allier	28/02/2011	0.69	41.79	5.00	1.52	40.35	3.889	0.016	122.4	33.46	11.91	0.019	0.010	0.032	0.10	<100	58.46	0.013	0.044	0.01	0.051	0.30	0.159	1.51	0.43	0.001	0.10	0.36	6.68
Allier	14/03/2011	3.57	21.53	17.24	2.18	16.89	5.184	0.067	115.6	119.89	37.57	0.093	0.052	0.418	0.51	<100	120.46	0.044	0.011	0.20	0.188	1.52	0.157	6.36	1.63	0.007	0.15	0.56	15.73
Allier	11/04/2011	3.29	29.95	25.67	1.95	22.31	3.664	0.066	114.4	11.46	42.44	0.015	0.017	0.064	0.08	<100	20.24	0.012	0.003	0.18	0.036	0.72	0.058	5.88	1.59	<0.000	0.22	0.74	6.80
Allier	26/04/2011	3.70	48.90	32.78	4.27	32.75	7.524	0.085	140.3	28.06	52.48	0.012	0.018	0.082	0.39	103	58.17	0.013	0.008	0.45	0.040	1.27	0.186	7.90	1.50	<0.000	0.41	0.92	14.76
Allier	09/05/2011	4.38	54.27	31.97	2.54	37.11	7.495	0.069	140.1	12.98	36.62	0.012	0.008	0.086	0.13	119	36.07	0.008	0.006	0.33	0.024	0.75	0.084	8.21	1.46	0.008	0.44	1.05	6.06
Allier	23/05/2011	5.19	56.66	35.97	1.82	39.74	5.467	0.062	138.6	11.79	33.70	0.011	0.006	0.076	0.11	116	28.97	0.009	0.010	0.34	0.024	0.77	0.062	9.35	1.51	0.002	0.35	1.17	4.52
Allier	06/06/2011	4.88	42.46	24.49	2.03	28.14	3.053	0.062	111.8	16.65	33.23	0.015	0.010	0.074	2.92	112	43.81	0.010	0.111	1.38	0.032	2.15	0.081	7.04	1.36	0.010	0.26	1.09	4.95
Allier	20/06/2011	5.76	67.49	36.74	2.50	41.64	6.092	0.069	148.6	24.10	72.57	0.017	0.013	0.094	0.12	108	54.95	0.015	0.001	0.39	0.040	1.55	0.145	10.04	1.37	0.000	0.50	1.51	5.54
Allier	04/07/2011	5.85	61.59	36.36	3.45	38.35	2.918	0.079	128.8	62.55	33.49	0.047	0.015	0.176	0.14	141	135.59	0.030	0.009	0.26	0.124	0.98	0.577	9.36	0.92	0.013	0.31	1.56	14.75
Allier	18/07/2011	5.25	68.67	36.79	1.79	42.42	3.063	0.074	135.9	8.87	34.57	0.017	0.007	0.073	0.11	126	53.28	0.011	0.002	0.36	0.038	0.94	0.112	9.67	1.04	<0.000	0.44	1.36	2.27
Allier	16/08/2011	1.13	61.42	8.69	0.93	46.51	8.325	0.046	159.0	1.91	19.64	0.007	0.007	0.021	0.06	132	12.01	0.003	0.038	0.11	0.006	0.05	0.093	0.84	0.43	0.106	0.91	0.75	45.51
Allier	29/08/2011	4.40	44.58	29.72	2.56	29.94	6.783	0.062	107.5	26.40	28.50	0.027	0.016	0.078	0.13	109	56.38	0.013	0.077	0.34	0.052	0.85	0.147	7.95	0.80	0.027	0.19	1.07	13.30
Allier	12/09/2011	6.13	59.39	38.08	2.23	37.77	10.199	0.067	129.7	68.12	33.23	0.027	0.012	0.133	0.17	120	153.22	0.024	<0.000	0.34	0.091	0.87	0.311	9.46	0.75	<0.000	0.36	1.46	6.51
Allier	26/09/2011	4.12	58.42	20.87	2.01	37.99	4.648	0.055	110.8	21.32	25.43	0.017	0.008	0.069	0.09	150	60.59	0.010	<0.000	0.31	0.031	0.58	0.151	8.37	0.64	0.007	0.27	0.91	8.05
Allier	10/10/2011	3.90	66.28	32.18	3.28	40.25	6.805	0.064	124.4	20.08	28.42	0.022	0.010	0.086	0.12	121	66.25	0.010	0.023	0.35	0.030	0.69	0.200	9.46	0.74	0.076	0.29	0.87	16.15
Allier	24/10/2011	3.71	67.01	29.14	6.51	42.42	4.919	0.070	123.4	17.47	27.22	0.024	0.013	0.084	0.23	102	59.82	0.010	0.018	0.35	0.025	0.73	0.176	9.03	0.68	0.094	0.34	0.71	22.90
Allier	07/11/2011	2.54	8.19	11.43	4.35	5.06	13.283	0.080	44.8	342.04	18.70	0.075	0.018	0.242	0.61	<100	308.15	0.093	0.011	0.14	0.394	1.54	0.569	3.91	0.78	0.049	0.38	1.18	5.03
Allier	21/11/2011	3.23	33.59	16.32	2.04	23.10	6.905	0.045	91.8	17.09	24.32	0.027	0.009	0.077	0.12	<100	67.17	0.013	0.004	0.20	0.038	0.66	0.121	5.43	1.10	0.007	0.31	0.70	14.88
Allier	05/12/2011	3.63	52.56	19.27	1.41	34.83	6.277	0.058	114.1	10.19	26.76	0.030	0.006	0.073	0.10	<100	63.73	0.009	0.002	0.28	0.025	0.48	0.064	7.48	1.03	<0.000	0.39	0.84	2.29
Allier	19/12/2011	2.34	17.15	14.89	2.54	14.77	6.038	0.057	76.0	109.51	15.29	0.039	0.012	0.128	0.36	<100	123.77	0.035	0.008	0.21	0.159	1.63	0.296	5.16	1.01	0.074	0.17	1.21	17.05
Allier	03/01/2012	2.43	10.65	0.76	4.59	7.71	5.197	0.055	69.4	148.85	15.40	0.034	0.011	0.134	0.40	<100	144.40	0.036	0.079	0.18	0.159	1.43	0.291	4.58	0.78	0.036	0.14	1.15	7.86
Allier	16/01/2012	2.64	17.82	1.25	3.23	16.42	7.473	0.057	92.4	28.72	19.50	0.028	0.008	0.098	0.17	<100	48.68	0.011	<0.000	0.16	0.044	0.79	0.216	5.13	0.94	<0.000	0.21	0.78	7.82
Allier	30/01/2012	2.83	27.93	18.42	1.69	22.40	6.862	0.059	98.4	21.11	21.39	0.030	0.008	0.089	0.18	<100	70.26	0.014	0.012	0.26	0.040	0.64	0.108	5.81	1.17	0.093	0.32	0.90	4.27
Allier	13/02/2012	3.60	32.80	21.91	1.44	26.65	10.756	0.076	123.6	57.13	26.19	0.033	0.006	0.125	0.55	<100	114.37	0.019	0.001	0.30	0.074	1.01	0.210	6.94	1.48	0.027	0.44	1.12	4.57
Allier	27/02/2012	2.46	18.49	15.41	1.51	15.68	4.463	0.067	79.0	97.63	18.06	0.032	0.006	0.108	0.31	<100	115.52	0.023	0.014	0.21	0.091	0.89	0.117	4.61	1.40	0.327	0.20	1.00	4.01
Allier	12/03/2012	3.07	31.58	7.81	1.76	22.49	6.006	0.089	108.1	17.42	23.49	0.018	0.003	0.074	0.08	<100	48.54	0.011	0.002	0.24	0.035	0.90	0.090	6.15	1.58	0.005	0.36	0.90	3.05
Allier	26/03/2012	3.68	37.56	11.87	1.54	27.11	9.109	0.084	117.6	14.91	25.78	0.020	0.006	0.092	0.08	<100	56.75	0.012	0.001	0.28	0.035	0.69	0.076	7.27	1.80	0.013	0.38	1.06	2.96
Allier	10/04/2012	3.92	37.68	10.27	1.97	29.40	9.242	0.080	111.5	12.25	24.20	0.025	0.009	0.100	0.13	<100	66.72	0.010	0.005	0.29	0.029	0.58	0.089	7.01	1.81	0.108	0.36	0.97	2.27
Allier	23/04/2012	2.69	14.26	<0.000	2.05	10.58	5.707	0.068	75.2	72.86	17.19	0.023	0.006	0.109	0.21	103	122.23	0.024	0.003	0.17	0.096	0.74	0.119	4.47	1.23	0.016	0.18	0.92	2.05
Allier	09/05/2012	3.71	11.33	5.95	3.53	11.23	2.426	0.060	76.5	326.72	23.34	0.108	0.024	0.318	0.81	<100	475.10	0.082	0.002	0.22	0.373	1.19	0.696	5.10	1.33	0.024	0.31	1.68	3.77
Allier	21/05/2012	3.23	18.95	4.47	2.84	15.01	4.865	0.045	89.6	167.96	21.36	0.040	0.011	0.140	0.35	<100	184.20	0.041	<0.000	0.20	0.160	1.24	0.161	5.72	1.71	<0.000	0.16	1.53	2.41
Allier	18/06/2012	4.89	29.92	26.79	1.32	20.36	6.619	0.052	106.3	23.37	27.01	0.044	0.005	0.085	0.20	<100	94.73	0.019	0.001	0.30	0.059	0.62	0.106	5.76	1.17	0.049	0.35	1.28	1.66
Allier	02/07/2012	5.74	44.97	30.76	1.61	31.54	7.357	0.059	123.6	12.89	28.59	0.017	0.005	0.075	0.11	105	61.73	0.013	0.001	0.35	0.036	0.47	0.088	7.66	1.10	0.002	0.36	1.41	2.47
Allier	16/07/2012	5.37	44.99	14.68	1.38	29.47	9.141	0.072	124.9	23.14	28.98	0.013	0.003	0.096	0.16	<100	86.11	0.015	0.004	0.35	0.044	0.94	0.112	8.06	1.32	<0.000	0.44	1.42	7.38
Allier	30/07/2012	5.52	55.57	26.15	1.29	29.21	10.578	0.061	123.8	8.08	28.27	0.001	0.001	0.093	0.09	111	37.91	0.008	0.003	0.35	0.024	0.86	0.071	8.87	1.00	<0.000	0.33	1.37	1.97
Allier	13/08/2012	5.01	45.55	19.61	1.37	29.34	9.475	0.049	100.3	13.31	24.92	0.027	0.007	0.076	0.10	113	51.19	0.007	0.003	0.30	0.027	0.38	0.090	7.42	0.95	0.005	0.23	1.06	2.25
Allier	27/08/2012	4.82	49.54	24.56	1.50	32.78	9.571	0.047	97.4	13.14	24.09	0.017	0.007	0.079	0.07	115	63.24	0.010	<0.000	0.31	0.032	0.54	0.146	7.37	0.75	0.008	0.26	1.02	3.80
Allier	24/09/2012	4.20	67.40	29.45	1.31	41.26	12.920	0.061	123.9	56.61	28.37	0.027	0.012	0.103	0.15	112	117.93	0.021	<0.000	0.33	0.071	0.54	0.217	9.38	0.58	<0.000	0.37	1.06	5.93
Allier	08/10/2012	4.10	70.60	29.00	1.06	45.21	7.968	0.033	122.5	9.76	26.87	0.026	0.008	0.069	0.26	107	55.22	0.011	0.005	0.34	0.021	0.54	0.079	9.01	0.79	<0.000	0.34	0.96	3.01
Allier	22/10/2012	3.77	63.20	24.18	1.04	40.05	9.381	0.039	111.3	7.43	24.83	0.022	0.007	0.071	0.09	103	62.04	0.009	0.001	0.29	0.023	0.51	0.089	8.54	0.65	<0.000	0.27	0.80	3.54
Allier	05/11/2012	3.55	53.23	18.12	1.07	33.02	9.065	0.075	105.3	20.58	23.57	0.019	0.003	0.065	0.12	117	101.89	0.014	0.005	0.33	0.040	0.51	0.084	7.87	0.96	0.003	0.31	0.88	3.25

Sample ID	Date	As	B	Br	Cu	Li	Mn	Se	Sr	Al	Ba	Be	Cd	Co	Cr	F	Fe	Gd	Hg	Mo	Nd	Ni	Pb	Rb	Sb	Sn	U	V	Zn
Cognet	14/02/2011	33.46	44.87	49.68	0.99	97.07	0.030	0.892	1223.7	3.87	8.34	0.001	0.002	0.033	0.70	383	1.29	0.001	0.001	3.54	0.001	0.97	0.030	14.70	0.24	0.007	5.79	4.99	0.45
Cognet	28/02/2011	33.28	43.93	46.47	1.07	95.60	0.029	0.862	1252.1	2.90	8.60	0.001	0.003	0.030	0.67	395	0.81	0.001	0.024	3.43	0.002	0.95	0.040	15.14	0.24	<0.000	5.92	5.05	0.18
Cognet	14/03/2011	32.81	42.28	45.40	1.37	93.05	0.092	0.839	1226.2	3.72	8.58	<0.000	0.005	0.028	0.69	379	1.02	0.001	0.182	3.35	0.001	0.87	0.040	14.89	0.21	0.006	5.99	4.86	0.10
Cognet	28/03/2011	31.91	46.60	51.91	1.40	101.59	0.026	0.891	1267.4	0.65	8.87	<0.000	0.004	0.028	0.66	372	0.00	0.001	0.004	3.46	<0.000	0.55	0.003	14.78	0.24	0.026	6.07	4.94	<0.000
Cognet	11/04/2011	36.43	44.25	48.09	0.50	102.32	<0.000	1.130	1258.0	3.27	8.17	0.001	0.028	0.027	0.85	386	1.45	0.000	0.004	3.66	0.000	1.04	0.027	13.61	0.19	<0.000	5.40	5.13	0.37
Cognet	26/04/2011	32.09	42.61	50.25	2.90	93.91	0.042	1.012	1204.2	2.48	8.69	0.002	0.005	0.035	0.71	387	0.59	0.001	0.005	3.35	0.002	0.99	0.027	14.84	0.23	0.012	5.68	5.16	2.14
Cognet	09/05/2011	33.80	46.41	51.04	2.46	104.99	0.042	1.064	1240.1	1.61	8.63	0.004	0.003	0.029	0.65	402	1.16	0.000	0.085	3.23	0.000	0.95	0.037	15.05	0.22	0.001	5.66	5.17	0.64
Cognet	23/05/2011	32.87	45.18	48.69	3.71	108.51	0.088	0.995	1237.3	3.05	8.42	0.003	0.005	0.039	2.73	385	5.65	0.001	0.012	4.10	0.001	1.98	0.030	14.76	0.24	0.035	5.72	5.04	0.36
Cognet	06/06/2011	32.38	44.11	46.07	3.53	99.99	0.301	0.988	1238.0	1.92	7.35	0.006	0.001	0.004	0.15	393	2.10	0.000	<0.000	0.35	0.002	0.47	0.074	0.64	0.09	<0.000	3.42	2.08	0.97
Cognet	20/06/2011	34.29	43.30	42.01	2.54	109.19	0.088	1.040	1217.6	8.04	9.25	0.004	0.005	0.052	0.66	388	8.72	0.003	0.010	3.47	0.015	1.10	0.046	16.17	0.23	0.018	6.05	5.25	0.25
Cognet	04/07/2011	34.31	45.58	53.05	3.93	106.52	0.262	1.016	1253.4	1.42	9.04	0.004	0.005	0.026	0.64	413	0.60	0.000	0.001	3.42	<0.000	1.00	0.091	15.61	0.22	<0.000	6.00	5.32	0.56
Cognet	18/07/2011	33.56	47.38	48.78	2.29	105.66	0.024	1.027	1225.1	10.26	12.18	0.007	0.008	0.036	0.87	415	1.97	0.001	0.010	4.41	0.001	1.31	0.073	19.62	0.30	0.048	7.69	6.70	0.39
Cognet	16/08/2011	33.75	45.96	54.07	3.12	99.86	0.039	1.140	1308.6	1.30	9.46	0.027	0.005	0.029	0.66	414	0.92	0.001	0.100	3.54	0.003	1.03	0.045	16.61	0.24	0.002	6.06	5.49	0.29
Cognet	29/08/2011	34.82	47.68	54.59	2.35	103.60	0.029	1.041	1271.1	5.95	9.54	0.011	0.008	0.031	0.70	391	4.44	0.000	0.001	3.64	0.004	1.15	0.178	15.72	0.21	<0.000	5.70	5.63	9.37
Cognet	12/09/2011	34.34	45.16	51.28	4.91	95.28	0.543	1.011	1263.0	1.54	9.40	0.003	0.006	0.067	0.73	413	1.27	0.001	<0.000	3.54	0.002	0.96	0.051	15.90	0.24	0.019	5.93	5.31	1.71
Cognet	26/09/2011	33.51	49.70	45.47	2.06	109.53	0.206	1.073	1235.5	0.39	9.32	0.000	0.003	0.026	0.61	446	<0.000	0.000	0.003	3.76	0.000	0.88	0.001	16.65	0.28	0.018	6.07	5.39	<0.000
Cognet	10/10/2011	38.26	45.57	45.32	0.61	105.11	0.001	1.455	1252.1	1.11	9.89	0.002	0.003	0.031	0.60	390	0.49	0.001	0.008	3.75	0.000	1.04	0.051	16.80	0.27	0.036	6.07	5.73	0.59
Cognet	24/10/2011	35.98	50.43	43.90	2.35	107.47	<0.000	1.198	1275.8	1.36	9.95	0.002	0.004	0.028	0.63	389	0.36	0.000	0.003	3.73	0.001	0.99	0.048	17.08	0.26	0.013	6.00	5.51	2.66
Cognet	07/11/2011	35.33	49.12	43.81	1.90	109.11	0.007	1.169	1269.0	0.99	9.40	0.002	0.005	0.032	0.59	422	<0.000	0.001	0.002	3.63	0.000	0.95	0.050	16.76	0.25	<0.000	5.89	5.51	<0.000
Cognet	21/11/2011	35.42	51.03	41.38	1.75	113.06	<0.000	1.058	1259.4	1.09	9.25	0.005	0.006	0.028	0.56	412	<0.000	0.000	0.001	3.65	<0.000	0.90	0.047	16.80	0.25	<0.000	5.74	5.44	0.06
Cognet	05/12/2011	35.10	49.60	38.89	1.75	111.91	<0.000	0.999	1236.8	2.05	8.88	0.004	0.005	0.028	0.64	403	0.81	0.001	0.003	3.62	0.001	0.98	0.053	15.91	0.25	0.004	5.37	5.59	0.90
Cognet	19/12/2011	34.64	47.55	44.04	1.82	107.40	<0.000	1.022	1189.5	1.29	8.55	0.005	0.004	0.038	0.58	409	0.54	0.000	<0.000	3.76	0.001	1.05	0.050	15.82	0.26	0.001	5.44	5.48	<0.000
Cognet	03/01/2012	35.23	42.26	31.83	1.69	103.00	0.037	1.025	1148.5	0.34	8.11	0.001	0.002	0.037	0.56	410	<0.000	0.001	<0.000	3.77	0.000	0.83	<0.000	15.67	0.26	0.011	5.13	5.27	<0.000
Cognet	16/01/2012	39.00	36.49	26.81	0.54	98.79	0.010	1.271	1115.6	1.53	8.82	0.003	0.002	0.035	0.58	374	0.44	0.001	0.007	4.01	0.001	1.01	0.047	15.94	0.29	0.042	5.59	5.51	0.17
Cognet	30/01/2012	36.20	41.90	45.78	1.97	102.26	0.010	1.007	1172.1	1.74	7.37	0.002	0.004	0.037	0.53	461	2.82	0.001	0.001	3.86	0.001	1.08	0.053	14.50	0.26	0.006	4.83	4.86	1.88
Cognet	13/02/2012	33.24	34.47	40.45	1.45	85.42	0.149	0.862	1048.5	1.80	6.69	0.013	0.002	0.039	0.55	404	1.19	0.001	0.007	3.60	0.002	0.88	0.044	13.15	0.24	0.062	4.85	4.74	0.28
Cognet	27/02/2012	30.65	43.45	45.36	3.81	102.06	0.062	0.900	1006.4	1.02	9.61	<0.000	<0.000	0.038	0.48	407	2.78	0.001	0.002	3.75	0.000	1.01	0.034	14.84	0.25	0.008	5.33	4.70	1.97
Cognet	12/03/2012	31.78	43.42	30.22	1.43	84.64	0.215	0.982	1143.1	1.16	8.66	<0.000	0.000	0.042	0.54	371	3.54	<0.000	0.001	3.83	0.000	1.28	0.043	15.40	0.27	0.012	5.85	5.26	2.18
Cognet	26/03/2012	33.73	47.59	34.28	2.54	97.27	0.302	1.118	1224.7	1.05	8.52	<0.000	0.005	0.042	0.58	381	3.58	0.000	0.002	3.50	0.000	0.96	0.052	15.01	0.27	0.037	5.85	4.85	2.12
Cognet	10/04/2012	32.76	41.76	34.90	1.55	98.33	0.344	1.102	1203.0	1.39	8.41	<0.000	0.003	0.031	0.55	433	0.54	0.000	0.002	3.38	<0.000	0.83	0.035	14.92	0.26	0.004	5.66	4.58	0.10
Cognet	23/04/2012	31.37	38.90	33.52	1.89	89.27	0.023	1.099	1205.5	2.37	8.44	0.016	0.007	0.047	0.83	421	2.51	0.001	0.006	3.53	0.002	1.03	0.070	14.97	0.27	0.337	5.67	4.96	1.02
Cognet	09/05/2012	32.34	39.44	38.57	1.65	97.91	0.116	1.096	1195.5	1.14	9.10	0.004	0.002	0.026	0.59	398	0.16	0.000	<0.000	3.34	<0.000	1.09	0.041	15.23	0.14	0.022	5.95	4.86	0.19
Cognet	21/05/2012	31.71	49.82	39.94	1.73	118.31	0.011	0.843	1211.4	1.77	8.48	0.000	0.005	0.027	0.66	424	5.30	0.000	<0.000	3.46	0.001	0.88	0.049	14.27	0.24	0.017	5.64	4.73	1.67
Cognet	04/06/2012	32.07	48.29	42.68	1.41	106.94	0.112	0.935	1283.4	0.87	9.02	<0.000	0.001	0.024	0.73	416	0.48	0.000	0.001	3.45	0.000	0.76	0.012	14.24	0.26	0.019	5.86	5.20	0.14
Cognet	18/06/2012	32.80	48.39	60.39	1.75	111.13	0.006	0.834	1278.2	0.99	8.93	<0.000	<0.000	0.022	0.70	420	1.02	<0.000	<0.000	3.41	0.000	0.72	0.009	14.55	0.24	<0.000	5.68	5.28	0.10
Cognet	02/07/2012	33.34	48.24	56.93	1.73	111.25	0.026	0.911	1318.6	1.02	9.74	<0.000	0.001	0.025	0.63	434	0.24	0.000	<0.000	3.92	0.000	0.97	0.042	16.11	0.27	<0.000	6.22	5.16	0.26
Cognet	16/07/2012	33.53	47.11	47.98	1.93	105.58	0.064	0.882	1300.5	0.05	9.55	<0.000	0.002	0.029	0.60	414	0.21	0.000	0.000	3.70	0.000	1.03	0.057	15.77	0.09	<0.000	6.21	5.25	<0.000
Cognet	30/07/2012	32.28	56.28	60.38	1.84	121.41	0.054	0.851	1293.9	0.87	9.10	0.001	0.005	0.027	0.62	407	0.30	<0.000	0.009	3.74	0.000	0.97	0.065	15.16	0.17	<0.000	5.79	5.30	0.49
Cognet	13/08/2012	33.23	52.20	61.67	1.64	108.46	0.090	0.870	1282.4	0.82	9.18	<0.000	0.004	0.028	0.65	430	0.21	<0.000	0.002	3.84	0.000	0.97	0.056	15.28	0.17	<0.000	5.68	5.42	<0.000
Cognet	27/08/2012	37.29	55.93	48.15	1.83	122.72	0.009	0.729	1256.6	1.17	8.98	<0.000	0.001	0.029	0.57	401	0.29	0.000	0.013	4.06	0.001	1.05	0.050	15.39	0.29	0.086	5.72	5.51	0.58
Cognet	10/09/2012	34.09	46.72	46.15	2.15	96.32	0.013	0.961	1318.3	3.14	8.40	0.000	0.003	0.030	0.94	397	2.55	0.000	0.043	3.24	0.001	1.08	0.028	14.70	0.23	<0.000	5.75	4.95	0.32
Cognet	24/09/2012	32.79	52.94	39.91	1.93	108.99	0.006	0.880	1288.6	1.98	9.38	<0.000	<0.000	0.027	0.76	420	0.85	0.001	0.007	3.58	0.001	1.39	0.044	16.03	0.26	<0.000	6.17	5.17	1.88
Cognet	08/10/2012	32.60	52.95	47.14	1.74	113.69	0.026	0.890	1224.6	1.21	9.24	<0.000	0.005	0.027	0.71	440	0.47	0.000	<0.000	3.62	0.001	1.03	0.039	15.72	0.25	0.028	6.18	5.08	0.49
Cognet	22/10/2012	32.44	56.42	48.34	1.78	117.86	0.006	0.782	1202.1	1.69	9.08	0.004	0.006	0.030	0.70	436	0.69	0.001	0.012	3.71	0.001	0.94	0.042	15.81	0.24	<0.000	6.11	5.18	0.77
Cognet	05/11/2012	32.62	56.80	49.02	1.42	115.02	0.040	0.818	1179.7	0.83	9.06	<0.000	0.004	0.028	0.73	424	0.15	0.000	<0.000	3.56	0.000	0.93	0.026	15.07	0.24	<0.000	6.03	5.82	0.07

Sample ID	Date	As	B	Br	Cu	Li	Mn	Se	Sr	Al	Ba	Be	Cd	Co	Cr	F	Fe	Gd	Hg	Mo	Nd	Ni	Pb	Rb	Sb	Sn	U	V	Zn
Jallat	14/02/2011	97.41	24.03	33.66	0.47	67.48	0.055	0.809	1283.3	4.04	117.58	0.001	0.001	0.033	0.14	590	1.67	0.001	0.000	1.52	0.003	1.00	0.219	17.78	0.28	0.001	5.56	0.95	0.70
Jallat	28/02/2011	94.96	23.17	32.47	0.40	67.18	0.043	0.865	1296.6	3.12	117.84	<0.000	0.000	0.028	0.13	586	1.33	0.001	0.094	1.50	0.002	1.05	0.183	18.68	0.27	<0.000	5.57	0.92	0.79
Jallat	14/03/2011	95.05	22.68	31.40	0.44	65.78	0.092	0.846	1312.3	3.39	118.65	<0.000	0.001	0.032	0.39	625	1.85	0.002	0.007	1.57	0.002	1.10	0.212	18.88	0.26	<0.000	5.60	0.86	0.80
Jallat	28/03/2011	93.15	24.20	33.54	0.49	70.01	0.050	0.847	1301.7	3.41	119.28	<0.000	0.003	0.031	0.13	585	1.11	0.003	2.222	1.62	0.002	1.01	0.224	18.67	0.27	0.007	5.63	0.86	0.37
Jallat	26/04/2011	91.73	22.23	33.24	1.37	66.89	0.069	0.992	1244.4	3.05	109.09	<0.000	0.005	0.029	0.35	581	1.64	0.001	0.015	1.74	0.001	1.21	0.230	17.51	0.22	<0.000	5.12	0.77	0.46
Jallat	09/05/2011	96.96	22.57	33.21	0.88	74.59	0.121	1.058	1274.5	3.82	118.40	0.004	0.007	0.036	0.14	619	1.02	0.004	0.004	1.64	0.005	1.13	0.254	18.57	0.27	0.010	5.42	0.87	6.00
Jallat	23/05/2011	97.00	25.20	34.38	0.42	75.14	0.044	1.044	1287.4	3.08	118.69	<0.000	0.003	0.030	0.14	560	1.15	0.001	0.061	1.65	0.001	1.12	0.263	19.26	0.27	<0.000	5.80	0.87	0.46
Jallat	06/06/2011	87.43	20.11	29.23	0.91	65.75	0.514	0.909	1230.0	3.30	114.90	0.011	0.004	0.036	2.89	621	6.85	0.001	0.037	2.42	0.002	2.33	0.288	16.97	0.25	0.070	5.07	0.77	1.25
Jallat	20/06/2011	96.26	24.25	34.67	0.69	73.40	0.072	1.073	1275.0	1.90	118.68	0.002	0.003	0.034	0.12	657	1.73	0.002	<0.000	1.67	0.005	1.08	0.271	19.04	0.27	<0.000	5.95	0.80	0.64
Jallat	04/07/2011	97.19	23.18	34.52	0.70	74.36	0.178	1.087	1286.3	2.70	119.51	0.003	0.003	0.032	0.20	715	2.29	0.002	0.003	1.70	0.004	1.10	0.285	20.42	0.27	0.012	5.79	0.82	2.38
Jallat	18/07/2011	98.15	23.45	32.66	1.15	75.10	0.474	1.150	1288.5	5.98	122.40	0.003	0.007	0.034	0.16	679	4.60	0.002	0.001	1.73	0.007	1.20	0.335	20.05	0.26	<0.000	5.95	0.86	15.44
Jallat	16/08/2011	92.86	21.78	34.92	0.50	69.14	0.063	1.155	1328.5	1.53	116.80	0.005	0.003	0.029	0.14	639	1.12	0.002	0.006	1.85	0.002	0.98	0.252	21.27	0.25	<0.000	5.74	0.80	0.41
Jallat	29/08/2011	92.21	21.53	31.87	0.67	69.59	0.040	1.067	1244.0	1.59	117.88	0.029	0.004	0.034	0.13	631	1.21	0.002	0.222	1.80	0.002	1.08	0.221	19.66	0.26	0.006	5.84	0.84	0.41
Jallat	12/09/2011	89.68	19.84	30.70	0.59	62.80	0.112	1.113	1234.3	2.85	114.87	0.002	0.005	0.032	0.09	789	2.78	0.002	<0.000	1.77	0.004	1.05	0.307	18.67	0.22	<0.000	5.58	0.87	0.49
Jallat	26/09/2011	89.64	21.62	25.56	0.39	74.37	0.117	1.190	1210.0	3.82	112.67	<0.000	0.005	0.031	0.12	697	7.34	0.002	<0.000	1.74	0.004	1.01	0.346	19.28	0.26	0.030	5.83	0.78	3.68
Jallat	10/10/2011	94.21	21.66	28.50	0.63	74.20	0.051	1.255	1275.8	2.17	115.46	0.001	0.003	0.029	0.11	583	1.24	0.001	0.012	1.79	0.003	1.08	0.379	19.95	0.28	0.033	6.08	0.84	0.57
Jallat	24/10/2011	95.72	20.66	25.67	0.47	72.37	0.069	1.342	1255.3	2.25	115.18	0.003	0.004	0.033	0.11	579	2.50	0.002	0.011	1.84	0.004	1.09	0.359	19.65	0.29	0.058	6.01	0.82	2.55
Jallat	07/11/2011	89.00	22.51	33.97	0.76	78.68	0.226	1.176	1271.8	4.32	117.43	0.003	0.003	0.034	0.25	606	4.08	0.002	0.002	1.74	0.005	1.09	0.288	19.39	0.30	0.010	5.81	1.00	1.33
Jallat	21/11/2011	91.76	22.69	28.23	0.46	81.51	0.086	1.160	1267.4	2.40	115.61	0.002	0.005	0.028	0.13	578	1.52	0.001	0.003	1.78	0.003	1.01	0.357	20.40	0.27	<0.000	5.99	0.88	1.07
Jallat	05/12/2011	93.10	21.48	23.57	0.55	79.11	0.132	1.162	1269.5	2.57	111.40	0.004	0.003	0.032	0.10	591	2.91	0.002	0.000	1.76	0.003	0.87	0.294	19.76	0.26	<0.000	5.96	1.02	1.30
Jallat	19/12/2011	93.49	19.59	27.48	0.64	74.36	0.019	1.239	1204.4	1.81	110.58	0.006	0.003	0.027	0.16	583	1.00	0.001	0.002	1.76	0.003	0.98	0.292	18.80	0.25	<0.000	5.73	0.92	0.89
Jallat	03/01/2012	97.22	19.00	16.98	0.60	75.63	0.198	1.297	1220.8	2.36	114.00	0.004	0.002	0.036	0.13	609	3.59	0.002	<0.000	1.85	0.004	1.09	0.318	19.47	0.28	0.004	6.11	0.99	0.91
Jallat	16/01/2012	98.57	16.93	16.24	0.18	73.88	0.014	1.497	1222.0	0.24	110.77	0.001	0.001	0.029	0.11	539	<0.000	0.001	<0.000	1.87	0.001	0.76	<0.000	20.22	0.27	0.058	5.98	0.85	<0.000
Jallat	30/01/2012	103.29	19.75	31.63	0.79	76.37	0.106	1.235	1265.1	2.63	120.78	0.003	0.000	0.032	0.14	671	2.35	0.002	0.006	1.89	0.003	1.11	0.314	20.55	0.30	0.029	6.46	0.96	0.57
Jallat	13/02/2012	101.65	17.03	30.80	0.72	69.94	0.099	1.225	1261.0	1.79	119.49	0.003	0.036	0.031	0.16	613	1.70	0.002	0.001	1.90	0.002	1.10	0.309	20.93	0.28	0.023	6.24	0.85	0.76
Jallat	27/02/2012	87.84	24.36	34.69	0.53	89.32	0.308	1.123	1235.2	2.23	116.49	0.003	0.000	0.036	0.18	573	3.63	0.002	0.005	1.71	0.004	1.06	0.248	19.67	0.26	0.040	5.96	1.00	1.46
Jallat	12/03/2012	94.66	23.57	21.78	0.79	71.71	0.219	1.218	1344.4	1.78	127.63	<0.000	<0.000	0.043	0.10	526	2.92	0.002	0.001	1.88	0.002	1.70	0.255	21.87	0.27	0.006	6.41	0.88	1.65
Jallat	26/03/2012	97.42	24.47	22.94	0.66	79.23	0.040	1.271	1378.3	1.53	126.90	0.001	0.004	0.032	0.09	587	0.49	0.003	0.001	2.02	0.003	1.36	0.324	22.05	0.30	0.002	6.55	0.98	0.34
Jallat	10/04/2012	96.90	21.75	21.07	0.64	79.29	0.367	1.232	1308.6	1.91	121.05	<0.000	0.002	0.036	0.15	596	4.63	0.002	0.002	1.92	0.002	1.11	0.296	21.35	0.29	0.022	6.36	0.89	2.28
Jallat	23/04/2012	93.14	19.24	18.49	1.10	69.78	0.131	1.287	1276.7	2.07	115.59	<0.000	0.002	0.034	0.28	641	5.10	0.002	0.001	1.93	0.003	1.17	0.283	20.92	0.27	<0.000	5.83	0.76	2.05
Jallat	09/05/2012	90.71	17.75	16.53	0.65	63.27	0.320	1.224	1270.9	3.23	124.25	0.009	0.002	0.033	0.14	547	1.83	0.002	<0.000	1.93	0.003	1.18	0.318	21.39	0.17	0.060	6.21	0.85	1.34
Jallat	21/05/2012	93.27	26.32	23.00	1.03	89.45	0.096	0.994	1265.0	3.18	116.42	0.000	0.003	0.033	0.09	639	2.91	0.002	<0.000	1.79	0.004	0.96	0.253	20.11	0.25	0.018	5.61	0.78	1.07
Jallat	04/06/2012	90.75	24.58	21.99	0.28	76.18	0.173	0.986	1267.6	3.38	124.92	<0.000	<0.000	0.030	0.13	638	3.38	0.002	0.000	1.69	0.003	0.85	0.208	19.22	0.29	0.016	5.67	0.84	0.64
Jallat	18/06/2012	95.15	26.17	37.36	0.47	79.41	0.252	0.784	1326.9	2.94	125.75	<0.000	0.003	0.024	0.16	589	3.12	0.003	<0.000	1.53	0.003	0.95	0.214	18.40	0.28	0.003	5.28	0.81	0.80
Jallat	02/07/2012	97.11	27.26	39.52	0.74	78.69	0.149	0.770	1334.9	3.91	129.76	<0.000	<0.000	0.028	0.15	609	2.67	0.003	0.005	1.65	0.004	1.34	0.226	19.62	0.29	<0.000	5.83	0.80	1.41
Jallat	16/07/2012	97.90	26.21	23.42	0.61	72.92	0.108	0.730	1338.2	2.84	124.78	<0.000	0.003	0.030	0.13	603	2.04	0.002	<0.000	1.65	0.003	1.05	0.229	18.92	0.28	0.021	5.74	0.79	0.65
Jallat	30/07/2012	95.65	30.99	43.50	0.42	84.74	0.073	0.689	1313.0	3.05	128.71	0.002	0.004	0.031	0.13	593	2.18	0.002	0.003	1.66	0.003	0.77	0.251	19.75	0.26	<0.000	5.85	0.70	1.23
Jallat	13/08/2012	95.32	27.24	26.85	0.48	73.32	0.059	0.798	1304.7	2.48	119.46	<0.000	0.003	0.031	0.10	621	1.63	0.003	<0.000	1.59	0.003	0.96	0.252	18.67	0.26	0.003	5.51	0.76	1.11
Jallat	27/08/2012	91.71	28.86	26.05	0.34	82.48	0.088	0.723	1252.4	4.12	129.56	<0.000	0.001	0.030	0.14	644	3.55	0.002	<0.000	1.76	0.004	1.17	0.281	20.56	0.28	<0.000	5.94	0.73	1.05
Jallat	10/09/2012	95.86	24.67	31.57	0.84	67.17	0.173	0.875	1351.9	3.18	125.46	<0.000	0.003	0.033	0.12	592	3.58	0.002	<0.000	1.69	0.005	1.19	0.293	19.63	0.10	<0.000	5.93	0.74	0.14
Jallat	24/09/2012	94.11	27.00	18.36	0.43	74.35	0.134	0.908	1286.9	5.46	120.63	0.002	0.003	0.029	0.12	639	3.99	0.002	0.005	1.70	0.005	1.11	0.323	19.45	0.18	<0.000	5.74	0.76	1.44
Jallat	08/10/2012	91.78	25.35	27.02	0.56	76.82	0.119	0.920	1253.5	5.90	120.61	<0.000	0.004	0.029	0.11	603	5.43	0.002	0.001	1.89	0.004	1.11	0.360	18.47	0.18	<0.000	5.75	0.70	1.23
Jallat	22/10/2012	89.68	26.94	27.83	0.49	83.50	0.186	0.904	1242.9	5.87	119.25	<0.000	<0.000	0.026	0.12	606	4.60	0.001	0.012	1.91	0.004	1.14	0.367	18.66	0.29	0.146	5.93	0.68	1.85
Jallat	05/11/2012	92.42	25.98	23.14	0.41	79.99	0.188	1.004	1240.4	2.82	119.28	<0.000	0.002	0.027	0.15	629	2.96	0.001	0.001	1.95	0.004	0.94	0.297	21.22	0.28	<0.000	6.12	0.78	1.90

Sample ID	Date	As	B	Br	Cu	Li	Mn	Se	Sr	Al	Ba	Be	Cd	Co	Cr	F	Fe	Gd	Hg	Mo	Nd	Ni	Pb	Rb	Sb	Sn	U	V	Zn
P13	14/02/2011	3.95	35.21	77.50	0.89	54.42	13.144	0.684	951.5	100.43	63.14	0.015	0.006	0.139	0.28	535	96.99	0.020	0.005	0.69	0.077	0.74	0.882	10.51	0.26	0.025	9.40	1.32	1.59
P13	28/02/2011	5.41	74.23	132.51	0.88	96.49	16.326	1.545	1232.7	127.42	66.03	0.012	0.006	0.184	0.43	655	108	0.018	0.269	1.23	0.081	0.91	0.728	19.19	0.32	<0.000	11.62	1.84	0.84
P13	14/03/2011	1.70	52.24	137.34	0.60	87.62	2.990	0.893	1480.4	30.42	41.57	0.005	0.005	0.033	0.35	567	23.05	0.008	0.000	0.19	0.030	0.30	0.151	1.03	0.09	<0.000	4.41	0.32	0.61
P13	11/04/2011	5.19	81.93	150.57	0.33	111.65	0.000	1.796	1156.3	74	51.62	<0.000	0.002	0.059	0.30	508	0.04	0.001	0.069	1.44	0.000	0.39	<0.000	22.19	0.30	0.002	11.09	1.63	<0.000
P13	26/04/2011	5.07	71.87	149.31	1.72	89.01	0.996	1.559	1260.5	8.68	62.15	0.007	0.006	0.076	0.61	491	9.13	0.006	0.050	1.44	0.018	0.83	0.190	19.33	0.31	0.098	11.71	1.69	0.62
P13	09/05/2011	5.43	69.88	146.70	1.32	86.69	11.154	1.711	1255.7	69.80	61.04	0.009	0.007	0.152	0.39	458	57.76	0.015	0.002	1.30	0.064	0.95	0.390	20.35	0.29	<0.000	11.84	1.84	0.29
P13	23/05/2011	5.00	79.96	144.45	0.68	114.70	5.645	1.738	1173.9	46.03	57.29	0.010	0.007	0.104	0.37	474	48.11	0.011	0.250	1.33	0.044	0.73	0.334	22.40	0.31	0.022	11.36	1.77	2.59
P13	06/06/2011	5.04	80.30	146.64	0.95	116.96	2.806	1.817	1198.3	20.17	59.44	0.008	0.007	0.088	3.05	484	16.54	0.007	0.019	2.42	0.022	1.85	0.067	22.85	0.31	0.018	11.37	1.81	0.53
P13	20/06/2011	5.53	84.05	160.84	0.98	112.14	6.743	1.942	1258.1	49.16	71.16	0.013	0.007	0.115	0.36	479	32.93	0.012	<0.000	1.36	0.048	0.77	0.269	21.76	0.34	<0.000	12.39	1.86	0.94
P13	04/07/2011	1.22	84.01	128.13	0.82	124.12	10.851	1.624	1390.2	82.79	27.75	0.013	0.007	0.108	0.19	451	164.76	0.021	<0.000	0.29	0.085	0.46	0.916	5.70	0.15	0.006	3.45	0.93	2.63
P13	18/07/2011	5.12	87.90	150.61	1.04	126.52	13.812	1.751	1058.0	160.4	43.24	0.013	0.008	0.185	0.44	613	139.05	0.026	0.001	1.68	0.121	0.95	0.663	28.28	0.31	<0.000	11.51	2.11	4.66
P13	16/08/2011	4.73	85.39	178.82	0.77	124.93	4.613	1.585	1133.7	45.70	38.50	0.011	0.008	0.091	0.29	636	30.78	0.012	0.058	1.92	0.039	0.66	0.262	31.87	0.33	<0.000	10.13	1.86	0.64
P13	29/08/2011	6.30	86.68	173.56	2.56	112.50	8.454	1.546	1215.9	619.7	76.49	0.066	0.017	0.684	0.81	542	497.9	0.091	0.062	1.21	0.405	2.37	3.415	24.17	0.51	0.011	10.10	2.85	1.90
P13	12/09/2011	6.76	75.15	169.28	2.83	107.65	11.099	1.446	1072.6	1632.7	50.81	0.087	0.019	1.084	1.17	482	1396.5	0.211	0.004	1.69	1.080	3.20	3.995	33.08	0.64	0.169	9.97	3.58	3.08
P13	26/09/2011	4.94	88.93	154.66	1.03	131.77	11.680	1.589	1037.1	97.96	41.41	0.009	0.011	0.133	0.35	634	60.78	0.015	<0.000	1.83	0.068	0.70	0.380	29.14	0.34	0.009	10.61	1.92	4.93
P13	10/10/2011	4.77	88.28	165.20	0.27	137.36	0.012	1.783	1033.1	N.A	35.22	<0.000	0.003	0.048	0.22	550	<0.000	0.001	0.003	2.34	0.000	0.45	0.000	32.60	0.38	<0.000	10.59	1.68	<0.000
P13	24/10/2011	5.58	91.54	158.00	1.28	131.63	4.102	1.522	1080.1	329.16	45.61	0.028	0.011	0.355	0.49	540	224.3	0.046	0.008	2.05	0.216	1.41	1.184	30.58	0.44	0.031	10.90	2.33	1.45
P13	07/11/2011	5.79	91.20	151.81	1.02	116.49	6.877	1.605	1246.8	45.07	74.48	0.011	0.009	0.104	0.73	513	36.48	0.011	0.009	1.77	0.045	0.84	0.401	22.20	0.72	0.025	11.97	2.02	1.71
P13	21/11/2011	4.91	95.01	151.03	7.49	135.33	7.115	1.409	1055.8	56.12	40.81	0.012	0.007	0.105	0.26	563	35.15	0.011	0.004	1.89	0.046	0.58	0.206	29.79	0.35	<0.000	10.81	1.92	0.44
P13	05/12/2011	5.52	89.18	140.88	0.86	112.63	2.243	1.348	1198.8	15.99	68.44	0.012	0.007	0.069	0.27	514	15.18	0.008	0.002	1.52	0.020	0.63	0.141	21.44	0.46	<0.000	11.17	1.90	1.16
P13	19/12/2011	4.73	90.85	152.52	0.93	131.93	3.083	1.419	1008.2	21.68	35.69	0.011	0.006	0.073	0.30	542	18.27	0.007	0.006	1.96	0.025	0.55	0.120	30.19	0.33	<0.000	9.37	1.86	1.56
P13	03/01/2012	4.90	86.45	146.15	0.73	133.38	0.609	1.362	1031.8	4.10	39.81	0.007	0.006	0.057	0.27	548	5.60	0.006	0.013	2.06	0.014	0.65	0.264	30.56	0.35	0.007	10.42	1.87	0.13
P13	16/01/2012	5.42	78.68	135.41	0.35	127.51	0.020	1.818	1031.0	0.17	41.19	0.002	0.002	0.050	0.23	534	<0.000	0.001	<0.000	1.94	0.002	0.57	0.000	28.99	0.35	0.001	10.03	1.76	<0.000
P13	30/01/2012	5.39	81.63	159.63	5.60	119.99	0.744	1.434	1096.8	4.37	46.43	0.047	0.003	0.076	0.26	489	10.00	0.005	0.008	1.85	0.014	0.69	0.068	28.17	0.37	0.010	10.99	2.03	3.65
P13	13/02/2012	6.27	74.03	158.15	1.86	112.04	8.981	1.404	1088.5	492.3	53.23	0.038	0.014	0.633	0.79	606	617.15	0.073	0.003	1.71	0.342	2.62	4.005	27.71	1.25	0.036	10.74	2.69	2.67
P13	27/02/2012	4.40	90.40	153.80	0.69	144.68	0.920	1.331	1003.8	3.52	38.97	0.009	0.004	0.060	0.27	534	7.69	0.005	0.006	1.86	0.011	0.66	0.038	27.81	0.32	0.029	10.33	1.81	2.68
P13	12/03/2012	5.16	90.04	140.55	1.01	106.05	7.169	1.629	1191.3	63.49	54.84	0.003	0.003	0.112	0.26	560	44.80	0.012	0.005	1.60	0.051	0.87	0.381	25.61	0.37	0.001	11.42	1.93	0.48
P13	26/03/2012	5.18	89.31	147.23	2.15	113.97	0.497	1.560	1206.6	6.25	52.84	0.005	0.006	0.067	0.23	498	10.84	0.005	0.003	1.76	0.018	0.91	0.143	26.51	0.37	0.015	11.42	1.92	7.57
P13	10/04/2012	4.89	80.04	150.87	3.32	115.50	3.161	1.503	1125.5	23.62	48.09	0.020	0.006	0.088	0.28	498	26.01	0.009	0.002	1.71	0.028	0.53	0.137	26.20	0.38	0.009	11.14	1.79	0.94
P13	23/04/2012	4.40	77.74	151.87	1.07	114.05	2.168	1.360	1023.7	19.49	37.17	<0.000	0.005	0.069	0.22	552	17.16	0.007	0.003	1.96	0.022	0.45	0.073	29.67	0.35	<0.000	10.18	1.59	0.62
P13	09/05/2012	4.35	80.11	148.97	0.97	128.90	2.552	1.274	989.7	15.72	37.41	0.019	0.008	0.077	0.44	562	15.09	0.007	0.005	2.19	0.022	0.57	0.113	29.72	0.36	0.148	9.92	1.70	1.73
P13	21/05/2012	5.16	103.73	150.39	1.01	139.75	0.332	1.126	1129.9	4.02	55.32	0.006	0.006	0.061	0.27	455	9.91	0.006	<0.000	1.62	0.016	0.70	0.047	25.58	0.44	0.014	10.40	1.84	0.91
P13	04/06/2012	4.27	95.49	150.88	0.66	152.09	0.722	0.989	1005.7	5.96	44.91	0.002	0.006	0.048	0.26	528	12.52	0.006	<0.000	1.96	0.012	0.62	0.021	30.56	0.23	<0.000	9.50	1.67	5.88
P13	18/06/2012	5.13	83.42	154.29	0.63	116.88	2.862	1.001	1142.2	30.47	53.00	<0.000	0.003	0.073	0.32	616	26.63	0.010	0.001	1.52	0.028	0.30	0.111	22.44	0.35	0.020	9.43	1.92	1.31
P13	02/07/2012	4.20	83.27	181.36	0.67	142.68	1.777	0.801	1035.5	25.54	44.98	<0.000	0.003	0.056	0.21	491	49.67	0.008	0.002	1.97	0.025	0.54	0.091	30.99	0.38	0.003	8.73	1.75	2.90
P13	16/07/2012	5.20	71.98	116.42	0.90	105.56	0.500	0.876	1240.1	3.59	67.63	<0.000	0.001	0.059	0.32	581	5.18	0.005	0.008	1.46	0.018	0.85	0.090	20.88	0.41	0.104	9.32	1.81	2.35
P13	30/07/2012	5.48	91.69	143.68	1.03	126.82	4.377	0.871	1209.7	37.52	69.01	0.007	0.006	0.093	0.30	375	25.53	0.010	<0.000	1.40	0.030	0.43	0.130	20.29	0.40	0.021	9.76	1.92	0.96
P13	13/08/2012	5.22	86.91	140.02	0.72	118.97	3.620	1.074	1186.0	33.31	58.72	0.010	0.007	0.086	0.31	539	25.04	0.009	0.010	1.57	0.025	0.22	0.133	24.50	0.34	<0.000	10.11	1.86	1.36
P13	27/08/2012	4.73	97.43	154.61	0.46	142.32	2.305	0.877	1071.6	20.77	44.72	<0.000	0.006	0.069	0.22	519	12.95	0.007	<0.000	1.78	0.022	0.30	0.053	27.87	0.32	0.000	9.78	1.86	0.35
P13	10/09/2012	5.46	77.63	146.81	1.22	101.37	0.311	1.016	1225.5	3.70	65.09	0.003	0.007	0.061	0.59	606	6.82	0.006	<0.000	1.65	0.014	0.80	0.090	24.18	0.89	0.076	10.09	1.90	4.51
P13	24/09/2012	5.46	92.76	138.16	0.61	116.99	0.818	1.034	1237.8	5.86	69.48	0.003	0.007	0.064	0.29	486	6.35	0.006	0.001	1.47	0.017	0.58	0.051	22.72	0.26	<0.000	10.53	1.97	0.23
P13	08/10/2012	4.74	98.41	180.65	0.84	140.63	1.506	0.998	1082.5	17.61	38.64	0.005	0.010	0.063	0.27	599	17.54	0.006	0.014	2.06	0.022	0.65	0.092	31.62	0.18	0.215	9.73	1.88	0.69
P13	22/10/2012	5.29	95.66	143.50	0.64	127.96	0.581	1.056	1158.9	3.65	63.37	0.004	0.006	0.056	0.27	559	4.50	0.005	0.006	1.60	0.014	0.42	0.064	21.98	0.36	<0.000	9.97	1.98	0.52
P13	05/11/2012	5.50	97.71	143.03	0.65	132.38	0.342	0.956	1112.4	3.40	58.97	<0.000	0.002	0.057	0.28	580	3.66	0.005	0.011	1.81	0.014	0.47	0.036	22.33	0.52	0.056	10.16	2.03	2.73

Traces for first campaign December 2010

Sample ID	As	B	Br	Cu	Li	Mn	Se	Sr	Al	Ba	Be	Cd	Co	Cr	Fe	Gd	Hg	Mo	Nd	Ni	Pb	Rb	Sb	Sn	U	V	Zn
B01	2.13	36.38	25.39	19.48	26.69	0.622	0.079	139.0	10.60	8.70	<0.000	0.002	0.072	0.098	16.9	0.005	0.005	0.295	0.011	0.230	0.141	7.13	1.12	0.010	0.20	0.91	2.86
B02	2.08	36.71	25.70	8.02	26.82	0.350	0.066	138.0	7.36	8.21	<0.000	0.002	0.068	0.083	9.3	0.005	0.003	0.306	0.011	0.106	0.049	7.18	1.07	0.012	0.18	0.84	1.51
B03	2.46	36.86	25.99	29.35	27.82	17.142	0.065	143.3	297.81	12.40	0.030	0.012	0.346	0.626	549.6	0.056	0.002	0.281	0.245	0.654	N.A	8.85	1.16	0.018	0.21	1.71	4.83
B04	2.01	38.88	26.52	6.23	28.19	0.654	0.067	139.9	12.81	8.48	0.001	0.002	0.069	0.112	17.7	0.005	0.002	0.306	0.014	0.118	0.031	7.27	1.12	0.000	0.18	0.96	2.56
B05	2.81	35.60	19.38	35.08	25.55	0.383	0.065	111.8	9.34	11.98	0.005	0.001	0.050	0.081	33.6	0.00	<0.000	0.33	0.011	0.189	0.024	6.14	1.48	0.001	0.09	1.02	0.43
B06	1.89	38.13	25.67	8.64	27.95	0.907	0.066	142.3	8.34	9.62	0.001	0.005	0.063	0.175	9.9	0.003	0.001	0.338	0.011	0.160	0.081	7.18	1.12	0.012	0.18	0.87	40.84
B07	2.32	34.10	20.97	24.16	25.19	0.207	0.053	120.7	4.63	9.38	<0.000	0.001	0.052	0.083	3.6	0.003	0.001	0.305	0.008	0.082	<0.000	6.62	1.34	<0.000	0.11	0.94	3.54
B08	1.98	39.22	26.06	15.13	27.69	0.374	0.045	151.9	5.26	10.17	<0.000	0.002	0.060	0.105	6.0	0.003	0.000	0.320	0.007	0.086	0.002	7.36	1.08	<0.000	0.28	0.91	3.76
B09	2.28	35.18	22.27	10.83	25.14	0.316	0.056	122.7	5.12	9.50	0.001	0.002	0.057	0.086	71.9	0.004	0.001	0.313	0.008	0.093	0.015	6.67	1.30	<0.000	0.12	0.96	1.12
B10	2.10	45.47	34.10	8.06	28.90	0.384	0.134	233.3	5.66	22.01	0.001	0.002	0.059	0.107	17.6	0.002	0.001	0.370	0.006	0.109	<0.000	8.65	0.93	<0.000	0.74	0.95	0.50
B11	3.21	34.95	22.70	51.04	25.40	0.178	0.075	118.0	6.55	9.58	0.003	0.002	0.054	0.091	5.3	0.004	0.031	0.349	0.011	0.076	0.008	6.81	1.51	0.115	0.07	1.01	3.24
B12	2.02	43.41	34.83	13.92	26.73	0.954	0.206	218.6	9.14	19.64	0.000	0.003	0.063	0.119	8.8	0.004	0.016	0.349	0.009	0.104	0.022	7.92	0.93	0.052	0.63	0.83	1.39
B13	2.82	31.52	20.32	17.26	22.49	0.226	0.087	120.0	9.46	13.20	0.001	0.002	0.046	0.092	6.4	0.005	0.010	0.321	0.013	0.116	0.012	5.98	1.47	0.028	0.09	0.96	1.79
B14	2.03	38.81	28.84	14.02	22.77	0.206	0.128	162.7	4.19	16.36	<0.000	0.001	0.083	0.117	3.2	0.002	0.007	0.366	0.006	0.098	<0.000	7.61	0.94	0.017	0.39	0.91	0.55
B15	2.31	37.88	22.25	1.39	26.94	0.181	0.058	128.7	4.16	6.77	<0.000	0.002	0.049	0.051	3.1	0.004	0.005	0.334	0.009	0.051	0.002	7.04	1.39	0.014	0.09	0.98	2.74
B16	1.93	38.59	30.69	0.84	21.49	1.976	0.089	145.3	3.69	10.71	0.002	0.002	0.101	0.091	38.3	0.003	0.022	0.393	0.008	0.104	0.002	7.36	1.04	0.034	0.25	0.96	1.81
B17	2.47	36.90	24.55	1.09	27.21	0.444	0.068	136.6	4.29	8.12	0.003	0.003	0.056	0.057	28.0	0.004	0.010	0.307	0.010	0.059	0.001	7.11	1.35	0.018	0.11	0.97	0.22
B18	1.73	36.90	28.41	0.83	25.92	0.435	0.046	136.6	2.47	9.68	0.002	0.003	0.081	0.089	2.4	0.003	0.008	0.290	0.004	0.095	0.009	6.93	0.80	0.013	0.23	0.87	1.71
B19	2.61	38.11	23.38	1.10	27.64	0.239	0.095	138.0	3.53	8.43	0.003	0.001	0.059	0.080	3.3	0.004	0.007	0.299	0.008	0.073	0.010	7.18	1.31	0.011	0.12	0.95	0.57
B20	2.18	34.08	24.26	1.79	28.32	0.104	0.055	151.9	3.78	13.51	<0.000	0.002	0.060	0.072	3.0	0.004	0.003	0.288	0.005	0.103	0.047	5.22	1.34	0.003	0.15	0.94	0.31
B21	2.00	41.41	31.16	2.11	28.33	12.588	0.191	227.8	35.30	21.64	0.002	0.004	0.072	0.159	42.7	0.010	0.002	0.464	0.039	0.191	0.106	7.26	1.25	0.004	0.95	0.98	2.41
B22	3.32	83.52	54.95	1.46	75.97	0.206	0.640	725.2	4.55	45.63	<0.000	0.005	0.072	0.187	1.8	0.005	0.002	1.942	0.010	0.350	0.018	14.35	1.03	<0.000	6.21	1.45	1.80
B23	5.32	92.83	58.63	1.40	168.57	0.301	1.119	1146.1	4.61	108.03	<0.000	0.008	0.098	0.215	1.3	0.006	0.002	2.788	0.013	0.653	0.003	15.19	0.99	<0.000	10.22	1.80	1.67
B24	10.84	84.07	45.32	1.60	215.31	0.091	0.931	968.2	5.04	102.86	<0.000	0.006	0.080	0.198	1.3	0.004	0.001	2.325	0.010	0.562	0.008	10.09	1.28	<0.000	6.24	2.31	1.90
B25	5.98	36.09	24.92	0.72	34.96	0.076	0.091	214.0	3.60	17.52	0.006	0.002	0.039	0.125	1.1	0.002	0.020	0.384	0.002	0.013	0.003	3.81	1.44	0.046	0.57	1.40	<0.000
B26	4.51	28.40	18.19	1.47	26.36	0.067	0.056	137.7	4.05	10.03	0.009	0.003	0.051	0.080	1.9	0.003	0.014	0.295	0.007	<0.000	0.019	5.00	1.29	0.028	0.22	1.00	0.05
B27	2.33	55.14	43.79	1.16	30.39	0.254	0.448	342.8	8.86	31.06	<0.000	0.006	0.062	0.191	11.3	0.004	0.002	0.751	0.013	0.184	0.012	9.12	1.04	<0.000	2.66	1.09	1.01
B28	3.57	95.78	78.63	1.17	62.40	0.105	0.675	674.3	3.90	67.69	<0.000	0.005	0.049	0.208	1.1	0.002	0.003	1.969	0.008	0.325	0.006	15.70	0.62	<0.000	6.37	1.44	0.52
B29	4.52	123.56	74.47	1.02	96.34	0.024	0.559	924.2	3.72	94.83	<0.000	0.008	0.089	0.174	0.8	0.005	0.003	3.929	0.011	0.521	0.003	17.92	0.51	<0.000	10.06	1.68	0.59
B30	2.95	31.04	21.74	1.40	29.23	0.491	0.049	126.6	6.48	8.46	0.002	0.003	0.059	0.096	4.0	0.005	0.006	0.271	0.012	0.150	0.016	6.28	1.29	0.006	0.13	0.97	1.98
B31	1.74	41.17	28.73	1.38	23.91	0.361	0.051	146.8	4.88	11.82	0.003	0.002	0.065	0.086	4.7	0.003	0.004	0.323	0.007	0.110	0.024	7.28	1.31	0.007	0.17	0.81	2.59
B31BIS	2.89	23.02	21.59	2.19	21.73	0.191	0.066	129.0	6.26	15.87	0.005	0.004	0.070	0.106	2.1	0.006	0.005	0.252	0.020	0.310	0.002	5.79	1.37	0.008	0.17	0.81	0.66
B32	2.89	35.20	23.18	1.25	25.46	0.206	0.083	130.8	4.82	11.08	0.000	0.002	0.053	0.089	3.9	0.003	0.004	0.367	0.009	0.113	0.010	6.69	1.36	0.021	0.12	0.97	1.44
B33	2.05	45.02	33.32	14.05	27.75	1.020	0.217	217.9	9.37	19.51	<0.000	0.002	0.063	0.108	9.0	0.004	0.002	0.362	0.008	0.100	0.021	7.88	0.94	<0.000	0.61	0.83	1.41
B34	3.41	36.38	26.24	1.84	32.91	86.440	0.040	155.1	4.80	9.54	<0.000	0.008	0.084	0.045	3.5	0.003	0.004	0.923	0.008	0.185	0.011	7.95	1.00	0.006	0.73	0.98	0.31
B35	6.34	38.35	31.01	0.81	35.87	1829.93	0.020	140.7	4.10	6.64	<0.000	0.022	0.209	0.020	14.9	0.002	0.005	0.184	0.003	0.167	0.014	7.63	0.50	0.002	0.59	0.91	3.89
B36	2.74	37.55	21.04	1.50	23.50	0.870	0.051	119.8	4.47	7.90	0.001	0.002	0.055	0.056	5.6	0.004	0.001	0.360	0.009	0.055	0.019	7.52	1.34	0.002	0.09	0.90	0.70
B37	3.15	42.56	28.25	2.46	30.05	327.65	0.010	149.3	4.05	8.65	0.001	0.020	0.235	0.035	21.1	0.005	0.002	0.646	0.011	0.334	0.035	8.60	1.18	<0.000	0.18	0.72	0.68
B38	14.03	30.08	21.88	0.18	52.03	340.56	0.005	148.2	4.32	4.96	<0.000	0.003	0.112	0.028	913.2	0.002	0.003	0.406	0.004	0.194	1.116	11.90	0.06	0.001	0.01	0.08	0.86
B39	22.81	39.52	28.84	1.00	30.27	369.96	0.028	155.2	6.49	34.34	0.004	0.004	0.637	0.060	1313.1	0.004	0.002	0.413	0.011	1.081	0.570	8.40	0.22	0.017	0.05	0.28	5.50
B40	16.91	34.51	20.52	0.57	44.53	192.33	0.011	133.8	3.54	3.91	<0.000	0.007	0.149	0.031	11.4	0.001	0.001	0.584	0.002	0.299	0.158	9.82	0.22	0.001	0.17	0.26	0.73
B41	3.84	31.37	22.13	1.26	48.80	3.352	0.103	209.8	4.49	24.44	0.007	0.004	0.061	0.151	3.8	0.003	0.009	0.619	0.008	0.100	0.011	5.49	1.27	0.016	0.80	1.03	0.49
B42	3.71	31.89	24.16	1.36	49.53	3.212	0.128	213.1	4.93	24.62	0.005	0.004	0.060	0.181	4.0	0.004	0.009	0.681	0.007	0.135	0.056	5.61	1.28	0.012	0.79	1.13	2.10
B43	3.81	30.28	21.42	1.84	46.57	3.202	0.082	202.4	9.38	23.98	0.006	0.006	0.063	0.169	7.2	0.004	0.006	0.682	0.012	0.173	0.261	5.45	1.29	0.022	0.69	1.10	10.51
B44	4.44	28.65	23.60	1.38	45.49	1.198	0.111	224.5	5.26	21.44	0.004	0.003	0.059	0.162	3.5	0.003	0.004	0.514	0.007	0.103	0.312	5.20	1.32	0.005	0.75	1.08	1.77
B45	4.30	32.20	21.22	1.44	51.16	0.149	0.164	222.7	4.66	19.11	0.005	0.004	0.050	0.135	1.6	0.003	0.004	0.779	0.006	0.056	0.303	4.96	1.40	0.007	0.90	1.06	1.50
B46	4.76	39.05	23.53	1.12	60.39	24.98	0.123	208.4	4.72	20.48	0.005	0.004	0.103	0.133	16.9	0.003	0.004	1.115	0.005	0.125	0.046	5.44	1.33	0.006	0.60	1.16	0.29
B47	3.39	26.52	18.02	1.45	31.63	0.172	0.077	131.1	5.59	14.52	0.007	0.003	0.054	0.128	3.2	0.004	0.003	0.585	0.008	0.072	0.061	5.02	1.51	0.000	0.15	1.10	1.20
B48	3.30	33.55	23.23	1.39	39.88	0.121	0.129	207.9	5.14	24.55	0.007	0.003	0.000	0.168	2.8	0.002	0.001	0.787	0.010	0.121	0.178	6.36	1.31	<0.000	0.47	1.01	0.93
B49	2.56	16.20	16.95	1.66	15.56	0.060	0.050	124.6	4.61	15.56	0.008	0.002	0.049	0.085	1.7	0.004	0.002	0.317	0.012	0.079	0.040	4.83	1.53	<0.000	0.09	0.78	0.17
B50	3.64	28.58	21.37	1.30	48.16	0.063	0.129	223.3	5.58	28.65	0.006	0.003	0.053	0.177	1.6	0.004	0.000	0.558	0.009	0.128	0.078	5.59	1.23	<0.000	0.87	1.08	0.92
B51	3.15	27.35	18.93	1.33	21.61	0.245	0.026	105.0	4.80	11.58	0.002	0.002	0.052	0.061	2.2	0.003	0.001	0.273	0.009	0.198	0.003	5.85	1.13	0.000	0.04	0.78	1.18
B52	2.98	24.19	17.29	1.50	20.63	0.222	0.043	100.2	5.81	12.55	0.003	0.005	0.048	0.116	3.8	0.004	0.001	0.248	0.010	0.257	0.008	5.47	1.14	<0.000	0.05	0.78	1.73
B53	4.58	31.35	17.41	1.44	25.17	2.055	0.032	107.9	4.05	11.75	0.004	0.003	0.062	0.044	2.3	0.003	0.001	0.267	0.008	0.195	0.009	6.88	0.97	<0.000	0.04	0.81	1.75
B54	2.83	26.51	17.82	1.66	23.51	0.257	0.073	118.8	13.78	9.79	0.006	0.003	0.100	0.081	7.0	0.007	0.002	0.329	0.020	0.307	0.013	6.21	0.90	0.001	0.09	0.82	3.40

B55	2.54	31.81	20.56	1.85	31.59	0.328	0.026	135.0	8.49	10.56	0.006	0.005	0.126	0.058	3.8	0.005	0.000	0.447	0.017	0.333	0.018	7.12	0.89	<0.000	0.07	0.97	6.96
B56	2.99	23.89	16.37	1.67	35.35	0.268	0.021	127.8	15.01	9.52	0.004	0.004	0.084	0.052	5.3	0.005	0.001	0.609	0.014	0.287	0.012	6.57	0.84	<0.000	0.12	0.92	0.85
B57	4.53	29.60	27.44	2.23	35.28	1.122	0.057	149.7	9.88	11.47	0.006	0.012	0.159	0.052	4.6	0.005	0.028	0.906	0.014	0.532	0.014	7.43	0.62	0.114	0.16	1.05	2.13
B58	2.86	28.89	22.54	1.44	40.32	0.419	0.044	134.0	40.50	12.14	0.009	0.003	0.070	0.106	17.1	0.007	0.013	0.537	0.025	0.332	0.018	7.18	0.83	0.052	0.09	1.06	0.98
B60	4.18	34.19	37.30	1.21	60.47	0.144	0.140	247.6	5.31	19.80	0.004	0.004	0.064	0.114	2.7	0.003	0.009	1.290	0.007	0.286	0.009	11.18	0.59	0.026	0.63	1.47	0.97
B61	3.38	32.72	30.82	1.39	48.69	0.989	0.115	222.3	8.33	16.21	0.004	0.002	0.077	0.149	9.4	0.003	0.003	0.895	0.009	0.282	0.026	9.34	0.93	0.015	0.58	1.19	1.74
B62	2.47	34.03	30.80	1.13	38.37	0.217	0.128	195.4	5.70	10.78	0.003	0.003	0.063	0.098	2.7	0.003	0.002	0.573	0.008	0.230	0.017	8.39	0.93	0.008	0.55	1.03	3.18
B63	3.47	33.17	28.95	1.54	36.05	0.120	0.086	195.9	5.04	25.95	0.003	0.002	0.062	0.074	2.2	0.003	0.001	0.531	0.009	0.291	0.013	7.35	1.24	0.005	0.44	0.88	1.30
B64	3.92	35.41	38.65	1.31	46.46	0.120	0.080	221.1	4.96	27.76	0.003	0.006	0.045	0.112	3.3	0.002	0.002	0.961	0.006	0.254	0.018	8.07	1.21	0.004	0.82	1.00	2.28
B65	4.34	40.13	47.37	0.76	58.58	0.122	0.135	264.1	5.12	34.99	0.001	0.005	0.022	0.142	1.4	0.001	0.002	1.583	0.004	0.212	0.021	9.56	1.20	0.002	1.40	1.11	3.34
B66	5.11	31.80	20.82	1.93	32.32	19.497	0.036	168.8	4.76	9.78	<0.000	0.007	0.081	0.033	5.1	0.003	0.001	0.609	0.006	0.210	0.071	6.74	0.96	<0.000	0.31	1.24	41.69
B69	7.63	27.07	19.58	2.01	33.71	261.906	0.032	151.1	25.72	10.41	0.002	0.013	0.396	0.374	434.8	0.007	0.017	0.658	0.028	0.629	0.059	6.02	0.81	0.048	0.42	0.96	1.78
B70	5.55	29.54	18.65	2.77	35.68	480.666	0.028	166.6	22.80	16.07	0.004	0.023	0.212	0.092	169.0	0.010	0.010	0.100	0.035	1.397	0.028	5.98	1.17	0.024	0.35	1.73	2.66
B71	2.49	36.07	23.91	1.06	25.44	1.389	0.069	169.4	7.09	9.81	0.003	0.005	0.049	0.078	5.7	0.003	0.001	0.376	0.005	0.197	0.025	4.92	0.87	<0.000	0.43	1.02	0.89
Allier	2.60	13.32	17.86	1.53	9.85	10.128	0.064	89.3	142.47	22.77	0.042	0.014	0.162	0.373	205.4	0.043	0.001	0.158	0.180	0.635	0.387	4.19	1.07	<0.000	0.33	0.96	5.38
P13	4.50	79.95	147.60	0.59	124.97	3.992	0.859	955.7	26.48	38.02	0.003	0.007	0.076	0.251	28.2	0.007	0.000	2.150	0.027	0.590	0.183	29.33	0.30	<0.000	9.14	1.73	4.45

Traces for the second campaign of June 2012

Sample ID	As	B	Br	Cu	Li	Mn	Se	Sr	Al	Ba	Be	Cd	Co	Cr	Fe	Gd	Hg	Mo	Nd	Ni	Pb	Rb	Sb	Sn	U	V	Zn
B01	2.23	27.83	9.19	340.88	23.41	7.572	0.038	110.1	22.07	9.06	0.002	0.004	0.135	0.183	250.6	0.006	<0.000	0.266	0.018	0.192	0.394	5.56	0.98	<0.000	0.12	0.85	6.90
B02	1.62	31.84	12.53	7.56	24.38	0.833	0.046	113.2	3.85	7.17	0.001	0.001	0.058	0.075	13.7	0.002	<0.000	0.239	0.005	0.026	0.027	5.54	0.75	<0.000	0.15	0.74	0.49
B03	2.53	25.54	8.16	101.01	21.29	0.770	0.069	91.7	9.15	8.64	0.004	0.002	0.060	0.101	14.6	0.004	<0.000	0.213	0.013	0.144	0.058	5.23	1.23	<0.000	0.08	0.80	2.16
B04	1.62	29.50	7.90	38.35	23.29	1.305	0.039	99.3	23.50	6.21	0.004	0.001	0.065	0.108	32.8	0.004	<0.000	0.252	0.016	0.033	0.087	5.25	0.94	<0.000	0.09	0.78	1.01
B05	2.16	29.78	6.64	61.00	21.50	1.002	0.028	93.7	13.73	8.12	0.002	0.001	0.054	0.103	48.4	0.004	<0.000	0.266	0.010	0.055	0.037	4.49	1.05	<0.000	0.08	0.76	0.84
B06	1.33	30.04	9.52	83.49	22.67	1.402	0.041	97.1	4.19	6.48	0.003	0.001	0.044	0.114	41.1	0.002	<0.000	0.298	0.004	0.048	0.009	5.31	1.12	0.129	0.06	0.65	1.06
B07	1.91	29.37	8.09	55.32	21.83	1.269	0.054	98.8	5.57	8.06	0.002	0.001	0.051	0.096	36.9	0.002	<0.000	0.262	0.007	0.167	0.025	4.87	1.11	0.034	0.09	0.73	1.33
B08	1.69	34.31	9.24	17.42	23.98	0.400	0.043	111.3	2.95	7.88	0.002	0.002	0.046	0.104	7.4	0.002	<0.000	0.321	0.003	0.068	0.019	5.59	0.94	0.003	0.16	0.88	0.59
B09	1.63	31.72	11.43	9.41	24.07	0.356	0.063	112.0	3.46	7.84	0.006	0.001	0.060	0.088	8.5	0.002	<0.000	0.242	0.004	0.031	0.037	5.35	0.85	<0.000	0.14	0.79	0.86
B10	1.748	36.366	14.644	11.107	24.73	0.127	0.117	146.3	1.23	12.21	0.002	0.002	0.047	0.106	3.2	0.001	<0.000	0.313	0.002	0.036	0.003	5.93	0.75	<0.000	0.32	0.79	0.35
B11	1.951	28.789	8.280	20.856	23.01	0.132	0.042	99.1	3.23	6.15	0.001	0.002	0.048	0.074	6.7	0.002	<0.000	0.237	0.005	0.030	0.006	4.85	0.94	<0.000	0.08	0.69	0.38
B12	1.726	46.260	17.357	76.523	32.80	0.299	0.075	148.0	1.71	12.13	0.001	0.001	0.054	0.115	1.5	0.002	<0.000	0.294	0.002	0.043	0.016	6.42	0.52	<0.000	0.39	0.87	1.37
B13	2.258	30.289	8.879	13.656	21.96	0.164	0.067	102.2	6.80	8.66	0.005	0.002	0.043	0.110	8.8	0.004	<0.000	0.259	0.008	0.168	0.031	4.72	1.11	0.047	0.08	0.84	0.94
B14	1.633	33.791	13.837	7.553	23.20	0.425	0.087	120.9	2.48	11.02	0.007	0.002	0.051	0.095	4.4	0.002	<0.000	0.262	0.003	0.037	0.018	5.54	0.75	0.013	0.18	0.82	1.13
B15	2.109	29.779	9.806	3.581	26.67	0.653	0.030	106.9	4.51	7.56	0.003	0.003	0.054	0.068	34.7	0.002	<0.000	0.300	0.006	11.242	0.018	5.43	1.05	0.005	0.15	0.78	1.07
B16	1.519	37.252	19.835	1.163	23.42	0.353	0.040	133.9	2.27	8.61	0.003	0.001	0.067	0.092	5.9	0.002	<0.000	0.296	0.004	0.044	0.014	6.48	0.77	<0.000	0.21	0.81	0.65
B17	1.726	29.773	9.027	1.507	23.86	3.332	0.041	102.0	5.44	6.43	0.001	0.002	0.060	0.068	20.3	0.002	<0.000	0.331	0.006	0.067	0.036	5.31	1.12	<0.000	0.12	0.73	1.24
B18	1.561	34.528	16.599	0.746	25.87	0.180	0.028	121.6	1.09	8.33	0.002	0.001	0.068	0.087	2.3	0.001	<0.000	0.234	0.002	0.018	0.004	5.88	0.61	<0.000	0.19	0.79	0.50
B19	1.86	30.07	10.74	1.60	24.95	0.140	0.046	107.8	2.09	5.93	0.002	0.001	0.049	0.075	5.2	0.003	<0.000	0.227	0.003	<0.000	0.040	5.28	0.90	<0.000	0.10	0.76	0.36
B20	1.789	30.995	8.748	1.641	26.90	0.014	0.043	121.4	1.03	9.58	0.002	0.002	0.049	0.071	2.4	0.002	<0.000	0.256	0.003	0.676	0.011	4.02	1.09	<0.000	0.09	0.84	0.47
B21	1.70	39.63	10.70	1.18	25.21	1.986	0.094	146.7	12.62	12.54	0.001	0.003	0.075	0.114	34.3	0.003	<0.000	0.430	0.008	0.050	0.036	5.40	1.09	<0.000	0.36	0.84	0.55
B22	2.94	63.41	25.29	1.35	62.68	0.217	0.322	429.2	1.70	26.38	<0.000	0.004	0.054	0.132	3.2	0.003	<0.000	1.631	0.004	0.158	0.039	9.48	0.90	<0.000	2.79	1.24	0.57
B23	4.493	77.406	35.012	1.189	156.95	0.180	0.798	811.1	1.12	76.82	0.001	0.007	0.068	0.160	2.5	0.005	<0.000	2.296	0.008	0.350	0.007	10.73	0.88	<0.000	5.57	1.48	0.42
B24	4.18	89.81	44.75	1.25	88.77	0.290	0.484	615.9	3.86	50.79	0.006	0.009	0.060	0.156	5.9	0.005	0.001	2.204	0.009	0.405	0.105	11.28	0.79	0.008	4.73	1.32	1.09
B25	6.44	36.77	10.39	1.12	34.23	0.471	0.062	168.2	3.38	13.13	0.009	0.003	0.050	0.120	7.7	0.003	0.000	0.395	0.003	0.207	0.043	3.12	1.34	0.011	0.28	1.48	2.41
B26	4.302	37.997	9.249	2.092	25.01	0.470	0.048	124.1	6.94	8.66	0.007	0.006	0.055	0.098	12.6	0.005	0.000	0.273	0.011	0.217	0.081	4.25	1.16	0.005	0.16	0.80	5.57
B27	2.024	52.743	12.456	0.814	28.15	0.050	0.114	162.0	1.65	11.99	<0.000	0.003	0.046	0.115	2.7	0.001	<0.000	0.792	0.002	0.024	0.023	6.02	0.91	<0.000	0.57	1.00	0.50
B28	2.95	86.09	51.02	0.79	61.84	0.110	0.633	506.8	1.77	49.76	0.000	0.004	0.049	0.178	1.7	0.002	<0.000	1.555	0.004	0.217	0.018	12.18	0.44	<0.000	3.76	1.27	1.28
B29	3.839	127.731	64.500	0.843	105.43	0.051	0.504	860.6	1.10	87.56	0.000	0.008	0.068	0.160	0.9	0.004	<0.000	3.687	0.008	0.351	0.007	17.02	0.37	<0.000	8.88	1.50	1.89

B30	2.72	24.59	10.30	2.06	22.78	0.376	0.085	98.7	7.11	7.77	0.006	0.001	0.061	0.098	11.4	0.004	<0.000	0.214	0.013	0.221	0.019	4.85	1.15	<0.000	0.11	0.93	0.48
B31	1.51	34.34	12.75	0.83	25.09	0.073	0.068	119.5	1.38	8.89	0.004	0.001	0.049	0.067	2.0	0.002	<0.000	0.262	0.004	<0.000	0.003	5.86	0.99	<0.000	0.14	0.66	0.21
B31BIS	2.58	28.66	10.57	1.30	20.32	0.110	0.088	129.7	2.70	18.44	0.003	0.002	0.050	0.108	3.2	0.002	<0.000	0.235	0.010	0.225	0.018	4.77	1.05	<0.000	0.28	0.71	0.22
B32	2.51	30.16	8.25	1.33	21.14	6.222	0.042	110.8	4.27	9.93	0.002	0.014	0.113	0.097	28.4	0.003	<0.000	0.243	0.006	0.155	0.012	5.79	0.97	<0.000	0.09	0.77	0.43
B33	3.252	29.809	8.828	1.686	21.708	0.153	0.062	96.3	7.00	9.40	0.003	0.001	0.054	0.086	4.6	0.004	<0.000	0.220	0.011	0.242	0.006	5.27	1.14	<0.000	0.07	0.90	0.31
B34	3.29	26.71	12.25	2.21	26.57	54.833	0.034	116.0	4.11	8.99	0.003	0.005	0.061	0.072	3.7	0.002	<0.000	0.443	0.010	0.306	0.021	5.75	0.97	<0.000	0.35	0.80	0.71
B35	10.76	42.75	9.63	0.67	40.56	280.983	0.025	103.9	2.09	5.65	<0.000	0.010	0.219	0.029	46.4	0.001	<0.000	0.261	0.001	0.295	0.025	6.88	0.32	<0.000	0.18	0.64	1.27
B36	2.51	34.13	7.88	1.42	21.99	2.573	0.064	107.8	2.39	7.80	0.000	0.001	0.050	0.092	2.2	0.003	<0.000	0.267	0.007	0.041	0.010	5.63	0.99	<0.000	0.11	0.73	0.55
B37	4.20	29.29	9.29	1.24	29.62	398.404	0.028	106.9	1.34	5.78	<0.000	0.010	0.158	0.022	32.9	0.002	<0.000	0.328	0.005	0.106	8.939	5.52	0.72	<0.000	0.11	0.56	0.37
B38	25.56	35.57	9.45	0.47	59.30	621.590	0.016	131.7	0.73	6.42	<0.000	0.001	0.095	0.013	1613.1	0.002	<0.000	0.592	0.003	0.007	0.200	10.69	<0.000	<0.000	0.00	0.07	0.52
B39	6.834	33.129	8.447	0.893	27.650	100.335	0.016	124.2	56.37	18.26	0.005	0.005	0.235	0.158	288.6	0.003	<0.000	0.260	0.007	0.463	1.346	7.41	0.25	0.019	0.04	0.18	0.79
B40	15.48	41.30	6.47	1.12	45.22	628.879	0.030	134.0	1.46	3.95	0.004	0.011	0.164	0.001	17.1	0.001	0.001	0.535	0.002	0.212	0.098	8.55	0.23	0.010	0.19	0.31	0.39
B41	20.09	57.82	34.12	1.87	180.08	0.425	0.257	488.9	2.18	39.93	0.009	0.007	0.051	0.107	2.8	0.003	<0.000	0.874	0.009	0.445	0.032	6.17	1.69	0.004	2.86	2.03	1.19
B42	5.11	42.17	14.68	1.51	49.49	0.803	0.178	208.9	6.66	19.84	0.004	0.005	0.048	0.174	8.4	0.003	<0.000	0.501	0.007	0.212	0.059	4.78	1.40	<0.000	0.87	1.11	0.47
B43	4.70	39.26	12.59	1.45	39.72	0.607	0.146	201.2	3.68	20.00	0.005	0.005	0.051	0.142	7.0	0.004	<0.000	0.395	0.007	0.337	0.045	4.76	1.35	0.001	0.52	1.03	0.55
B44	3.73	38.56	12.69	1.18	31.98	0.129	0.110	187.4	3.51	14.89	0.005	0.005	0.044	0.128	2.5	0.006	<0.000	0.294	0.007	0.245	0.041	4.35	1.19	<0.000	0.46	0.87	0.38
B45	5.09	48.62	20.44	1.24	67.37	0.177	0.298	309.1	2.40	24.10	0.005	0.006	0.052	0.138	3.3	0.004	<0.000	0.562	0.007	0.279	0.014	5.37	1.24	<0.000	2.07	1.05	0.26
B46	4.99	58.96	24.45	1.46	101.15	18.794	0.429	386.0	2.25	36.03	0.004	0.006	0.080	0.283	30.8	0.004	<0.000	1.055	0.006	0.311	0.011	6.77	1.15	<0.000	3.26	1.05	0.25
B47	3.17	41.12	11.72	1.21	39.24	0.406	0.105	172.3	6.54	17.16	0.004	0.004	0.047	0.135	23.6	0.003	<0.000	0.651	0.008	0.236	0.039	5.10	1.22	<0.000	0.49	0.96	0.96
B48	2.59	30.46	6.14	1.53	19.03	5.361	0.042	106.4	8.06	12.33	0.004	0.004	0.224	0.100	138.5	0.004	<0.000	0.300	0.008	0.460	0.129	6.24	2.18	<0.000	0.08	0.90	1.75
B49	3.10	28.71	16.86	3.06	22.54	0.295	0.084	154.4	9.87	19.41	0.010	0.007	0.070	0.117	7.8	0.006	<0.000	0.270	0.018	0.494	0.194	5.14	1.37	0.002	0.20	0.79	10.57
B50	3.146	32.858	10.187	1.930	34.579	0.308	0.099	180.1	5.98	22.06	0.008	0.004	0.069	0.151	6.7	0.006	<0.000	0.342	0.014	0.366	0.078	4.73	1.41	<0.000	0.46	0.91	1.77
B51	2.91	33.88	6.35	1.62	23.71	2.213	0.048	97.2	6.14	9.61	0.006	0.002	0.064	0.072	4.8	0.004	<0.000	0.202	0.010	0.124	0.095	5.50	1.22	0.002	0.04	0.68	0.93
B52	3.36	26.48	7.13	3.94	19.72	0.525	0.060	89.7	9.97	12.91	0.007	0.005	0.056	0.133	6.5	0.006	<0.000	0.237	0.019	0.300	0.101	5.20	1.48	<0.000	0.06	0.82	1.01
B53	3.22	31.69	5.07	2.90	23.93	0.276	0.041	104.3	3.18	10.74	0.006	0.002	0.052	0.083	2.5	0.002	<0.000	0.197	0.007	0.058	0.020	5.36	1.13	<0.000	0.05	0.56	1.70
B54	2.08	38.87	10.14	1.18	42.98	0.207	0.121	152.3	4.62	7.44	0.004	0.003	0.077	0.077	4.0	0.004	<0.000	0.434	0.009	0.104	0.020	8.07	0.78	<0.000	0.28	0.85	0.77
B55	2.39	37.62	11.17	1.41	47.85	0.997	0.050	163.8	6.37	10.29	0.004	0.005	0.098	0.042	6.1	0.004	<0.000	0.676	0.008	0.173	0.023	7.80	0.75	<0.000	0.29	0.91	0.59
B56	3.230	25.866	5.245	1.947	30.030	0.303	0.036	101.4	44.93	7.70	0.010	0.004	0.075	0.075	14.4	0.007	<0.000	0.559	0.020	0.225	0.021	5.88	0.97	<0.000	0.06	0.87	0.50
B57	3.68	32.99	11.60	1.69	40.86	0.926	0.052	148.2	18.36	9.29	0.007	0.008	0.122	0.056	8.5	0.005	<0.000	1.352	0.016	0.168	0.025	6.66	0.60	<0.000	0.24	0.88	0.70
B58	3.07	34.91	17.02	1.34	49.25	0.340	0.069	180.2	17.36	12.56	0.005	0.005	0.101	0.075	8.6	0.004	<0.000	1.213	0.013	0.161	0.038	7.84	0.65	0.010	0.44	1.10	0.94
B59	4.30	39.53	29.24	0.72	61.92	0.116	0.144	259.0	7.15	21.81	0.005	0.005	0.063	0.119	3.5	0.003	<0.000	2.033	0.005	0.128	0.007	10.60	0.55	0.002	0.72	1.41	0.52
B60	3.74	39.39	22.70	1.42	62.31	1.404	0.117	226.4	6.61	17.14	0.004	0.007	0.079	0.080	20.9	0.003	<0.000	2.253	0.008	0.496	0.046	10.70	0.73	0.009	0.70	1.19	4.31
B61	3.50	43.03	35.90	1.09	68.94	0.163	0.262	285.6	5.35	17.84	0.004	0.004	0.073	0.156	4.0	0.003	<0.000	1.559	0.006	0.183	0.021	11.21	0.69	0.003	0.97	1.18	1.22
B62	2.47	39.46	20.53	0.89	42.48	0.186	0.114	198.9	4.68	9.80	0.004	0.003	0.074	0.075	2.6	0.002	<0.000	0.676	0.007	0.057	0.008	8.87	0.90	0.001	0.63	0.98	0.46
B63	3.42	40.71	31.99	1.26	48.90	0.069	0.193	236.0	1.88	27.00	0.034	0.003	0.051	0.109	1.4	0.004	0.006	0.924	0.009	0.291	0.014	7.70	1.13	0.091	0.96	0.82	1.77
B64	3.50	46.24	38.71	0.86	58.30	0.040	0.169	256.1	1.78	24.68	0.018	0.003	0.034	0.090	1.5	0.002	0.005	0.955	0.004	0.218	0.011	8.77	0.96	0.039	1.20	0.92	0.64
B65	3.820	45.884	34.275	0.631	64.547	0.047	0.190	255.0	1.55	22.70	0.014	0.004	0.023	0.145	1.1	0.002	0.004	1.452	0.004	0.201	0.010	8.96	0.99	0.024	1.21	1.06	1.03
B69	2.96	34.48	7.57	0.89	41.41	25.891	0.115	162.3	5.01	9.44	0.003	0.005	0.160	0.102	102.7	0.003	<0.000	0.503	0.007	0.306	0.031	5.07	0.84	<0.000	0.24	0.96	1.36
B70	6.72	30.93	8.39	1.52	28.51	189.121	0.064	132.3	6.05	10.65	0.004	0.009	0.226	0.044	132.9	0.005	0.000	0.385	0.011	0.432	0.032	4.50	0.98	<0.000	0.25	0.79	1.04
B71	2.645	41.239	17.970	1.112	30.062	0.865	0.070	189.1	4.05	10.86	0.009	0.003	0.058	0.125	7.8	0.003	0.001	0.381	0.006	0.248	0.037	5.10	0.99	0.015	0.57	0.99	4.57
P13	4.275	95.486	150.877	0.656	152.086	0.722	0.989	1005.7	5.96	44.91	0.002	0.006	0.048	0.259	12.5	0.006	<0.000	1.965	0.012	0.623	0.021	30.56	0.23	<0.000	9.50	1.67	5.88

APPENDIX D

Pharmaceuticals and pesticides data (µg/l)

Analyzed pharmaceutical and pesticide molecules with detection limits (DL) and analytical methods

Parametes	DL (µg/l)	Analytical method	Parametes	DL (µg/l)	Analytical method
MICROPOLLUANTS ORGANIQUES			Fénothrine	<0.021	GC / MS après extraction L/L
Tributyl phosphate	<0.052	GC / MS après extraction L/L	Fluvalinate-tau	<0.054	GC / MS après extraction L/L
PESTICIDES ARYLOXYACIDES			Tefluthrine	<0.022	GC / MS après extraction L/L
2,4 D	<0.025	LC / MS-MS	Tralométhrine	<0.024	GC / MS après extraction L/L
MCPA	<0.010	LC / MS-MS	**PESTICIDES DIVERS**		
Dichlorprop	<0.050	LC / MS-MS	AMPA	<0.050	Dérivation/HPLC-MSMS
Mécoprop	<0.005	LC / MS-MS	Chlorméquat	<0.100	SPE/HPLC/MSMS
Imazamethabenz méthyl	<0.005	LC / MS-MS	Glufosinate	<0.050	Dérivation/LC-MSMS
Ioxynil	<0.010	LC / MS-MS	Glyphosate	<0.050	Dérivation/LC-MSMS
Triclopyr	<0.050	LC / MS-MS	Mépiquat	<0.100	SPE/LC/MSMS
Dicamba	<0.100	LC / MS-MS	Aclonifen	<0.010	GC / MS après extraction L/L
Fluroxypir méthyl heptyl ester	<0.054	GC / MS après extraction L/L	Bentazone	<0.005	LC / MS-MS
Dichlofop méthyl	<0.005	GC / MS après extraction L/L	Cyprodinil	<0.005	LC / MS-MS
Dinoseb	<0.005	LC / MS-MS	Diflufénican	<0.006	GC / MS après extraction L/L
Dinoterbe	<0.050	LC / MS-MS	Diméthomorphe	<0.005	LC / MS-MS
Fenoxaprop-p-éthyl	<0.005	LC / MS-MS	Fenpropidine	<0.005	LC / MS-MS
Haloxyfop méthyl	<0.005	LC / MS-MS	Fenpropimorphe	<0.005	LC / MS-MS
Fluroxypyr	<0.050	LC / MS-MS	Flurochloridone	<0.011	GC / MS après extraction L/L
Fluazifop-P-butyl	<0.005	LC / MS-MS	Prochloraze	<0.010	LC / MS-MS
Quizalofop	<0.005	LC / MS-MS	Trifluraline	<0.006	GC / MS après extraction L/L
Quizalofop éthyl	<0.005	LC / MS-MS	Azoxystrobine	<0.005	LC / MS-MS
DNOC (2-méthyl-4,5-dinitrophénol)	<0.050	LC / MS-MS	Sulcotrione	<0.010	LC / MS-MS
Quinmérac	<0.010	LC / MS-MS	Oxadiazon	<0.012	GC / MS après extraction L/L
2,4 D - Esters	<0.025	Saponification - LC / MS-MS	Anthraquinone	<0.012	GC / MS après extraction L/L
Triclopyr - Esters	<0.050	Saponification - LC / MS-MS	Bifenox	<0.012	GC / MS après extraction L/L
MCPA - Esters	<0.010	Saponification - LC / MS-MS	Chlorothalonil	<0.013	GC / MS après extraction L/L
Clodinafop-propargyl	<0.042	GC / MS après extraction L/L	Clomazone	<0.012	GC / MS après extraction L/L
Mécoprop - Esters	0.005	Saponification - LC / MS-MS	Ethofumésate	<0.005	LC / MS-MS
PESTICIDES CARBAMATES			Flurtamone	<0.025	LC / MS-MS
Carbendazime	<0.005	LC / MS-MS	Vinchlozoline	<0.011	GC / MS après extraction L/L
Carbofuran	<0.005	LC / MS-MS	Pipéronil butoxyde	<0.011	GC / MS après extraction L/L
Prosulfocarbe	<0.005	LC / MS-MS	Picoxystrobine	<0.005	LC / MS-MS en ligne
Carbétamide	<0.005	LC / MS-MS	Pyraclostrobine	<0.005	LC / MS-MS en ligne
Thiodicarbe	<0.005	LC / MS-MS	Trifloxystrobine	<0.005	LC / MS-MS en ligne
Carbofuran-3-hydroxy	<0.005	LC / MS-MS	Bromacil	<0.005	LC / MS-MS en ligne
Aldicarbe	<0.010	LC / MS-MS	Cymoxanyl	<0.005	LC / MS-MS en ligne
Aldicarbe sulfone	<0.010	LC / MS-MS	Fipronil	<0.011	GC / MS après extraction L/L
Aldicarbe sulfoxyde	<0.010	LC / MS-MS	Fludioxonil	<0.005	LC / MS-MS
Carbaryl	<0.010	LC / MS-MS	Imidaclopride	<0.010	LC / MS-MS
Diallate	<0.024	GC / MS après extraction L/L	Mésotrione	<0.005	LC / MS-MS
Ethiofencarbe	<0.010	LC / MS-MS	Métosulame	<0.010	LC / MS-MS
Fenoxycarbe	<0.005	LC / MS-MS	Oryzalin	<0.005	LC / MS-MS
Méthiocarb	<0.010	LC / MS-MS	Oxadixyl	<0.005	LC / MS-MS
Méthomyl	<0.005	LC / MS-MS	Pyridabène	<0.010	GC / MS après extraction L/L
Pyrimicarbe	<0.005	LC / MS-MS	Pyrifenox	<0.010	LC / MS-MS
Triallate	<0.011	GC / MS après extraction L/L	Pyriméthanil	<0.010	LC / MS-MS
Carbosulfan	<0.023	GC / MS après extraction L/L	Clopyralid	<0.500	LC / MS-MS
Diethofencarbe	<0.010	LC / MS-MS	2,6-dichloroaniline	<0.026	GC / MS après extraction L/L
Iprovalicarbe	<0.010	LC / MS-MS	Bromoxynil	<0.010	LC / MS-MS
Phenmédiphane	<0.025	LC / MS-MS	Captane	<0.056	GC / MS après extraction L/L
Dimétilan	<0.050	LC / MS-MS	Dichlobénil	<0.013	GC / MS après extraction L/L
Iodopropanyl butyl carbamate (IPBC)	<0.005	LC / MS-MS	Fénazaquin	<0.011	GC / MS après extraction L/L
Molinate	<0.020	GC / MS après extraction L/L	Folpel	<0.059	GC / MS après extraction L/L
Thiabendazole	<0.025	LC / MS-MS	Méfenpyr-diéthyl	<0.010	LC / MS-MS
Thiobencarde	<0.005	LC / MS-MS	Procymidone	<0.011	GC / MS après extraction L/L
PESTICIDES ORGANOCHLORES			Propetamphos	<0.056	GC / MS après extraction L/L
Hexachlorobenzène	<0.027	GC / MS après extraction L/L	Propiconazole	<0.005	LC / MS-MS
DDD 2,4"	<0.006	GC / MS après extraction L/L	Propoxur	<0.010	LC / MS-MS
DDE 2,4"	<0.006	GC / MS après extraction L/L	Pyridate	<0.010	LC / MS-MS
DDT 2,4' + DDD 4,4'	<0.036	GC / MS après extraction L/L	Thiacloprid	<0.050	LC / MS-MS
DDE 4,4"	<0.006	GC / MS après extraction L/L	Tolyfluanide	<0.050	LC / MS-MS
DDT 4,4'	<0.006	GC / MS après extraction L/L	Dichlorobenzamide-2,6	<0.100	GC / MS après extraction L/L
Aldrine	<0.013	GC / MS après extraction L/L	Acifluorfen	<0.010	LC / MS-MS e
HCH Alpha	<0.014	GC / MS après extraction L/L	Amidosulfuron	<0.025	LC / MS-MS e
HCH Béta	<0.007	GC / MS après extraction L/L	Benoxacor	<0.022	GC / MS après extraction L/L
HCH Delta	<0.014	GC / MS après extraction L/L	Biphényl	<0.053	GC / MS après extraction L/L
HCH Epsilon	<0.011	GC / MS après extraction L/L	Chlorprophame	<0.058	GC / MS après extraction L/L
Lindane (HCH Gamma)	<0.013	GC / MS après extraction L/L	Cléthodim	<0.010	LC / MS-MS
Chlordane cis	<0.006	GC / MS après extraction L/L	Cycloxydime	<0.063	GC / MS après extraction L/L
Chlordane trans	<0.006	GC / MS après extraction L/L	Ethephon	<0.500	LC / MS-MS
Dicofol	<0.023	GC / MS après extraction L/L	Fluazinam	<0.063	GC / MS après extraction L/L
Dieldrine	<0.012	GC / MS après extraction L/L	Fomésafen	<0.025	LC / MS-MS
Endosulfan alpha	<0.026	GC / MS après extraction L/L	Iprodione	<0.061	GC / MS après extraction L/L
Endosulfan beta	<0.024	GC / MS après extraction L/L	Isoxaflutole	<0.005	LC / MS-MS
Endosulfan sulfate	<0.022	GC / MS après extraction L/L	Quinoxyfen	<0.054	GC / MS après extraction L/L
Endrine	<0.022	GC / MS après extraction L/L	Spiroxamine	<0.083	GC / MS après extraction L/L
Heptachlore	<0.006	GC / MS après extraction L/L	Métaldéhyde	<1.020	GC / MS après extraction L/L
Heptachlore époxyde	<0.024	GC / MS après extraction L/L	Acétamipride	<0.005	LC / MS-MS
Isodrine	<0.025	GC / MS après extraction L/L	Benfluraline	<0.012	GC / MS après extraction L/L
Pentachlorobenzène	<0.028	GC / MS après extraction L/L	Bifenthrine	<0.021	GC / MS après extraction L/L
HCH (Total)	<0.059	GC / MS après extraction L/L	Boscalid	<0.025	LC / MS-MS
Endrine aldéhyde	<0.023	GC / MS après extraction L/L	Bromadiolone	<0.100	LC / MS-MS
Endosulfan total	<0.072	GC / MS après extraction L/L	Bupirimate	<0.069	GC / MS après extraction L/L
Fénison	<0.025	GC / MS après extraction L/L	Buprofézine	<0.057	GC / MS après extraction L/L
Hexachlorobutadiène	<0.034	GC / MS après extraction L/L	Butraline	<0.022	GC / MS après extraction L/L
Quintozène	<0.023	GC / MS après extraction L/L	Cadusafos	<0.059	GC / MS après extraction L/L
PESTICIDES ORGANOPHOSPHORES			Captafol	<0.054	GC / MS après extraction L/L

Trichlorfon	<0.050	LC / MS-MS	Carfentrazone éthyl	<0.025	LC / MS-MS
Dichlorvos	<0.005	LC / MS-MS	Chinométhionate	<0.054	GC / MS après extraction L/L
Oxydéméton méthyl	<0.005	LC / MS-MS	Cloquintocet mexyl	<0.022	GC / MS après extraction L/L
Azamétiphos	<0.005	LC / MS-MS	Déméton S méthyl	<0.022	GC / MS après extraction L/L
Azinphos éthyl	<0.022	GC / MS après extraction L/L	Difénacoum	<0.025	LC / MS-MS
Bromophos éthyl	<0.012	GC / MS après extraction L/L	Hexythiazox	<0.025	LC / MS-MS
Bromophos méthyl	<0.013	GC / MS après extraction L/L	Imazalile	<0.010	LC / MS-MS
Chlorfenvinphos	<0.023	GC / MS après extraction L/L	Naptalame	<0.025	LC / MS-MS
Chlormephos	<0.024	GC / MS après extraction L/L	Nuarimol	<0.053	GC / MS après extraction L/L
Chlorpyriphos éthyl	<0.011	GC / MS après extraction L/L	Ofurace	<0.010	LC / MS-MS
Chlorpyriphos méthyl	<0.012	GC / MS après extraction L/L	Perméthrine	<0.059	GC / MS après extraction L/L
Coumaphos	<0.051	GC / MS après extraction L/L	Pymétrozine	<0.010	LC / MS-MS
Déméton S méthyl sulfoné	<0.005	LC / MS-MS	Tébufenpyrad	<0.023	GC / MS après extraction L/L
Diazinon	<0.013	GC / MS après extraction L/L	Flumioxazine	<0.075	GC / MS après extraction L/L
Diméthoate	<0.005	LC / MS-MS	Silthiofam	<0.057	GC / MS après extraction L/L
Ethion	<0.006	GC / MS après extraction L/L	POLY CHLORO-BROMO BIPHENYLS		
Ethoprophos	<0.021	GC / MS après extraction L/L	PCB 101	<0.001	GC / MS après extraction L/L
Fenclorphos	<0.024	GC / MS après extraction L/L	PCB 105	<0.001	GC / MS après extraction L/L
Fenitrothion	<0.012	GC / MS après extraction L/L	PCB 118	<0.001	GC / MS après extraction L/L
Fenthion	<0.013	GC / MS après extraction L/L	PCB 125	<0.001	GC / MS après extraction L/L
Isazophos	<0.014	GC / MS après extraction L/L	PCB 126	<0.001	GC / MS après extraction L/L
Malathion	<0.021	GC / MS après extraction L/L	PCB 128	<0.001	GC / MS après extraction L/L
Méthidathion	<0.056	GC / MS après extraction L/L	PCB 138	<0.001	GC / MS après extraction L/L
Parathion éthyl	<0.022	GC / MS après extraction L/L	PCB 149	<0.001	GC / MS après extraction L/L
Parathion méthyl	<0.057	GC / MS après extraction L/L	PCB 153	<0.001	GC / MS après extraction L/L
Phorate	<0.024	GC / MS après extraction L/L	PCB 156	<0.001	GC / MS après extraction L/L
Phosalone	<0.011	GC / MS après extraction L/L	PCB 169	<0.006	GC / MS après extraction L/L
Phosmet	<0.011	GC / MS après extraction L/L	PCB 170	<0.001	GC / MS après extraction L/L
Phoxime	<0.005	LC / MS-MS	PCB 18	<0.005	GC / MS après extraction L/L
Profenofos	<0.055	GC / MS après extraction L/L	PCB 180	<0.001	GC / MS après extraction L/L
Pyrazophos	<0.011	GC / MS après extraction L/L	PCB 194	<0.006	GC / MS après extraction L/L
Pyrimiphos éthyl	<0.005	LC / MS-MS	PCB 209	<0.006	GC / MS après extraction L/L
Quinalphos	<0.005	LC / MS-MS	PCB 28+31	<0.003	GC / MS après extraction L/L
Terbuphos	<0.012	GC / MS après extraction L/L	PCB 35	<0.006	GC / MS après extraction L/L
Tétrachlorvinphos	<0.023	GC / MS après extraction L/L	PCB 44	<0.001	GC / MS après extraction L/L
Tétradifon	<0.023	GC / MS après extraction L/L	PCB 52	<0.001	GC / MS après extraction L/L
Azinphos méthyl	<0.021	GC / MS après extraction L/L	PCB 54	<0.001	GC / MS après extraction L/L
Mévinphos	<0.063	GC / MS après extraction L/L	PCB 77	<0.006	GC / MS après extraction L/L
Oxyfluorfene	<0.011	GC / MS après extraction L/L	**PESTICIDES AZOTES**		
Pyrimiphos méthyl	<0.005	LC / MS-MS	Atrazine	<0.005	LC / MS-MS
Méthamidophos	<0.100	LC / MS-MS	Atrazine déséthyl	<0.025	LC / MS-MS
Carbophénotion	<0.054	GC / MS après extraction L/L	Atrazine déisopropyl (DIA)	<0.005	LC / MS-MS
Déméton	<0.04	GC / MS après extraction L/L	Hexazinone	<0.005	LC / MS-MS
Dichlofenthion	<0.024	GC / MS après extraction L/L	Métamitrone	<0.005	LC / MS-MS
Etrimfos	<0.026	GC / MS après extraction L/L	Métribuzine	<0.010	LC / MS-MS
Fonofos	<0.020	GC / MS après extraction L/L	Simazine	<0.010	LC / MS-MS
Formothion	<0.078	GC / MS après extraction L/L	Atrazine-2-hydroxy	<0.005	LC / MS-MS
Hepténophos	<0.072	GC / MS après extraction L/L	Fluthiamide (Flufénacet)	<0.010	LC / MS-MS
Iodofenphos	<0.025	GC / MS après extraction L/L	Terbuthylazine-2-hydroxy	<0.005	LC / MS-MS
Propargite	<0.051	GC / MS après extraction L/L	Améthrine	<0.005	LC / MS-MS
Sulfotepp	<0.021	GC / MS après extraction L/L	Cyanazine	<0.005	LC / MS-MS
Triazophos	<0.061	GC / MS après extraction L/L	Desétylterbutylazine	<0.025	LC / MS-MS
Trichloronate	<0.011	GC / MS après extraction L/L	Desméthrine	<0.005	LC / MS-MS
Vamidothion	<0.005	LC / MS-MS	Pendiméthaline	<0.025	LC / MS-MS
Isofenphos	<0.011	GC / MS après extraction L/L	Prometon	<0.025	LC / MS-MS
PESTICIDES AMIDES-ACETAMIDES			Prométhrine	<0.005	LC / MS-MS
Alachlore	<0.005	LC / MS-MS	Propazine	<0.010	LC / MS-MS
Acétochlore	<0.011	GC / MS après extraction L/L	Sébutylazine	<0.005	LC / MS-MS
Diméthénamide	<0.005	LC / MS-MS	Secbuméton	<0.005	LC / MS-MS
Métazachlore	<0.005	LC / MS-MS	Terbuméton	<0.005	LC / MS-MS
Métolachlore	<0.005	LC / MS-MS	Terbutryne	<0.005	LC / MS-MS
Napropamide	<0.005	LC / MS-MS	Terbuthylazine	<0.005	LC / MS-MS
Isoxaben	<0.005	LC / MS-MS	Atrazine déséthyl déisopropyl	<0.020	LC / MS-MS
Propachlore	<0.005	LC / MS-MS	Kresoxim-méthyle	<0.023	GC / MS après extraction L/L
Propyzamide	<0.012	GC / MS après extraction L/L	**NITROPHENOLS ET ALCOOLS**		
Diméthachlore	<0.005	LC / MS-MS	Bromoxynil octanoate	<0.060	GC / MS après extraction L/L
Métalaxyle	<0.025	LC / MS-MS	**PESTICIDES AZOLES**		
Mépronil	<0.008	GC / MS après extraction L/L	Aminotriazole	<0.10	Dérivation/LC/FLUO
Tébutam	<0.010	LC / MS-MS	Cyproconazole	<0.005	LC / MS-MS en ligne
Bénalaxyl	<0.005	LC / MS-MS	Epoxiconazole	<0.010	LC / MS-MS en ligne
Fenhexamid	<0.010	LC / MS-MS	Flusilazole	<0.005	LC / MS-MS en ligne
Zoxamide	<0.005	LC / MS-MS	Hexaconazole x	<0.005	LC / MS-MS en ligne
Dichlormid	<0.059	GC / MS après extraction L/L	Tebuconazole	<0.010	LC / MS-MS en ligne
Carboxine	<0.027	GC / MS après extraction L/L	Metconazol	<0.025	LC / MS-MS en ligne
Dichlofluanide	<0.020	GC / MS après extraction L/L	Chloridazone	<0.005	LC / MS-MS en ligne
Furalaxyl	<0.005	LC / MS-MS	Tétraconazole	<0.010	LC / MS-MS en ligne
Mefenacet	<0.058	GC / MS après extraction L/L	Myclobutanil	<0.010	LC / MS-MS en ligne
Métalaxyl-M	<0.010	LC / MS-MS	Bromuconazole	<0.010	LC / MS-MS en ligne
Pretilachlore	<0.020	GC / MS après extraction L/L	Difénoconazole	<0.010	LC / MS-MS en ligne
PESTICIDES UREES			Fenbuconazole	<0.010	LC / MS-MS en ligne
Flazasulfuron	<0.005	LC / MS-MS	Paclobutrazole	<0.010	LC / MS-MS en ligne
Chlortoluron	<0.005	LC / MS-MS	Penconazole	<0.010	LC / MS-MS en ligne
Diflubenzuron	<0.005	LC / MS-MS	Triadiméfon	<0.025	LC / MS-MS en ligne
Diuron	<0.005	LC / MS-MS	Florasulam	<0.050	LC / MS-MS en ligne
Isoproturon	<0.010	LC / MS-MS	Propoxycarbonazole sodium	<0.010	LC / MS-MS en ligne
Linuron	<0.010	LC / MS-MS	Triazamate	<0.025	LC / MS-MS en ligne
Méthabenzthiazuron	<0.010	LC / MS-MS	Bitertanol	<0.050	LC / MS-MS en ligne
Sulfosulfuron	<0.005	LC / MS-MS			
Thifensulfuron méthyl	<0.010	LC / MS-MS	**COMPOSES PHARMACEUTIQUES**		
Trinéxapac éthyl	<0.005	LC / MS-MS	Acide clofibrique	<0.001	SPE/HPLC/MSMS

1-(3,4-dichlorophényl)-3-méthylurée	<0.005	LC / MS-MS	Acide fenofibrique	<0.001	SPE/HPLC/MSMS
1-(3,4-dichlorophényl)-urée	<0.010	LC / MS-MS	Altrenogest	<0.005	SPE/HPLC/MSMS
Buturon	<0.010	LC / MS-MS	Amlodipine	<0.010	SPE/HPLC/MSMS
Chlorbromuron	<0.010	LC / MS-MS	Atenolol	<0.001	SPE/HPLC/MSMS
Chloroxuron	<0.005	LC / MS-MS	Bezafibrate	<0.001	SPE/HPLC/MSMS
Chlorsulfuron	<0.010	LC / MS-MS	Bromazepam	<0.005	SPE/HPLC/MSMS
Diméfuron	<0.010	LC / MS-MS	Caféine	<0.010	SPE/HPLC/MSMS
Ethidimuron	<0.005	LC / MS-MS	Carbamazépine	<0.001	SPE/HPLC/MSMS
Fénuron	<0.005	LC / MS-MS	Chloramphénicole	<0.001	SPE/HPLC/MSMS
Hexaflumuron	<0.005	LC / MS-MS	Clindamycine-2-phosphate	<0.005	SPE/HPLC/MSMS
Iodosulfuron méthyl sodium	<0.005	LC / MS-MS	Dicyclanil	<0.10	SPE/HPLC/MSMS
Métobromuron	<0.005	LC / MS-MS	Doxycycline	<0.001	SPE/HPLC/MSMS
Métoxuron	<0.005	LC / MS-MS	Epoxycarbamazépine	<0.005	SPE/HPLC/MSMS
Metsulfuron méthyl	<0.010	LC / MS-MS	Estriol	<0.001	SPE/HPLC/MSMS
Monolinuron	<0.005	LC / MS-MS	Fenofibrate	<0.010	SPE/HPLC/MSMS
Monuron	<0.005	LC / MS-MS	Fluoxetine	<0.005	SPE/HPLC/MSMS
Néburon	<0.050	LC / MS-MS	Furosemide	<0.001	SPE/HPLC/MSMS
Nicosulfuron	<0.010	LC / MS-MS	Fluvoxamine	<0.005	SPE/HPLC/MSMS
Norflurazon	<0.005	LC / MS-MS	Gemfibrozil	<0.001	SPE/HPLC/MSMS
Pencycuron	<0.005	LC / MS-MS	Hydrochlorothiazide	<0.005	SPE/HPLC/MSMS
Rimsulfuron	<0.010	LC / MS-MS	Ifosfamide	<0.001	SPE/HPLC/MSMS
Teflubenzuron	<0.005	LC / MS-MS	Indométhacine	<0.005	SPE/HPLC/MSMS
Triasulfuron	<0.005	LC / MS-MS	Iopromide	<0.005	SPE/HPLC/MSMS
Triflumuron	<0.005	LC / MS-MS	Levamisol	<0.005	SPE/HPLC/MSMS
Desméthylisoproturon (IPPMU)	<0.010	LC / MS-MS	Lincomycine	<0.010	SPE/HPLC/MSMS
Flupyrsulfuron méthyl sodium	<0.050	LC / MS-MS	Losartan	<0.005	SPE/HPLC/MSMS
Foramsulfuron	<0.010	LC / MS-MS	Méthotréxate	<0.010	SPE/HPLC/MSMS
Mésosulfuron méthyl	<0.010	LC / MS-MS	Metoprolol	<0.001	SPE/HPLC/MSMS
Prosulfuron	<0.010	LC / MS-MS	Naproxène	<0.001	SPE/HPLC/MSMS
Tribénuron méthyl	<0.010	LC / MS-MS	Paracétamol	<0.010	SPE/HPLC/MSMS
1-(4-isopropylphenyl)-urée	<0.010	LC / MS-MS	Oxytétracycline	<0.10	SPE/HPLC/MSMS
Flurfénoxuron	<0.025	LC / MS-MS	Pravastatine	<0.001	SPE/HPLC/MSMS
Triticonazole	<0.025	LC / MS-MS	Progestérone	<0.001	SPE/HPLC/MSMS
PESTICIDES PYRETHRINOIDES			Penicilline G	<0.005	SPE/HPLC/MSMS
Cyperméthrine	<0.034	GC / MS après extraction L/L	Propanolol	<0.001	SPE/HPLC/MSMS
Alphaméthrine	<0.022	GC / MS après extraction L/L	Ramipril	<0.005	SPE/HPLC/MSMS
Deltaméthrine	<0.053	GC / MS après extraction L/L	Ranitidine	<0.005	SPE/HPLC/MSMS
Lambda cyhalothrine	<0.010	GC / MS après extraction L/L	Roxithromycine	<0.005	SPE/HPLC/MSMS
Méthoxychlore	<0.024	GC / MS après extraction L/L	Sulfamérazine	<0.005	SPE/HPLC/MSMS
Esfenvalérate	<0.040	GC / MS après extraction L/L	Sulfaméthazine	<0.001	SPE/HPLC/MSMS
Acrinathrine	<0.012	GC / MS après extraction L/L	Sulfaméthizole	<0.005	SPE/HPLC/MSMS
Bioresmethrine	<0.013	GC / MS après extraction L/L	Sulfaméthoxazole	<0.001	SPE/HPLC/MSMS
Cyfluthrine	<0.052	GC / MS après extraction L/L	Tétracycline	<0.10	SPE/HPLC/MSMS
Dépallethrine	<0.045	GC / MS après extraction L/L	Testosterone	<0.005	SPE/HPLC/MSMS
Fenpropathrine	<0.021	GC / MS après extraction L/L	Trimétazidine	<0.10	SPE/HPLC/MSMS
			Triméthoprime	<0.001	SPE/HPLC/MSMS

Pharmaceuticals and pesticides detected in sampled points (Allier, P13, B29, and B33)

Sample ID	Date	Parameter type	Compounds	Conc. (µg/L)	Sample ID	Date	Parameter type	Compounds	Conc. (µg/L)
Allier	24/10/2011	Pesticide	Atrazine déisopropul	0.0110	**Allier**	10/04/2012	pharmaceutical	Hydrochlorothiazide	0.0130
Allier	24/10/2011	pharmaceutical	Acide fenofibrique	0.0022	**Allier**	10/04/2012	pharmaceutical	Iopromide	0.0420
Allier	24/10/2011	pharmaceutical	Atenolol	0.0034	**Allier**	10/04/2012	pharmaceutical	Pravastatine	0.0018
Allier	24/10/2011	pharmaceutical	Bezafibrate	0.0025	**Allier**	10/04/2012	pharmaceutical	Sulfaméthoxazole	0.0020
Allier	24/10/2011	pharmaceutical	Caféine	0.0240	**Allier**	09/05/2012	Pesticide	Thifensulfuron méthyl	0.0110
Allier	24/10/2011	pharmaceutical	Carbamazépine	0.0039	**Allier**	09/05/2012	Pesticide	Chloridazone	0.0060
Allier	24/10/2011	pharmaceutical	Furosemide	0.0043	**Allier**	09/05/2012	pharmaceutical	Caféine	0.0150
Allier	24/10/2011	pharmaceutical	Gemfibrozil	0.0019	**Allier**	09/05/2012	pharmaceutical	Doxycycline	0.0018
Allier	24/10/2011	pharmaceutical	Iopromide	0.0150	**Allier**	09/05/2012	pharmaceutical	Iopromide	0.0064
Allier	24/10/2011	pharmaceutical	Pravastatine	0.0037	**Allier**	09/05/2012	pharmaceutical	Naproxène	0.0012
Allier	24/10/2011	pharmaceutical	Propanolol	0.0010	**Allier**	09/05/2012	pharmaceutical	Sulfaméthoxazole	0.0015
Allier	24/10/2011	pharmaceutical	Sulfaméthoxazole	0.0010	**Allier**	04/06/2012	Pesticide	Diflufénican	0.0070
Allier	21/11/2011	Pesticide	Diflufénican	0.0060	**Allier**	04/06/2012	pharmaceutical	Acide fenofibrique	0.0018
Allier	21/11/2011	Pesticide	Cymoxanyl	0.0120	**Allier**	04/06/2012	pharmaceutical	Atenolol	0.0030
Allier	21/11/2011	Pesticide	Atrazine	0.0090	**Allier**	04/06/2012	pharmaceutical	Carbamazépine	0.0012
Allier	21/11/2011	Pesticide	Simazine	0.0140	**Allier**	04/06/2012	pharmaceutical	Furosemide	0.0018
Allier	21/11/2011	pharmaceutical	Acide fenofibrique	0.0089	**Allier**	02/07/2012	Pesticide	Métolachlore	0.0060
Allier	21/11/2011	pharmaceutical	Atenolol	0.0031	**Allier**	02/07/2012	Pesticide	Diuron	0.0080
Allier	21/11/2011	pharmaceutical	Bezafibrate	0.0055	**Allier**	02/07/2012	Pesticide	AMPA	0.1500
Allier	21/11/2011	pharmaceutical	Caféine	0.0270	**Allier**	02/07/2012	Pesticide	Diflufénican	0.0120
Allier	21/11/2011	pharmaceutical	Carbamazépine	0.0031	**Allier**	02/07/2012	pharmaceutical	Atenolol	0.0085
Allier	21/11/2011	pharmaceutical	Furosemide	0.0029	**Allier**	02/07/2012	pharmaceutical	Bezafibrate	0.0020
Allier	21/11/2011	pharmaceutical	Gemfibrozil	0.0022	**Allier**	02/07/2012	pharmaceutical	Caféine	0.0380
Allier	21/11/2011	pharmaceutical	Hydrochlorothiazide	0.0150	**Allier**	02/07/2012	pharmaceutical	Carbamazépine	0.0022
Allier	21/11/2011	pharmaceutical	Iopromide	0.0990	**Allier**	02/07/2012	pharmaceutical	Doxycycline	0.0011
Allier	21/11/2011	pharmaceutical	Naproxène	0.0033	**Allier**	02/07/2012	pharmaceutical	Furosemide	0.0026
Allier	21/11/2011	pharmaceutical	Pravastatine	0.0023	**Allier**	02/07/2012	pharmaceutical	Gemfibrozil	0.0015
Allier	21/11/2011	pharmaceutical	Propanolol	0.0013	**Allier**	02/07/2012	pharmaceutical	Hydrochlorothiazide	0.0210
Allier	21/11/2011	pharmaceutical	Sulfaméthoxazole	0.0011	**Allier**	02/07/2012	pharmaceutical	Iopromide	0.0240
Allier	19/12/2011	pharmaceutical	Acide fenofibrique	0.0046	**Allier**	02/07/2012	pharmaceutical	Metoprolol	0.0011
Allier	19/12/2011	pharmaceutical	Bezafibrate	0.0014	**Allier**	02/07/2012	pharmaceutical	Naproxène	0.0037
Allier	19/12/2011	pharmaceutical	Gemfibrozil	0.0020	**Allier**	02/07/2012	pharmaceutical	Paracétamol	0.0250
Allier	19/12/2011	pharmaceutical	Paracétamol	0.0370	**Allier**	02/07/2012	pharmaceutical	Pravastatine	0.0180
Allier	16/01/2012	pharmaceutical	Acide fenofibrique	0.0081	**Allier**	02/07/2012	pharmaceutical	Propanolol	0.0016
Allier	16/01/2012	pharmaceutical	Atenolol	0.0052	**Allier**	02/07/2012	pharmaceutical	Sulfaméthoxazole	0.0010
Allier	16/01/2012	pharmaceutical	Caféine	0.0370	**Allier**	27/08/2012	Pesticide	AMPA	0.1300

Allier	16/01/2012	pharmaceutical	Gemfibrozil	0.0039	**Allier**	27/08/2012	Pesticide	Diflufénican	0.0080
Allier	16/01/2012	pharmaceutical	Hydrochlorothiazide	0.0150	**Allier**	24/09/2012	Organic micro-pollutant	Tributyl phosphate	0.1380
Allier	16/01/2012	pharmaceutical	Iopromide	0.0097	**Allier**	24/09/2012	Pesticide	Carbendazime	0.0070
Allier	16/01/2012	pharmaceutical	Pravastatine	0.0074	**Allier**	24/09/2012	Pesticide	Glyphosate	0.0560
Allier	13/02/2012	Pesticide	Alachlore	0.0690	**Allier**	24/09/2012	Pesticide	Bentazone	0.0060
Allier	13/02/2012	Pesticide	Diuron	0.0080	**Allier**	24/09/2012	Pesticide	Diflufénican	0.0070
Allier	13/02/2012	pharmaceutical	Acide fenofibrique	0.0190	**Allier**	24/09/2012	pharmaceutical	Caféine	0.0780
Allier	13/02/2012	pharmaceutical	Atenolol	0.0070	**Allier**	24/09/2012	pharmaceutical	Epoxycarbamazépine	0.0460
Allier	13/02/2012	pharmaceutical	Caféine	0.0810	**Allier**	24/09/2012	pharmaceutical	Naproxène	0.0200
Allier	13/02/2012	pharmaceutical	Carbamazépine	0.0033	**Allier**	24/09/2012	pharmaceutical	Paracétamol	0.2000
Allier	13/02/2012	pharmaceutical	Hydrochlorothiazide	0.0350	**Allier**	22/10/2012	Organic micro-pollutant	Tributyl phosphate	0.0820
Allier	13/02/2012	pharmaceutical	Naproxène	0.0093	**Allier**	22/10/2012	Pesticide	Carbendazime	0.0070
Allier	13/02/2012	pharmaceutical	Pravastatine	0.0065	**Allier**	22/10/2012	Pesticide	1-(3,4-dichlorophénol)-3-méthylurée	0.0070
Allier	13/02/2012	pharmaceutical	Sulfaméthoxazole	0.0041	**Allier**	22/10/2012	pharmaceutical	Hydrochlorothiazide	0.0420
Allier	12/03/2012	Pesticide	Mépronil	0.0130	**P13**	24/10/2011	pesticide	Pipéronil butoxyde	0.0190
Allier	12/03/2012	pharmaceutical	Acide fenofibrique	0.0012	**P13**	21/11/2011	pesticide	Diuron	0.0080
Allier	12/03/2012	pharmaceutical	Atenolol	0.0047	**P13**	21/11/2011	pesticide	Atrazine déséthyl	0.0300
Allier	12/03/2012	pharmaceutical	Bezafibrate	0.0046	**P13**	21/11/2011	pesticide	Hexaconazole	0.0160
Allier	12/03/2012	pharmaceutical	Carbamazépine	0.0017	**P13**	19/12/2011	pesticide	Atrazine déséthyl	0.0270
Allier	12/03/2012	pharmaceutical	Gemfibrozil	0.0046	**P13**	13/02/2012	pesticide	AMPA	0.0770
Allier	12/03/2012	pharmaceutical	Hydrochlorothiazide	0.0270	**P13**	10/04/2012	pesticide	Atrazine déisopropyl	0.0070
Allier	12/03/2012	pharmaceutical	Iopromide	0.0750	**P13**	04/06/2012	pesticide	Atrazine déséthyl déisopropyl	0.0410
Allier	12/03/2012	pharmaceutical	Naproxène	0.0082	**P13**	02/07/2012	pesticide	Pipéronil butoxyde	0.0110
Allier	12/03/2012	pharmaceutical	Pravastatine	0.0024	**P13**	02/07/2012	pharmaceutical	Doxycycline	0.0011
Allier	12/03/2012	pharmaceutical	Roxithromycine	0.0076	**P13**	27/08/2012	pesticide	Sébutylazine	0.0060
Allier	10/04/2012	Pesticide	MCPA- Esters	0.0120	**P13**	24/09/2012	organic micro-pollutants	Tributyl phosphate	0.0920
Allier	10/04/2012	Pesticide	Carbendazime	0.0080	**P13**	24/09/2012	pesticide	Bentazone	0.0060
Allier	10/04/2012	Pesticide	Métolachlore	0.0150	**P13**	24/09/2012	pesticide	Dilflufénican	0.0080
Allier	10/04/2012	Pesticide	Diflufénican	0.0080	**P13**	24/09/2012	pesticide	Atrazine déséthyl	0.0320
Allier	10/04/2012	Pesticide	Métamitrone	0.0730	**P13**	22/10/2012	organic micro-pollutants	Tributyl phosphate	0.0980
Allier	10/04/2012	pharmaceutical	Acide fenofibrique	0.0064	**P13**	22/10/2012	pesticide	Quizalofop	0.0130
Allier	10/04/2012	pharmaceutical	Atenolol	0.0039	**P13**	22/10/2012	pesticide	Azametiphos	0.0160
Allier	10/04/2012	pharmaceutical	Bezafibrate	0.0040	**P13**	22/10/2012	pesticide	Sulfosulfuron	0.0170
Allier	10/04/2012	pharmaceutical	Caféine	0.0520	**P13**	22/10/2012	pesticide	Atrazine déséthyl	0.0310
Allier	10/04/2012	pharmaceutical	Carbamazépine	0.0040	**P13**	22/10/2012	pesticide	Simazine	0.0110
Allier	10/04/2012	pharmaceutical	Furosemide	0.0055	**P13**	22/10/2012	pesticide	Atrazine déséthyl déisopropyl	0.0610
B29	24/10/2011	pesticide	Dichlorvos	0.0160	**B29**	24/09/2012	organic micro-pollutant	Tributyl phosphate	0.0600
B29	24/10/2011	pesticide	Métamitrone	0.0280	**B29**	24/09/2012	pesticide	Bentazone	0.0060
B29	24/10/2011	pharmaceutical	Carbamazépine	0.0056	**B29**	24/09/2012	pesticide	Atrazine	0.0100
B29	24/10/2011	pharmaceutical	Epoxycarbamazépine	0.0080	**B29**	24/09/2012	pesticide	Simazine	0.0200
B29	24/10/2011	pharmaceutical	Sulfaméthoxazole	0.0028	**B29**	22/10/2012	organic micro-pollutant	Tributyl phosphate	0.0860
B29	21/11/2011	pesticide	Sulfosulfuron	0.0260	**B29**	22/10/2012	pesticide	Carbendazime	0.0090
B29	21/11/2011	pesticide	Foramsulfuron	0.0100	**B29**	22/10/2012	pesticide	Atrazine	0.0110
B29	21/11/2011	pesticide	Cyproconazole	0.0070	**B29**	22/10/2012	pesticide	Atrazine déisopropyl	0.0130
B29	21/11/2011	pharmaceutical	Carbamazépine	0.0032	**B29**	22/10/2012	pesticide	Simazine	0.0120
B29	21/11/2011	pharmaceutical	Sulfaméthoxazole	0.0011	**B29**	22/10/2012	pesticide	Chloridazone	0.0060
B29	19/12/2011	pesticide	Sulfosulfuron	0.0160	**B33**	24/10/2011	pesticide	Hexaconazole	0.0050
B29	19/12/2011	pesticide	Atrazine	0.0120	**B33**	24/10/2011	pharmaceutical	Carbamazépine	0.0019
B29	19/12/2011	pharmaceutical	Carbamazépine	0.0022	**B33**	24/10/2011	pharmaceutical	Sulfaméthoxazole	0.0016
B29	16/01/2012	pesticide	Atrazine	0.0120	**B33**	21/11/2011	pesticide	Thiodicarbe	0.0060
B29	16/01/2012	pharmaceutical	Epoxycarbamazépine	0.0075	**B33**	21/11/2011	pharmaceutical	Carbamazépine	0.0018
B29	13/02/2012	pesticide	AMPA	0.1400	**B33**	21/11/2011	pharmaceutical	Hydrochlorothiazide	0.0060
B29	13/02/2012	pharmaceutical	hydrochlorothiazide	0.0140	**B33**	19/12/2011	pharmaceutical	Carbamazépine	0.0015
B29	13/02/2012	pharmaceutical	Sulfaméthoxazole	0.0018	**B33**	16/01/2012	pharmaceutical	Hydrochlorothiazide	0.0084
B29	12/03/2012	pesticide	Mépronil	0.0090	**B33**	13/02/2012	pesticide	Atrazine déisopropyl	0.0060
B29	12/03/2012	pesticide	Atrazine	0.0090	**B33**	13/02/2012	pharmaceutical	Carbamazépine	0.0027
B29	12/03/2012	pesticide	Simazine	0.0130	**B33**	13/02/2012	pharmaceutical	Epoxycarbamazépine	0.0065
B29	12/03/2012	pharmaceutical	Carbamazépine	0.0013	**B33**	13/02/2012	pharmaceutical	Gemfibrozil	0.0280
B29	10/04/2012	pesticide	Atrazine	0.0110	**B33**	13/02/2012	pharmaceutical	Hydrochlorothiazide	0.0370
B29	10/04/2012	pharmaceutical	Carbamazépine	0.0034	**B33**	13/02/2012	pharmaceutical	Iopromide	0.1800
B29	10/04/2012	pharmaceutical	Epoxycarbamazépine	0.0056	**B33**	13/02/2012	pharmaceutical	Losartan	0.0077
B29	10/04/2012	pharmaceutical	Sulfaméthoxazole	0.0022	**B33**	13/02/2012	pharmaceutical	Sulfaméthoxazole	0.0020
B29	09/05/2012	pesticide	Atrazine	0.0100	**B33**	12/03/2012	pharmaceutical	Carbamazépine	0.0010
B29	09/05/2012	pesticide	Atrazine déisopropyl	0.0060	**B33**	12/03/2012	pharmaceutical	Hydrochlorothiazide	0.0200
B29	04/06/2012	pharmaceutical	Carbamazépine	0.0053	**B33**	12/03/2012	pharmaceutical	Sulfaméthoxazole	0.0028
B29	04/06/2012	pharmaceutical	Epoxycarbamazépine	0.0081	**B33**	10/04/2012	pesticide	MCPA- Esters	0.0130
B29	04/06/2012	pharmaceutical	Sulfaméthoxazole	0.0044	**B33**	10/04/2012	pesticide	Atrazine déisopropyl	0.0060
B29	02/07/2012	pesticide	Métolachlore	0.0380	**B33**	10/04/2012	pharmaceutical	Carbamazépine	0.0026
B29	02/07/2012	pesticide	Atrazine	0.0160	**B33**	10/04/2012	pharmaceutical	Hydrochlorothiazide	0.0100
B29	02/07/2012	pesticide	Métamitrone	0.0960	**B33**	10/04/2012	pharmaceutical	Sulfaméthoxazole	0.0035
B29	02/07/2012	pesticide	Simazine	0.0130	**B33**	04/06/2012	pharmaceutical	Carbamazépine	0.0020
B29	02/07/2012	pharmaceutical	Carbamazépine	0.0030	**B33**	02/07/2012	pharmaceutical	Hydrochlorothiazide	0.0083
B29	02/07/2012	pharmaceutical	Doxycycline	0.0014	**B33**	24/09/2012	pesticide	Sulfosulfuron	0.0060
B29	02/07/2012	pharmaceutical	Epoxycarbamazépine	0.0058	**B33**	24/09/2012	pesticide	Bentazone	0.0060
B29	02/07/2012	pharmaceutical	Sulfaméthoxazole	0.0029	**B33**	22/10/2012	pesticide	Carbendazime	0.0070
B29	27/08/2012	pesticide	Atrazine	0.0130	**B33**	22/10/2012	pesticide	Atrazine déséthyl déisopropyl	0.0710
B29	28/08/2012	pesticide	Simazine	0.0120	**B33**	22/10/2012	pharmaceutical	Hydrochlorothiazide	0.0280

APPENDIX E

Article 1: Isotopic and geochemical identification of main groundwater supply sources to an alluvial aquifer, the Allier River valley (France)

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Isotopic and geochemical identification of main groundwater supply sources to an alluvial aquifer, the Allier River valley (France)

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SUMMARY

Hydrodynamic, hydrochemical, and isotopic investigations were carried out on 18 points, including boreholes, piezometers, and surface waters, from February 2011 to August 2012, to assess groundwater quality in the unconfined shallow alluvial aquifer of the Allier River (one of the main tributary of the Loire River). The study area, located near the city of Clermont-Ferrand (France), plays an important socio-economic role as the alluvial aquifer is the major source of drinking water for about 100,000 inhabitants. The objective of the project aims at understanding the functioning of alluvial aquifers that occupy a pre-eminent position in the hydrogeologic landscape both for their economic role – production of drinking water and agricultural development – and for their ecological role. Moreover, this study also targets at determining the factors and processes controlling shallow groundwater quality and origin. The water circulates from the south, with a natural alimentation from the hills in the non-pumped part of the alluvial aquifer. In the pumping zone, this general behaviour is altered by the pumping that makes the water from the Allier River enter the system in a large proportion. Four end-members have been identified for the recharge of the alluvial groundwater: rainfall, Allier River, surrounding hills' aquifer and the southern non-pumped part of the alluvial system. Results indicate that, despite the global Ca–HCO_3 water type of the groundwater, spatial variations of physico-chemical parameters do exist in the study area. Ionic concentrations increase from the Allier River towards east due either to the increase in the residence time or a mixing with groundwater coming from the aquifer's borders. Stable isotopes of the water molecule show the same results: boreholes close to the river bank are recharged by the Allier River (depleted values), while boreholes far from the river exhibit isotopic contents close to the values of hills' spring or to the southern part of the alluvial aquifer, both recharged by local precipitation. One borehole (B65) does not follow this scheme of functioning and presents values attesting of a probable sealing of the Allier River banks. Based on these results, the contribution of each end-member has been calculated and the functioning of the alluvial system determined.

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1. Introduction

The Allier River (French Massif Central) is one of the main tributary of the Loire River nowadays considered as "the last wild river in the western Europe" owing to the relative absence of large dams and the consequent semi-natural condition of the river, notably in its upper reaches. For these reasons, the European Program "Plan Loire Grandeur Nature" has been settled in 1994 with the aims of ensuring the security of Loire valley's residents in case of floods, responding to the needs of water supply and protecting and restoring the river's biodiversity. This study is a part of the third phase of the Plan Loire (2007–2013) and is dedicated to the characterization

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of the alluvial aquifer of the Allier River considering its fundamental ecological and socio-economical role in the Auvergne region.

In fact, due to their permeable nature, alluvial aquifers play a fundamental role by supplying large quantities of water for drinking, industrial, and agricultural purposes in many countries (Doussan et al., 1997; Guo and Wang, 2004; Chkirbene et al., 2009; Lorite-Herrera and Jimenez-Espinosa, 2008). Alluvial aquifers have a fundamental ecological significance for they sustain various aquatic and terrestrial ecosystems of high patrimonial values and an economic role bound to the presence of easily irrigable fertile zones and to the production of industrial or drinkable water in advantageous costs. Therefore, they contribute to give these systems a pre-eminent place in the socio-economical management of an area (Klove et al., 2011). In the hydrogeology of the alluvial aquifer, what is determining is not only the extension of the alluvium formations but also the relationships that these can maintain with the surroundings aquifers, the substratum and the connected surface waters. Three models of functioning of alluvial aquifers can be proposed according to their geological context: (1) either the aquifer behaves as a drain which collects and leads to the superficial water network flow stemming from neighbouring aquifers, (2) or as a very permeable environment connected to the river which recharges the aquifer with the water coming from the upstream part of the basin (3) or as a combination of both models, each playing a variable role according to the location of the investigated well with regard to both limits (Huggenberger et al., 1998). The existence of these flows of diverse origins is translated, in open limits of the alluvial systems, by waters of different chemical composition.

Groundwater chemistry of alluvial aquifers depends on natural factors such as leaching and soil–rock–water interactions (Scheytt, 1997; Stigter et al., 1998), hydrodynamical characteristics of the aquifer, quality of recharge water and interaction with surface water or neighbouring aquifers (Stallard and Edmond, 1983). Moreover, anthropogenic activities such as industrial processes, agricultural practices and the development of population (Kelly, 1997; Stigter et al., 1998; Kraft et al., 1999; Böhlke, 2002) can alter these fragile systems, either by polluting them or by modifying the hydrological cycle to such an extent that the use of groundwater becomes limited.

The study site is the main water catchment of Clermont-Ferrand, the biggest town of the Auvergne region, and provides drinking water for around 100,000 inhabitants. Land occupations with agricultural activities and population centres extend from year to year. Consequently, there is a critical need to increase the knowledge of the system from quantitative, hydrodynamic and qualitative perspectives to sustain the groundwater resource, as also required by the Water Framework Directive (European Parliament, 2000) and the Groundwater directive (European Parliament, 2006). The purpose of this study is to improve ecological and socio-economical water management not only at the site scale but also at the whole scale of the Allier watershed. In this context, hydrochemical and isotopic methods were used to identify the sources, types and quantities of various components of groundwater and to describe their spatial and temporal variations.

2. Study area sittings

2.1. General settings and geology of Allier basin

This study was performed in the Quaternary shallow alluvial aquifer of the Allier River, located in the Allier basin covering a surface of 14,310 km^2 (Fig. 1). The climate of the Allier basin is subjected to high spatial variability due to altitude variations from

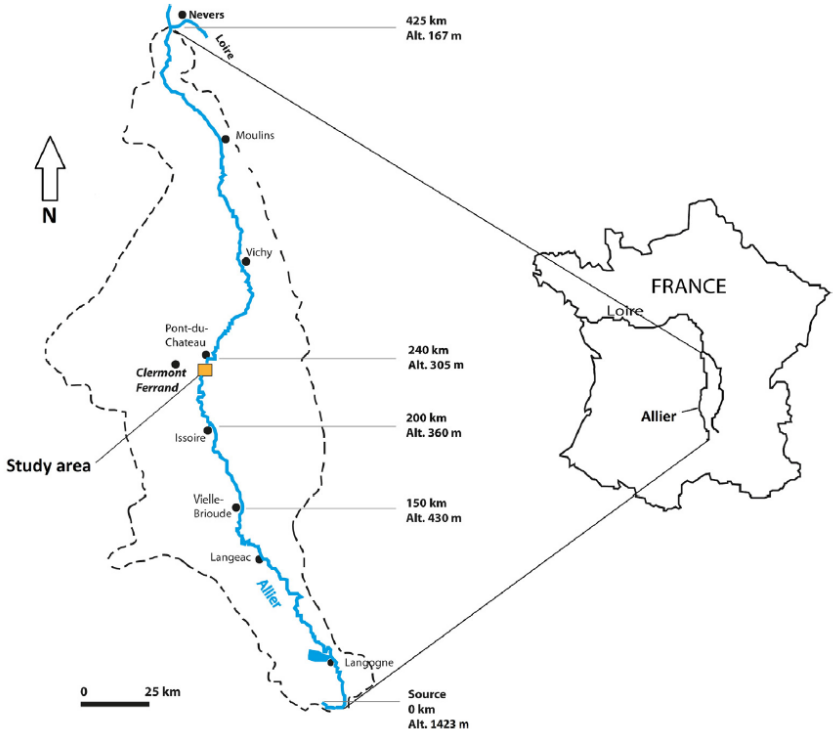

Fig. 1. The Allier River basin and the study area location.

167 to 1423 m.a.s.l. with a mean altitude of 900 m.a.s.l. and to the mixed influences of oceanic, continental climate as well as Mediterranean incomes in the southern part (Bertrand et al., 2008; Négrel and Roy, 1998). Rainfall is often different from location to another, such as in the mountainous area (upstream of study area); the maximum values are reached in winter and late spring (about 2000 mm), and the minimum ones in the summer (about 570 mm). Allier basin receives on average 800 mm of rain annually, with an average annual temperature comprised between 5 and 6 °C in the higher altitudes of the basin and 11.7 °C in the lower altitudes (Bertrand et al., 2010, 2013). The Allier River, the main tributary of the Loire River, originates in the Massif Central (La Maure de Gardille, 1423 m.a.s.l.) and flows roughly from South toward North with a total length of 410 km long; it joints the Loire River at the Bec d'Allier, near Nevers.

Geologically, the Allier River basin occupies the Limagne rift valley, an elongated tectonic depression in the Hercynian crystalline Massif Central, France (Dèzes et al., 2004). The drainage basin is underlined by Hercynian crystalline basement rocks (58%), with Cenozoic volcanic rocks (22%) mainly along the margins of the rift valley and partly calcareous Oligocene fluvio-lacustrine sediments (20%) as a rift valley fill (Korobova et al., 1997). Strong uplift of the Massif Central from the beginning of the Quaternary onwards (Dèzes et al., 2004; Ziegler and Dèzes, 2005) has forced the Allier to incise deeply into the underlying bedrock, thus forming many terraces. Furthermore, there was on-going volcanism in the uplifted rim west of the rift valley. The Allier terrace deposits are gravelly and sandy sediments poor in clay and encompassing silicate components of granitic-gneissic and basaltic origins from Massif Central, reflecting the different lithologies within the Allier basin. However, this composition is not linearly correlated with basin lithology, the volcanic components usually predominate while the Oligocene rocks are usually rare (Veldkamp and Feijtel, 1992). Common heavy minerals of the Allier terraces are augite, green and brown hornblende, olivine, mica and opaques (Van Dorsser, 1969; Rudel, 1963; Pelletier, 1971; Pastre, 1986; Tourenq, 1986). The opaque component, which can comprise more than 50% of the fine sand fraction, is predominantly composed of basaltic rock fragments. The sediment composition has known many changes in time due to incision of the Allier, glaciations of the higher parts in the basin and volcanic eruptions (Kroonenberg et al., 1988). The ancient alluvial deposits of Allier are distinguished from recent alluvial deposits. The former (Early Pleistocene) are thin, about several meters, and are consisting of quartz, sand and little clay whereas the latter alluvium is composed of sand, gravel and rocks covered with layer of silt. These alluvial deposits are mainly located over the marly calcareous deposits of the Limagne or directly on the crystalline basement (Dadet et al., 1979). The alluvial layer is 6–15 m thick (10 m on average) and their scope ranges from a few meters to several kilometres on each side of the river.

The total alluvial aquifers represent about 6% of the Allier basin, and then the total estimated volume of water contained in this alluvial layer is about 2 billion cubic meters (Livet et al., 2006). The basin's alluvial plain is used primarily for animal husbandry and agriculture (maize and cereal) which occupies about 71% of land cover of the basin, forest and grassland come next with 24% and urbanization with only 5%. The alluvial aquifer is unconfined and is in direct contact with surface water so it can be affected by surface recharge and discharge.

2.2. Settings of the sampling site

The study site is located about 20 km from the east of the city Clermont-Ferrand, France (Fig. 1). The climate of the study area is quite clement with fairly hot summer that temperatures climb to 27 °C in July and August and cold winter, temperatures of just below 0 °C in December and January. The study area has an average rainfall of 570.9 mm which is one of the lowest rates in France. Most of the rainfall falls between May and September.

Regarding to the geology (Fig. 2), the study site is in accordance with the lithology previously described with a succession of Quaternary alluvial deposits overlying Oligocene terrains consisting in marl, clay and limestone. The alluvial sediments are surrounded by hills constituted of Oligocene sediments or volcano-sediments (peperite) and Miocene volcanic formations. These terrains are characterised by high permeability and supply many springs generally located at hill foot.

Due to its importance as a fundamental source for the drinking water supply, the study area is protected and fenced. The site is active since the 1930s and accounts nowadays 71 boreholes distributed on a total surface of 2 km^2 (Fig. 3), most of them being located in the riverbanks of the Allier River. These boreholes allowed obtaining a general overview about the hydrogeological settings of the area. Water table is shallow with a depth varying from 2 to 4 m. Alluviums have a permeability ranging from 10^{-3} to 10^{-4} m/s and an efficient porosity of 8–10% (Frémion, 1995, 2007). From hydrodynamical point of view, groundwater–surface water interactions are supposed to be important along the Allier River, mainly because the river discharge and the piezometric variations are buffered in regards to the local high climate variability (Livet et al., 2006). According the water circulation/recharge and pumping, four end-members can be hypothesized: Allier River which is supposed to be the main source, surrounding hills groundwater, the southern part of the alluvial aquifer (characterised by a large non-pumping zone), and direct local recharge by effective rainfall.

3. Sampling and analytical methods

75 points (70 pumping boreholes, 3 piezometers including P13, (Fig. 3) in the no-pumping southern part of the alluvial aquifer, 1 spring emerging from the surrounding hills, and the aquifer-connected river) were sampled during two intensive field campaigns, in December 2010 (low flow conditions) and June 2012 (high flow conditions). Among these 75 points, 18 were selected for a temporal monitoring and have been sampled bi-weekly from February 2011 to August 2012 for physico-chemical and isotopic analysis. A total of 841 water samples were collected during the study period (including 684 groundwater samples from boreholes, 80 water samples from piezometers, 38 water samples from spring, and 39 Allier River water samples). In order to characterize the local recharge, 42 rainfall samples were collected weekly within the study area, during the same period, by a 614 cm^2 pluviocollector with automatic aperture (Eigenbrodt Automatic Precipitation Sampler NSA 181). By using narrow diameter submersible pump, water samples were collected in clean polyethylene bottles for major ions measurements (Ca^{2+}, Mg^{2+}, Na^+, and K^+, HCO_3^-, Cl^-, NO_3^- and SO_4^{2-}) and for silica (H_4SiO_4), and 20 mL glass bottles with poly-sealed lids for water isotopes. Sampling bottles, at the time of sampling, were thoroughly rinsed 2 times using the water to be sampled. In situ measurements including EC, pH and temperature were achieved by using a WTW Multi 3420 set C. The discharges of the springs were measured through a volumetric gauging method with a 1-L container and a chronometer. Water level of each borehole and piezometer were recorded by water-level dipper. All collected samples were transported in ice-boxes to the municipal laboratory of Clermont-Ferrand for major elements analysis.

Major cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) were analysed using mass spectrometer ICP-MS-7700, major anions (Cl^-, NO_3^- and SO_4^{2-}) were analysed using ion chromatography ICS-1000, and H_4SiO_4 was analysed by spectrophotometry. HCO_3^- was determined

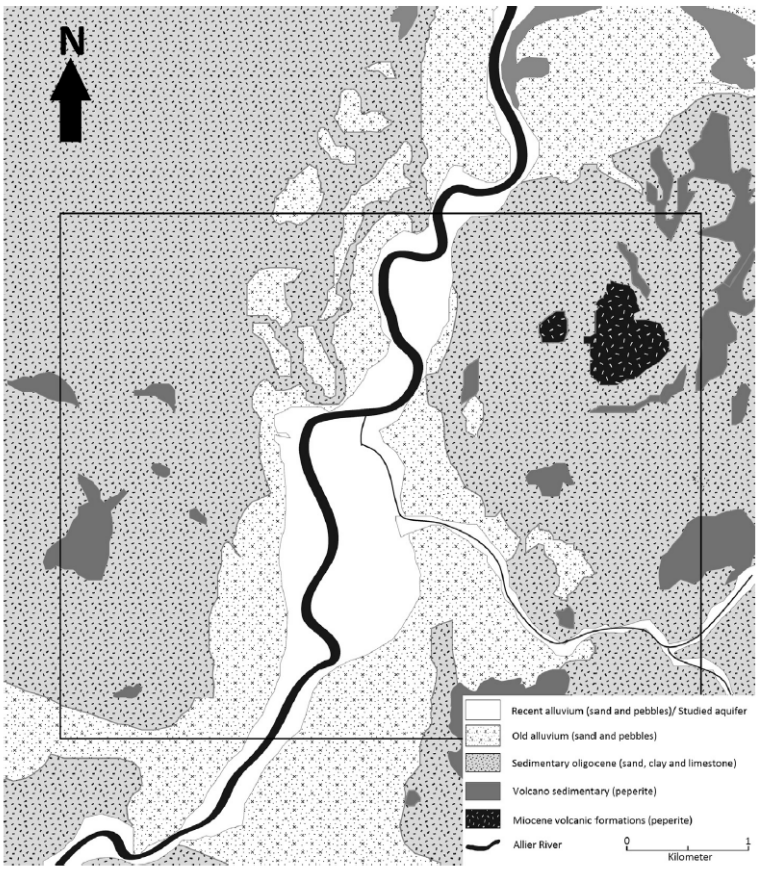

Fig. 2. Geological settings of the study site.

by titration with H_2SO_4. These analyses were run immediately after sampling. The quantification limits for was 0.1 mg/l for major cations, 1 mg/l for major anions and 0.1 mg/l for H_4SiO_4.

Isotopic analysis were performed in the Hydrogeology Department of the University of Corsica (CNRS UMR 6134 SPE), and both stable isotopes of the water molecule were characterized using a liquid-water stable isotope analyser DLT-100 (Los Gatos Research) according to the analytical scheme recommended by the IAEA (Aggarwal et al., 2009; Penna et al., 2010). The accuracy was 1‰ for δ^2H and up to 0.1‰ for $\delta^{18}O$. The isotopic data is reported in the standard delta notation in part per thousand relative to Vienna Standard Mean Ocean Water (Clark and Fritz, 1997).

4. Results and discussion

The minimum, maximum, average and standard deviation of physico-chemical, chemical and isotopic data of the 18 points used for the temporal monitoring of the system are summarized in Table 1.

4.1. End-member characteristics

Taking into account the circulations of water in alluvial system, the chemical composition of groundwater is influenced by four potential end-members: Allier River, hills located in the east side, southern non-pumped alluvial aquifer, and local precipitation. Direct recharge from Allier River is the main source of groundwater in the pumping area. The river flow rate is described through three different periods (Fig. 4a): (1) low flow rate of around 9.6 $m^3 s^{-1}$, during the two or three warmest months in the summer, (2) high flow in winter with flood impulses that can reach 377.6 $m^3 s^{-1}$, and (3) high flow in spring (176 $m^3 s^{-1}$) that corresponds to snow melting in the higher part in the basin; the average flow rate is of 40.4 $m^3 s^{-1}$. The electrical conductivity of the Allier River is generally low (mean for the sampling period = 183 µS/cm) and do not present any significant seasonal variation (Fig. 4d). However, a significant negative correlation between flow rate and electrical conductivity observed in Allier River (Fig. 4a and d). As a surface water, seasonal variation of temperature has been detected (Fig. 4c) with values that vary from 0 °C (14/2/2012) to 21.2 °C (14/8/2011). The Allier River's water type is Ca–Na–Mg/HCO_3–Cl (Fig. 5) in accordance with the leaching of the water catchment's basement mainly constituted of granitic and gneissic rocks. One exception concerns the 7/11/2011 analysis characterized by a Ca–Na–Mg/Cl–HCO_3 facies. This particular water has been during a flood event and then corresponds to major dilution effect with an electrical conductivity of 79 µS/cm; the change in water facies could be explained by the low concentration in ions.

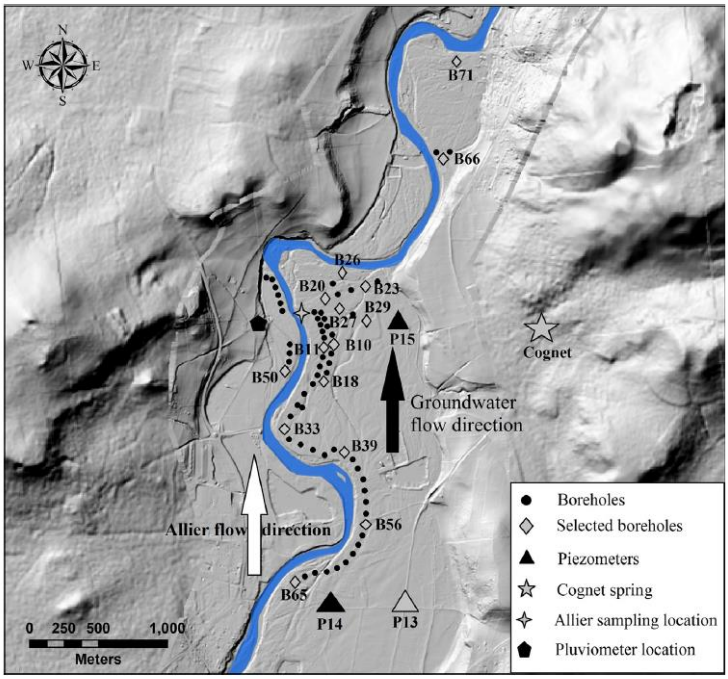

Fig. 3. Locations of sampling points.

Water coming from the hills constitutes the natural recharge origin of the alluvial groundwater. This source is represented by Cognet spring which shows a high EC varying from 818 to 1061 µS/cm (Fig. 4d). This sampled point is also characterised by high content of nitrate, sulphate and potassium with a mean concentrations of 49.6, 36.7 and 17.9 mg/l, respectively. These ions are primarily anthropogenic and mainly from agricultural sources, since the hills are extensively using for agricultural practises. The temperature varies seasonally from 9.6 to 14.8 °C but in lesser degree compare to Allier (Fig. 4c). The flow rate of Cognet demonstrates a continuous decrease in 2011 and starts to increase in the beginning of 2012 till the end of July. No correlation is observed between Cognet spring's flow rate and precipitation height, highlighting possible extractions of groundwater that, for agricultural or individual supplies within Cognet's basin up the spring (Fig. 4b). The dominating water type for Cognet is Ca–Mg/HCO_3 (Fig. 5) correlated with the circulation within Oligocene sediments.

The southern alluvial aquifer (non-pumped area) also accounts in the recharge of the alluvial system. This part is represented by piezometer P13 and has the highest EC recorded within the site, during the sampling period, that reaches 1541 µS/cm, what might likely be due to the slow circulation of groundwater in this non-pumping area (mean EC = 1194 µS/cm). Except for the measurement of 28/02/2011, the EC values are stable and do not show any seasonal variations (Fig. 4d). Furthermore, it contains very significant amounts of [NO_3^-] and [SO_4^{2-}] with mean concentrations of 38.1 mg/l and 117.5 mg/l respectively showing anthropogenic influence from agriculture. Temperature changed seasonally in this piezometer similarly to Cognet (Fig. 4c), nevertheless, no seasonal evolution is detected in piezometric level that remains unchanged during the study period, since it is located in the no-pumping zone (Fig. 4b). This point is featured by Ca–Mg/HCO_3 water types (Fig. 5).

Lastly, local precipitation is a natural source of recharge but contains very low amounts of ions. Minimum and maximum values of each chemical parameter of rainfall (Table 1) highlight the high variability of the chemical composition and mineralization of rainwater. Bertrand et al. (2008) and Négrel and Roy (1998) found similar values at Opme station (15 km to the West from our study location) and Sainte-Marguerite (9 km to the South from our site), respectively, and argue that this variability can either be due to the rain amount (Hicks and Shannon, 1979) or to diversity in the origins of air masses (Celle-Jeanton et al., 2009). Concentrations supplied by rainfall to groundwater can be calculated by using the following equation (Appelo and Postma, 1993):

$$\text{Concentration factor} = (P/Peff) * WM_{ion} \quad (1)$$

where P is the total volume of annual precipitation, Peff refers to the efficient rainfall (Peff = the total volume of annual precipitation – total annual evapotranspiration) and WM is the volume-weighted mean of each ionic concentration for the period of measurements. The calculations give the major ion concentrations of the local recharge by rainfall (HCO_3^- = 17.8 mg/l, Cl– = 4.8 mg/l, NO_3^- = 3.5 mg/l, SO_4^{2-} = 1.1 mg/l, Ca^+ = 1.2 mg/l, Mg^{2+} = 0.1 mg/l, Na^+ = 0.4 mg/l, K^+ = 0.1 mg/l, values are volume-weighted means).

4.2. Geochemical characteristics of alluvial groundwater

Groundwater from the 71 boreholes sampled during the study present a Ca/HCO_3 facies due to both lithology and the dissolution ability of the minerals' ions; this type is recognize in many alluvial systems around the world (in Europe: e.g. Andrade and Stigter, 2011, in Asia: e.g. Chkirbene et al., 2009). Based on secondary cations, this water type evolves from Ca–Na–Mg/HCO_3–Cl, Ca–Mg–Na/HCO_3–Cl recorded in the closest boreholes from the riverbanks to Ca–Mg/HCO_3 for the boreholes located in the eastern part of the

Table 1
Physico-chemical measurements, major ions concentrations (mg/l), oxygen-18 and deuterium data (‰ VSMOW).

Sample ID		T (°C)	pH	EC (µS/cm)	H_2SiO_4	HCO_3	Cl	NO_3	SO_4	Ca	Mg	Na	K	δ^2H (‰)	$\delta^{18}O$ (‰)
Rainfall	Min		5.6	3.1		2	<1	<1	<1	<1	<1	<1	<1	−133.6	−17.5
	Max		8.5	32		43	4	7.5	2.4	3.1	0.3	1.7	0.8	−8.2	−1.9
	Av		7.1	14.1		7.6	0.4	1.6	0.5	0.6	0.1	0.3	0.1	−47.2	−6.3
	V-WM		6.6	11.1		7.0	0.09	1.3	0.4	0.5	0.03	0.13	0.04	−46.3	−6.4
	SD		0.6	7.5		8.7	0.9	1.6	0.7	0.7	0.1	0.4	0.2	26.1	3.4
Allier	Min	2.5	7.1	79	6.2	24	6.7	2.5	4.5	6.2	2.2	5.6	1.7	−65.7	−9.4
	Max	21.2	7.9	350	16.3	98	20.8	6.9	10.4	20.3	6.8	17.9	6.2	−49.5	−7.0
	Av	13.4	7.5	183	11.6	68.9	15.2	4.6	8.1	14.3	5	12.5	3.4	−55.4	−8.1
	SD	5.9	0.2	48.2	2.6	16	3.8	1	1.4	3.2	0.9	3	0.8	3.4	0.6
	Min	9.6	6.9	818	19.9	421	29.6	38.3	31.7	102.8	32.3	14.1	14.5	−51.0	−7.5
Cognet	Max	14.8	7.7	1061	47.7	521	50.2	55	41.9	148.4	41.8	19.6	22.9	−49.0	−6.7
	Av	12.9	7.3	951.3	38.8	484.5	35.3	49.6	36.7	123.5	38.1	15.8	17.9	−50.3	−7.0
	SD	1.2	0.2	53.1	5.3	23.2	5.4	4.1	2.3	9.9	1.8	1	1.6	0.5	0.2
	Min	9.1	6.6	1099	21	489	57.2	29.4	91.8	129.3	48.9	28.6	9.3	−48.8	−6.8
P13	Max	14.7	7.3	1541	42.4	554	109	51.2	143.8	168.9	58.5	44.1	14.3	−44.6	−5.8
	Av	12.2	7.1	1192	31.1	513.7	68.4	38.2	117.5	142.4	52.5	34.1	10.9	−46.6	−6.2
	SD	1.4	0.1	77.2	3.8	13.1	9.2	5.8	12.8	8.2	2.3	3.8	1.2	1.0	0.3
	Min	9	6.8	221	7.7	90	15.7	4.3	10.1	21.7	7.2	11.9	2.6	−56.4	−8.6
B10	Max	14.6	7.3	509	22.6	203	29.5	20.7	46.3	56	18	20.1	6	−51.1	−7.1
	Av	12.4	7.1	358.2	19.3	147.6	21.1	10.5	24.1	35.5	12	16	4.3	−54.1	−7.9
	SD	1.4	0.1	85.6	2.6	31.1	4.4	5.8	11	10	3.3	2.1	0.9	1.4	0.4
	Min	8.5	6.8	152	4.4	59	10.4	2	6.4	11.4	3.9	8.9	2.1	−59.4	−8.9
B11	Max	16.7	7.5	271	21.2	96	20.3	7.3	9.7	20.7	6.1	15.4	5	−50.0	−7.1
	Av	12	7.1	195.3	14.6	75.9	14.5	4.4	8	15.9	5.1	11.6	3	−55.6	−8.2
	SD	2.2	0.1	25.9	2.7	11.5	2.7	1.4	0.8	2.7	0.6	1.5	0.7	2.7	0.5
	Min	9.6	6.9	203	7.2	87	13.3	<1	6.5	18.9	5.2	9.8	2.3	−58.1	−8.7
B18	Max	15.9	7.3	244	22	116	16.7	3.2	8.1	25.8	6.5	13.9	3.7	−54.1	−7.8
	Av	12.7	7.1	221.9	17.9	99.7	14.8	1.1	7.2	21.2	5.9	12.1	2.9	−56.0	−8.3
	SD	1.3	0.1	7.7	3.2	4.9	1	0.7	0.4	1.6	0.3	0.8	0.4	1.0	0.2
	Min	9.5	6.9	188	7.7	76	11.3	1.6	7.2	15.3	4.6	8.9	2.3	−59.1	−8.8
B20	Max	14.5	7.3	251	20	107	19.4	5.3	9.9	22.5	7.1	14.4	4.2	−50.8	−7.3
	Av	12.2	7.1	210.4	16.5	87	15	3.7	8.7	18.8	5.7	11.9	3.1	−55.8	−8.2
	SD	1.2	0.1	18.4	2.3	8.8	2.3	1.2	0.6	2	0.6	1.2	0.5	2.3	0.4
	Min	9.8	6.8	384	6.8	189	18.5	7.5	22.7	36.2	15.6	15	6.1	−52.4	−7.8
B23	Max	15.1	7.5	1001	37.5	526	42	26.2	91.4	130.7	51.2	31.4	13.6	−45.1	−5.2
	Av	12.6	7.3	830.3	21.7	400.6	33	18.9	62.4	90	37	24.6	10	−49.6	−7.0
	SD	1.4	0.1	162.9	5.8	103.1	6.1	4.3	16.1	24.9	9.7	3.4	1.6	2.0	0.5
	Min	6.6	6.9	154	4.2	63	9.8	<1	6.1	12.5	3.8	9	1.1	−60.5	−9.0
B26	Max	19.5	7.7	250	20.5	104	21.2	7.2	11.5	25.5	7.2	16.3	4.7	−50.0	−7.0
	Av	12.3	7.3	205.2	14.3	83.4	15.2	4.2	8.5	18.5	5.3	12	2.9	−55.8	−8.2
	SD	4.4	0.2	25.4	3.1	11.6	3.4	1.8	1.2	3	0.7	1.9	0.8	3.0	0.5
	Min	9.3	7	265	9	117	14.4	5.4	12	25.4	8.5	13.3	2.9	−55.5	−8.3
B27	Max	14.6	7.3	682	21.8	292	38.3	19.6	58.1	75.2	26.5	28.6	7.7	−47.5	−6.3
	Av	12.7	7.2	459	18.3	197.6	25.1	12.5	34.9	47.7	16.5	19.1	4.7	−51.5	−7.4
	SD	1.3	0.1	119.6	2.9	48.1	6.8	5.5	14.8	14.9	5	3.5	1.1	2.1	0.5
	Min	9.2	6.9	912	10.1	451	42.5	12.8	69	76.2	44.9	30.2	9.4	−47.1	−6.3
B29	Max	15.6	7.5	1005	35.8	503	54.5	26.2	83.7	117.3	64.3	58.1	18.5	−42.5	−5.6
	Av	13.1	7.3	972.8	22.7	474	48.7	21.1	76.3	96.8	49.9	37.8	11.5	−45.2	−6.0
	SD	1.5	0.1	19.2	4.3	11.8	2.3	2.6	3.7	6.2	3.3	4.5	1.6	1.1	0.2
	Min	6.2	6.8	155	5.4	61	9.2	1.6	6.4	11.5	4.1	10.1	2	−58.7	−8.9
B33	Max	19.4	7.6	242	24.7	90	21.2	6.8	11	19	6.3	17.5	5.2	−50.1	−7.0
	Av	12.4	7.1	193.1	14.5	74.2	14.8	4.7	8.2	15.3	5.2	12.4	3.2	−55.3	−8.1
	SD	4.3	0.2	24.6	2.8	9.2	3.5	1.4	1.1	2	0.5	2	0.8	2.6	0.5
	Min	9.8	6.9	181	6.3	73	10.7	<1	4.9	13.9	4.5	8.9	2.2	−59.0	−8.8
B39	Max	16	7.8	252	21.9	116	19.9	3.7	7.9	25	7.2	14.9	4.8	−49.7	−7.2
	Av	12	7.3	205.1	17.2	89.4	14.5	0.9	6.4	17.2	5.8	11.8	3.3	−55.4	−8.3
	SD	1.9	0.2	21.8	3.2	11.4	2.4	0.7	0.8	2.5	0.7	1.5	0.6	2.8	0.5
	Min	8.1	6.8	179	6.6	72	10	3.7	7.8	17.3	4.9	8.8	2.5	−59.8	−8.9
B50	Max	18.3	7.4	808	22.2	345	43.1	35.4	62	68.9	35.7	38.1	16.3	−50.1	−6.9
	Av	13.1	7.2	377.3	16.4	158.5	22.7	12.8	23.1	37.3	11.9	18.1	5.5	−54.5	−8.0
	SD	3	0.1	142.6	2.8	63.4	8.5	6.8	12.4	14.4	6.3	5.9	2.8	2.5	0.5
	Min	7.4	6.7	159	9.5	68	9.4	1.5	7.1	14	4.7	9.2	2.5	−58.7	−8.7
B56	Max	15.1	7.6	552	21.9	233	30.2	21	36.9	57	22.3	18.7	6.9	−48.7	−7.2
	Av	11.4	7.1	310.5	17.8	131.4	18.5	7.3	17.3	29.9	10.8	13.3	4.3	−53.8	−7.9
	SD	1.9	0.2	98	2.6	42.6	5.2	4.8	8.9	11.3	4.4	2.4	1	2.0	0.4
	Min	10.4	6.8	338	8.8	161	15.8	<1	19.7	33.7	12.8	15	3.5	−44.1	−5.9
B65	Max	14.6	7.4	467	24.5	227	24.4	10.1	31.2	53.4	18.5	21.6	7	−29.3	−2.4

Table 1 (*continued*)

Sample ID		T (°C)	pH	EC (µS/cm)	H_2SiO_4	HCO_3	Cl	NO_3	SO_4	Ca	Mg	Na	K	δ^2H (‰)	$\delta^{18}O$ (‰)
	Av	12.8	7.1	425.7	19.8	200.2	21.5	1.9	26.5	42.2	15.1	19	5	−35.3	−3.9
	SD	1.1	0.1	31.4	3.5	17.2	2	2	2.6	4.2	1.2	1.5	0.8	4.2	1.0
	Min	8.8	6.9	224	5.1	98	11.9	<1	5.4	20.2	6.2	10.6	2.2	−57.6	−8.6
B66	Max	19.3	7.5	351	21	154	22.6	9.2	17.2	33.5	12.9	25.3	6.4	−49.9	−7.1
	Av	13.1	7.2	260.9	16.4	116.4	16.4	3.7	10.4	24.9	8.1	13.8	3.5	−54.6	−8.0
	SD	3.1	0.1	35	2.6	15.7	2.6	2.9	3	3.7	1.9	2.5	0.9	2.2	0.4
	Min	8.4	6.9	240	6.7	106	14.9	<1	8.7	22.8	7	10.1	2	−57.0	−8.4
B71	Max	14.3	7.5	422	24.8	185	26.6	14.6	37.5	46.1	17.8	17.3	6.4	−49.8	−7.0
	Av	12	7.2	289.6	19.6	128	17.3	4.7	13.4	29	8.9	13.8	3.2	−54.5	−8.0
	SD	1.6	0.1	57.1	3	23.6	2.8	3.4	7.2	6.6	3	1.6	1	1.8	0.4

T: temperature, EC: electrical conductivity, Min: minimum, Max: maximum, Av: arithmetic average, SD: standard deviation, V-WM: volume-weighted mean for precipitation.

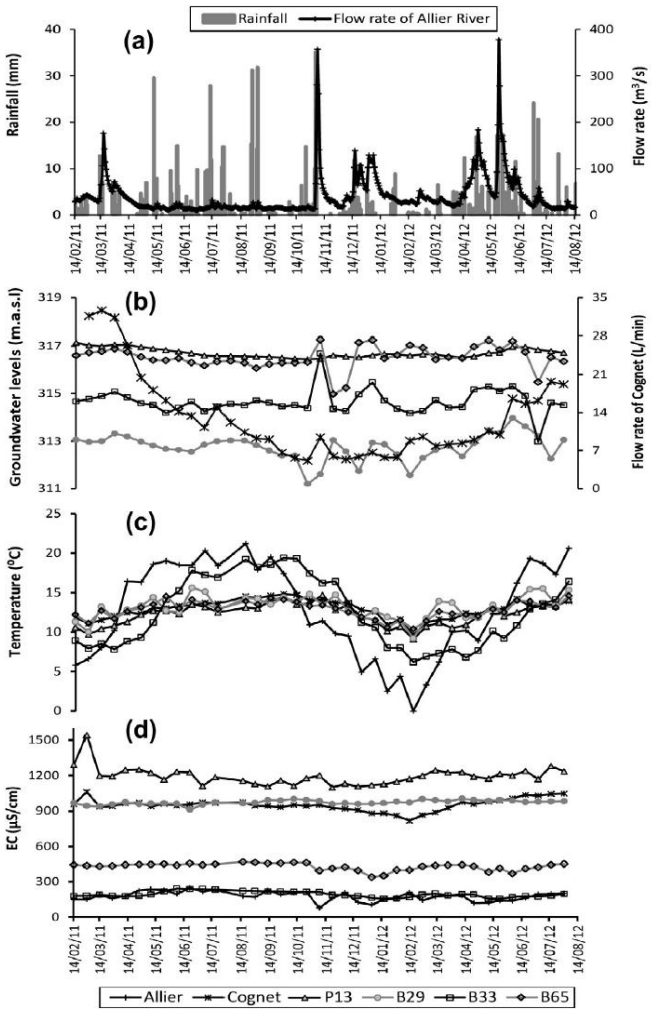

Fig. 4. Relation of (a) precipitation and Allier River flow, (b) groundwater level and Cognet spring flow, (c) temperature, and (d) electrical conductivity of selected points during study period.

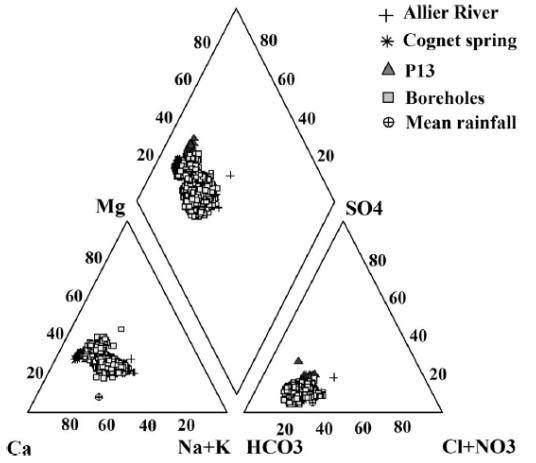

Fig. 5. Piper diagrams illustrating the chemical water types of the 18 points selected for the temporal following.

site (Fig. 5). The pH varies from 6.69 to 7.78, these values fall within natural water pH usually ranging between 6.5 and 9.5. Electrical conductivity (EC) values measured during the 2 intensive campaigns, carried out in December 2010 (low flow conditions) and June 2012 (high flow conditions), show a great spatial variation in boreholes and vary from 151 to 1005 µS/cm from the Allier River's banks to the hills' foot; values acquired in spring are lower due to the high flow period (Fig. 6). These punctual observations are completed by the following time sampling: mean ECs of the 15 boreholes sampled every 15 days show the same evolution (Fig. 7).

Variations in temperature and water level of the 15 boreholes confirm this eastward evolution. Fig. 4a–d presents the water level, temperature and EC evolutions for the four end-members and a selection of 3 boreholes: B33 close to Allier River, B29 close to hills' foot and B65, the most southern borehole. The temperature recorded in B33 shows a clear seasonal evolution, a little bit attenuated (temperature ranges between 6.2 and 19.4 °C) and with a small delay compare to Allier River. These modifications, compared to the evolution of Allier River parameters, are greater for B29 where temperature varies only from 9.2 to 15.6 °C. B29, B65, P13 and Cognet spring present the same evolution of temperature, highlighting an attenuation of air temperature variation. The same observation can be made for water level. B33 presents an evolution that corresponds to the one of the Allier River flow rate. B29 presents some high peaks that can be correlated to the increase in the River flow rate; however, the beginning of the curve shows a clear high water level that may be due to another factor. Concerning the electrical conductivity, values of B33 are in the same range of order than Allier and are low compare to the other points. The highest EC is the one of P13 (mean of 1192 µS/cm), for this point is located in a no-pumped zone. Allier flow rates show direct influence on the ionic concentrations of some boreholes, such as B10, B11, B23, P26, P33, B50, B56, B65, and B66, while the rest of boreholes show not affected. This correlation is shown in Fig. 4a and d for some boreholes.

These first observations, increase in EC and modifications of groundwater facies, highlight a general spatial evolution of groundwater chemistry from the Allier River to the eastern part of the study area. This could be due either by an increase in the residence time within the aquifer that results in higher EC and modification of water type, thanks to the dissolution of in-situ minerals, or a mixing with water from another origin, more concentrated and characterised by a different geochemical water type.

4.3. Stable isotope (δ^2H and $\delta^{18}O$) composition of water

In order to confirm these first hypotheses on the sources of recharge, stable isotopes of the water molecule have been used (Fontes, 1980; Gonfiantini, 1986; Nativ and Riggio, 1989; Wood and Sanford, 1995; Clark and Fritz, 1997). The relationships between δ^2H (‰ vs. SMOW) and $\delta^{18}O$ (‰ vs. SMOW) are shown in Fig. 8 for water collected from 18 sampling points. The 42 rain samples collected weekly define the local meteoric water line (LMWL: $\delta^2H = (7.7 \pm 0.2)\ \delta^{18}O + (1.7 \pm 1.1)$); the volume-weighted mean of

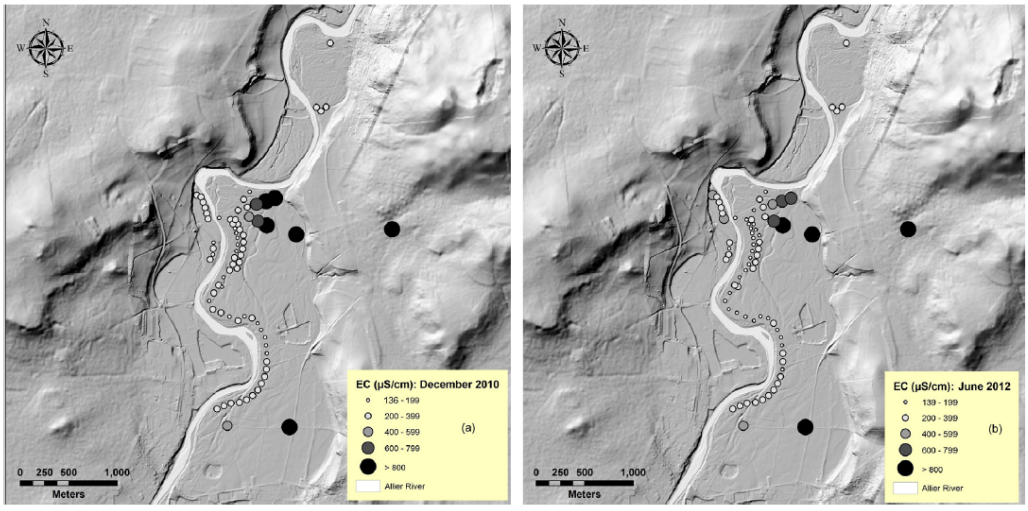

Fig. 6. Spatial distribution of electrical conductivity of 75 points during the two intensive campaigns, (a) December 2010 (low flow period) and (b) June 2012 (high flow period).

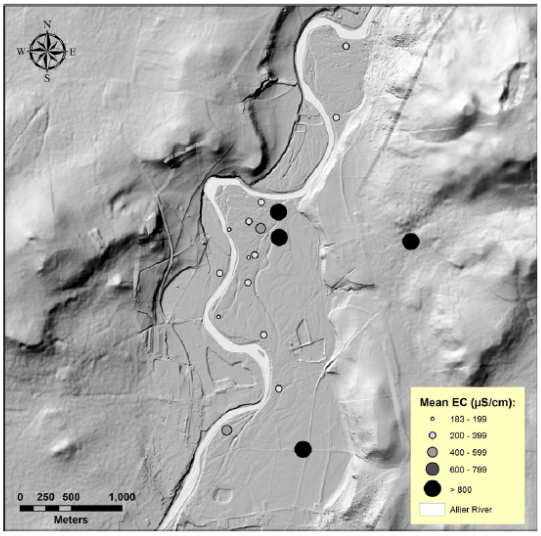

Fig. 7. Spatial distribution of the mean electrical conductivity of the 18 points selected for the temporal following. The mean value is calculated for the February-2011 to August-2012 period.

$\delta^{18}O$ and $\delta^{2}H$ for local precipitation are −6.4‰ and −46.3‰, respectively. The LMWL of the study site can be compared to the meteoric water line found in the region by by Bertrand ($\delta^{2}H = 7.9\ \delta^{18}O + 7.3$, 2009) for the Argnat Basin localized in the Chaîne des Puys (elevation = 550 m) and Gal ($\delta^{2}H = 7.8\ \delta^{18}O + 5.5$, 2005) in Saint-Just-Saint-Rambert (elevation = 420 m). Slopes are quite similar and correspond to the WMWL; difference of y-intercepts may be due to an increase of evaporation within the air column below the air masses considering that our sampling site is situated at a lower elevation. The developed LMWL is controlled by local climatic factors i.e. the origin of vapour mass, re-evaporation during rainfall and the seasonality of precipitation (Clark and Fritz, 1997) and then differs from the Global Meteoric Water Line (GMWL; $\delta^{2}H = 8\ \delta^{18}O + 10$) defined by Craig (1961). Such a difference mainly lies with a secondary evaporation during rainfall (Friedman et al., 1962) as the study site is characterised by very warm summer and generally low intensity rain events. Consistently, only 38% of the total rainfall amounts participate to the recharge (Bertrand et al., 2008).

In the 15 selected boreholes, $\delta^{18}O$ varies from −9.0‰ to −2.4‰ with an average value of −7.5‰ ($n = 560$); $\delta^{2}H$ varies between −60.5‰ and −29.3‰ with an average value of −52.4‰. The mean isotopic content of the Allier River (−8.1 $\delta^{18}O$‰ and −55.5 $\delta^{2}H$‰) which represents the input signal on the whole upstream watershed (altitude from 305 to 1423 m.a.s.l.), falls on the GMWL, in agreement with Négrel et al. (2003). P13 and Cognet spring present values close to the LMWL, testifying of a recharge of local precipitation. The isotopic signatures of most boreholes fall on, or close to the GMWL and behave similarly to Allier, demonstrating a strong interaction with the Allier River. Few boreholes (B23, B27, and B29) present more enriched values, close to the values of Cognet and P13 and drop into LMWL, indicating that these points could partly or highly be recharged by other sources than Allier River. Likewise, waters from boreholes are distributed along a line with a smaller slope than the LMWL that may indicate either evaporation or mixing trend between the two poles defined by Allier River and local recharge. This last hypothesis is consistent with the fact that the isotopic content of groundwater varies along with the distance from the two end members. In contrast to this general trend, borehole B65, harbouring the most enriched $\delta^{18}O$ and $\delta^{2}H$, (ranging from −5.9‰ to −2.4‰ and from −44.1‰ to −29.3‰, respectively), shows evidence of some additional isotopic enrichment by either stronger evaporative process or mixing with geothermal water. Indeed, the Allier basin is characterized by the availability of localized geothermal springs (Rihs et al., 2000; Bertrand et al., 2013). Measurements in carbon-13 of total dissolved inorganic carbon show that this geothermal effect cannot be implied as the values of B65 are comprised between −16.3 $\delta^{13}C$‰ and −10.3 $\delta^{13}C$‰ PDB far from the local signature of mantellic CO_2 degassed in the Chaîne des Puys (−6.6 ± 0.8 $\delta^{13}C$‰) determined by Batard et al. (1982).

From the temporal monitoring of selected points in the plain, a clear simultaneous seasonal evolution on $\delta^{18}O$ can be quoted for Allier River and B33 with a little delay in B33 peaks, highlighting this borehole is mainly supplied by the Allier River (Fig. 9). B29, Cognet spring and P13 present enriched and more stable values, demonstrating the absence of a rapid supply to the system for these points. The particular B65 point seems to be disconnected from the variations of rainfall height, but is however related to the fluctuations of the Allier River flow rate. Recorded isotopic values of B65 decrease during high flow periods and increase during low flow; this could imply a sealing of a part of the banks of the riv-

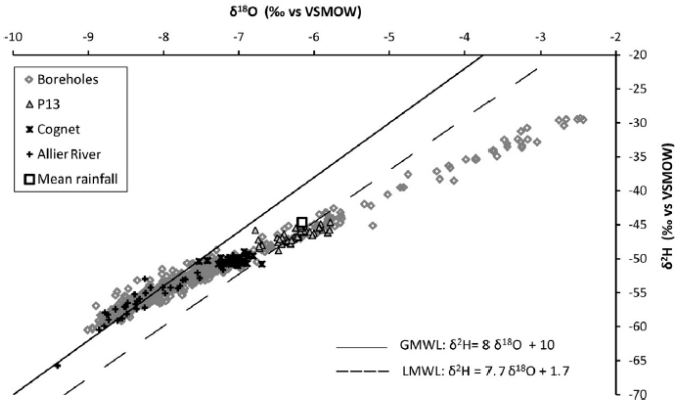

Fig. 8. $\delta^{18}O$ versus $\delta^{2}H$ (‰ vs. SMOW) in the 18 points selected for the temporal following.

er near B65. The water infiltrated from the Allier River or coming from the southern part of the aquifer evaporates during the low flow periods and is mixed with new water coming from a reconnection of the Allier River during the high flow periods. The spatial and temporal distribution of stable isotopes of $\delta^{18}O$ and $\delta^{2}H$ of the 75 sampling points during the two campaigns are shown in the Fig. 10.

The results of isotopes confirm the hypothesis formulated thanks to physico-chemical parameters, with a possible increase of the residence time of water that may lead to evaporation in such shallow aquifers (Mook, 2000) and consequently to an isotopic enrichment. A secondary supply with water isotopically enriched could also explain this hypothesis. In order to precise the geochemical processes involved along with the groundwater flow-path, the spatio-temporal evolution of mineral dissolution is discussed in the following.

4.4. Water–rock interactions

The plot of Na/Ca vs HCO_3^- for the 15 selected boreholes reflects the geology of the water basin (Fig. 11a). The Allier River that totalises the influences of the whole watershed clearly presents enrichment in $[Na^+]$ in relation with the crystalline nature of the basement. The boreholes samples present a progressive enrichment in $[Ca^{2+}]$ and $[HCO_3^-]$ between Allier River end-member and a pole represented by Cognet spring/P13. This evolution is confirmed by Fig. 11b plotting Ca + Mg vs HCO_3^-. A progressive enrichment in $[Ca^{2+}]$, $[Mg^{2+}]$ and $[HCO_3^-]$ is registered from the Allier River to the hills/southern aquifer that suggests an increase in the residence time within the aquifer and might reflect carbonate dissolution as the presence of significant proportion of carbonates in the basin has already been reported (Négrel et al., 2004). A mixing with water that circulates in carbonates is also possible as the abundance of Ca^{2+}, Mg^{2+} and Na^+ ions can be associated with minerals available in the alluvial terraces in the study area such as augite, green and brown hornblende, olivine, mica and opaque (Pelletier, 1971; Pastre, 1986; Tourenq, 1986). The presence of H_4SiO_4 in Cognet spring, boreholes, P13 and surface water suggests that crystalline rock fragments form a major component of aquifer matrix. H_4SiO_4 is present in all water samples at high concentrations but Cognet spring had the maximum concentration with a mean value of 38.8 mg/l, higher than the mean value of 17.7 mg/l in boreholes.

Thus, weathering and erosion of rocks or soil, and chemical reactions beneath the land surface control the natural composition of groundwater (Bullen et al., 1996; Kim, 2002). In this study, saturation indices (SI) of carbonate minerals (calcite and dolomite), and siliceous minerals (quartz and chalcedony) were calculated by using PHREEQC program (Parkhurst and Appelo, 2003). The summary statistics of saturation indices of some common mineral phases is presented in Table 2 and Fig. 12. All the samples are saturated with respect to quartz and/or chalcedony confirming the crystalline nature of the basin basement. Boreholes close to Allier River (e.g. B33) are undersaturated with respect to carbonate minerals indicating either that the groundwater originates from an environment where carbonate minerals are poorly available or/and due possibly to the short residence time of groundwater within this borehole, so that there is inadequate time for mineral phases to react to reach equilibrium. While, water samples from Cognet spring, P13 as well as both boreholes B23 and B29 are shown over saturated with respect to carbonate and siliceous minerals, suggesting that waters involved in their chemical composition have possibly longer residence time and consequently have dissolved more minerals.

The results show a progressive increase in the SI with respect to chalcedony and quartz from the Allier River to Cognet (B33–B10–B29) in relation with the dissolution of alluviums of crystalline origin (siliceous pebbles, sands, silts) and the volcano-sedimentary nature of the hills. This could suggest that the increase in the residence time is a major process in the chemical composition of waters. Regarding the evolution of SI with respect to dolomite and calcite, B33 and B10 are clearly undersaturated and show

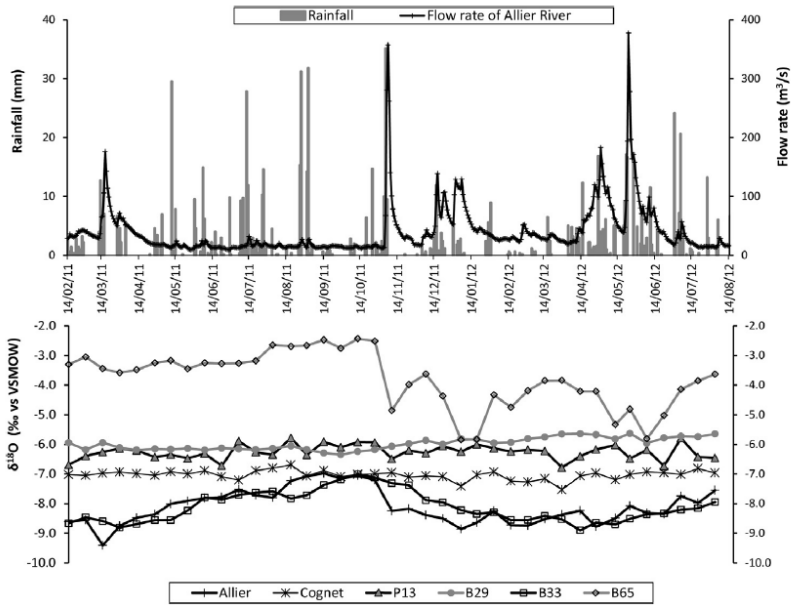

Fig. 9. Temporal variations in Allier flow rate and $\delta^{18}O$ of three boreholes (B33, B65, B29), Allier River, Cognet spring and piezometer P13.

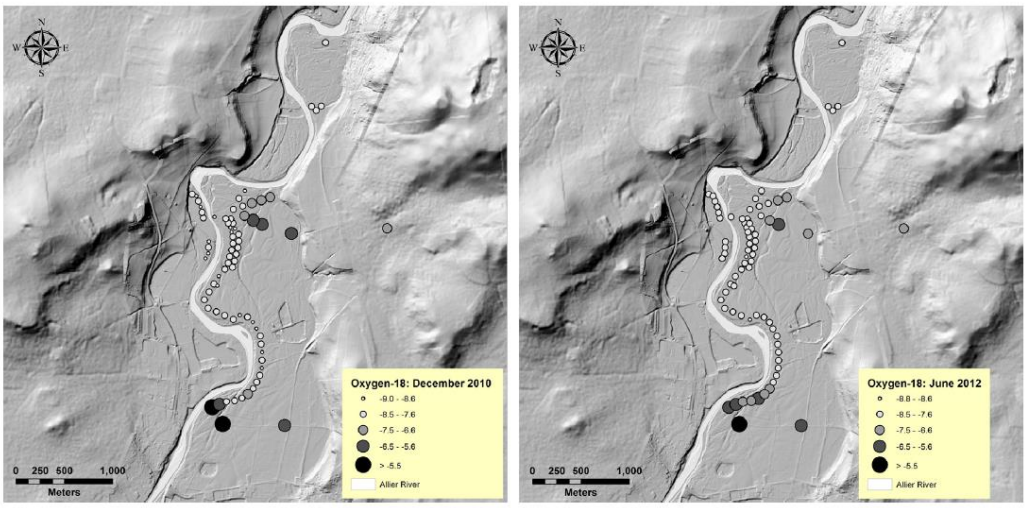

Fig. 10. Spatial distribution of $\delta^{18}O$ of 75 points during the two intensive campaigns, (a) December 2010 (low flow period) and (b) June 2012 (high flow period).

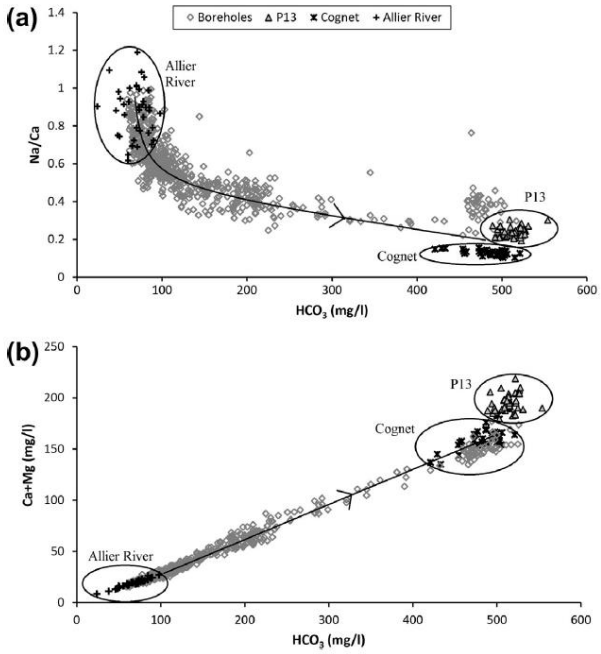

Fig. 11. (a) Na^+/Ca^{2+} vs HCO_3^- and (b) $Ca^{2+} + Mg^{2+}$ vs HCO_3^- plot.

the same variations compared to the Allier River indicating to rapid recharge by water from Allier River, since these points located very close to the Allier River. Whereas, B29 and P13 are oversaturated with carbonate minerals and present a trend similar to Cognet spring demonstrating that these points are recharged partly or mostly by water from hills rather than Allier. This implies, as previously suggested by isotopes, a mixing of the alluvial groundwater with groundwater coming from the hills or from the southern part of the alluvial aquifer.

4.5. Mixing between different sources of recharge

Chloride, nitrate and sulphate ions cannot be related to the dissolution of minerals from the bedrock. Moreover, for these 3 elements, the calculated groundwater concentrations due to rainfall (Cl^- = 4.8 mg/l, NO_3^- = 3.5 mg/l, SO_4^{2-} = 1.1 mg/l) are largely lower than the measured concentrations. These 3 elements could then be attributed to an anthropogenic origin: fertilizers can be implied for [Cl^-], [NO_3^-] and [SO_4^{2-}] in association with [K^+] (Widory et al.,

Table 2
Average values with standard deviation of saturation indices (SI) for carbonate and siliceous minerals.

Sample ID	SI calcite	SI dolomite	SI chalcedony	SI quartz
Allier	−0.9 ± 0.3	−1.9 ± 0.6	−0.2 ± 0.1	0.3 ± 0.1
Cognet	0.5 ± 0.1	0.9 ± 0.3	0.4 ± 0.1	0.8 ± 0.1
P13	0.4 ± 0.1	0.6 ± 0.3	0.3 ± 0.1	0.7 ± 0.1
B10	−0.7 ± 0.2	−1.4 ± 0.3	0.1 ± 0.1	0.5 ± 0.1
B11	−1.2 ± 0.2	−2.6 ± 0.3	−0.1 ± 0.1	0.4 ± 0.1
B18	−1.0 ± 0.1	−2.1 ± 0.2	0.0 ± 0.1	0.4 ± 0.1
B20	−1.1 ± 0.1	−2.4 ± 0.2	−0.0 ± 0.1	0.4 ± 0.1
B23	0.3 ± 0.2	0.6 ± 0.3	0.1 ± 0.1	0.5 ± 0.1
B26	−0.9 ± 0.2	−2.1 ± 0.3	−0.1 ± 0.1	0.3 ± 0.1
B27	−0.4 ± 0.2	−0.8 ± 0.4	0.3 ± 0.1	0.5 ± 0.1
B29	0.4 ± 0.1	0.8 ± 0.2	0.2 ± 0.1	0.6 ± 0.1
B33	−1.3 ± 0.1	−2.6 ± 0.3	−0.1 ± 0.1	0.4 ± 0.1
B39	−0.9 ± 0.2	−1.9 ± 0.4	0.0 ± 0.1	0.4 ± 0.1
B50	−0.6 ± 0.4	−1.3 ± 0.7	−0.0 ± 0.1	0.4 ± 0.1
B56	−0.7 ± 0.2	−1.6 ± 0.5	0.0 ± 0.1	0.5 ± 0.1
B65	−0.4 ± 0.1	−0.9 ± 0.2	0.1 ± 0.1	0.5 ± 0.1
B66	−0.7 ± 0.2	−1.5 ± 0.3	−0.0 ± 0.1	0.4 ± 0.1
B71	−0.6 ± 0.1	−1.4 ± 0.3	0.1 ± 0.1	0.5 ± 0.1

2005), waste waters for NO_3^-, and de-icing salt for $[Cl^-]$ (Meybeck, 1983; Négrel, 1999). In our study area, NO_3^- range from below detection limit (<1) in the boreholes close to Allier River up to 55 mg/l (Table 1) with an average of 15.1 mg/l, and only 5% of the water samples have a concentration of $[NO_3^-]$ higher than the drinking water standard of 50 mg/l (EEA, 2003). These contaminated waters correspond to samples taken from P13 and Cognet spring (not used for drinking purposes). Fig. 13 shows the spatial distribution of $[NO_3^-]$ measured during the two intensive campaigns achieved in December 2010 (low flow) and June 2012 (high flow). No strong difference can be quoted between the two periods emphasizing a continuous supply of nitrate within the field. It is an argument in favour of an origin in connection with residual waters. In the 15 selected boreholes, the highest $[NO_3^-]$ concentrations are recorded in the eastern and southern parts of the site. In alluvial groundwater, mean $[Cl^-]$ varies (Table 1) from 14.5 ± 2.7 mg/l (B11) to 48.7 ± 2.3 mg/l (B29) and demonstrates a general increase toward east. These values are in the range of the concentrations measured for the end-members: mean chloride content is of 15.2 ± 3.8 mg/l in the Allier River, 35.3 ± 5.4 mg/l in Cognet spring; the highest $[Cl^-]$ value 109 mg/l is recorded the 16/07/12 in piezometer P13 (mean value of 68.4 ± 9.2 mg/l). Same observations can be realised for $[SO_4^{2-}]$ generally associated with K^+. Boreholes present concentrations that vary from 6.4 ± 0.8 mg/l (B39) to 76.3 ± 3.7 mg/l (B29) and from 2.9 ± 0.8 mg/l (B26) to 11.5 ± 1.6 mg/l (B29) for $[SO_4^{2-}]$ and $[K^+]$, respectively. The end-members are characterized by concentrations of 8.1 ± 1.4 mg/l $[SO_4^{2-}]$, 3.4 ± 0.8 mg/l $[K^+]$ for Allier River, 36.7 ± 2.3 mg/l $[SO_4^{2-}]$, 17.9 ± 1.6 $[K^+]$ mg/l for Cognet spring, 117.5 ± 12.8 $[SO_4^{2-}]$ mg/l, 10.9 ± 1.2 $[K^+]$ mg/l for P13 (Fig. 14). Therefore, according to the boreholes' concentrations in $[Cl^-]$, $[SO_4^{2-}]$ and $[K^+]$ falling into the range of the ones of the determined end-members and to the independence of these parameters from the lithology, $[Cl^-]$, $[SO_4^{2-}]$ and $[K^+]$ can be used to determine the participation rate of each end-member to the chemistry of boreholes within the alluvial system.

The mathematical resolution of the 3 equations system with 3 unknown values (Jeuken, 2004) leads to the mean participation percentages of each end-member to the chemical composition of the boreholes selected for the following time investigation (Table 3). The mathematical equations can be written as:

$$X_B = F_a X_a + F_h X_h + F_{sa} X_{sa}$$

$$Y_B = F_a Y_a + F_h Y_h + F_{sa} Y_{sa}$$

$$Z_B = F_a Z_a + F_h Z_h + F_{sa} Z_{sa}$$

where X, Y, and Z are the concentrations of $[Cl^-]$, $[SO_4^{2-}]$ and $[K^+]$ respectively for each borehole (B) and end-members: Allier River (a), hills' aquifer (h) and southern aquifer (sa); F is the contribution of each end-member to the borehole's chemistry.

Based on our dataset that includes only the hills' aquifer and the southern aquifer in the right bank of the Allier River, the contribution of end-members has not been calculated for B50. The results of recharge calculations show that eight boreholes are only recharged by the Allier River (Fig. 15). In parallel, Boreholes B27, B56 and B65 are mainly supplied by the Allier River, but present a secondary

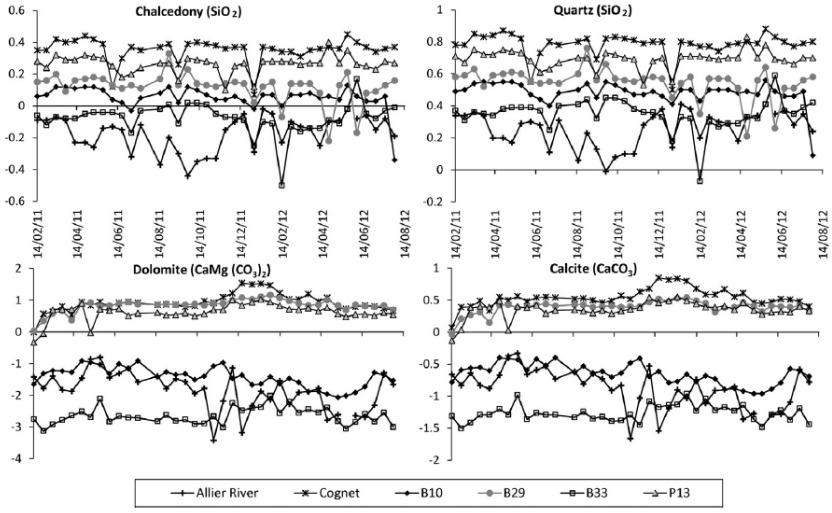

Fig. 12. Plot of saturation indexes (SI) for Allier River, Cognet spring, P13, B33, B10 and B29.

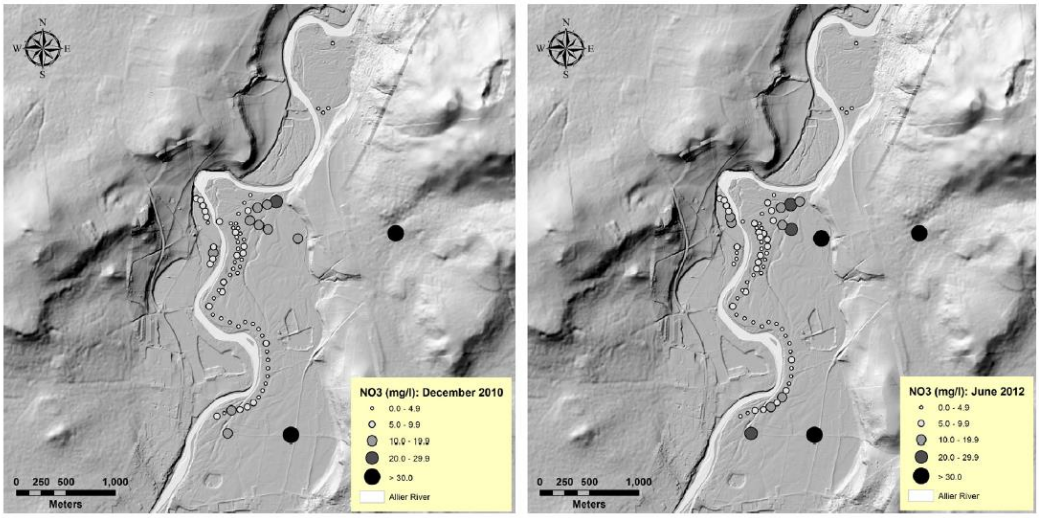

Fig. 13. Spatial distribution of nitrates of 75 points during the two intensive campaigns, (a) December 2010 (low flow period) and (b) June 2012 (high flow period).

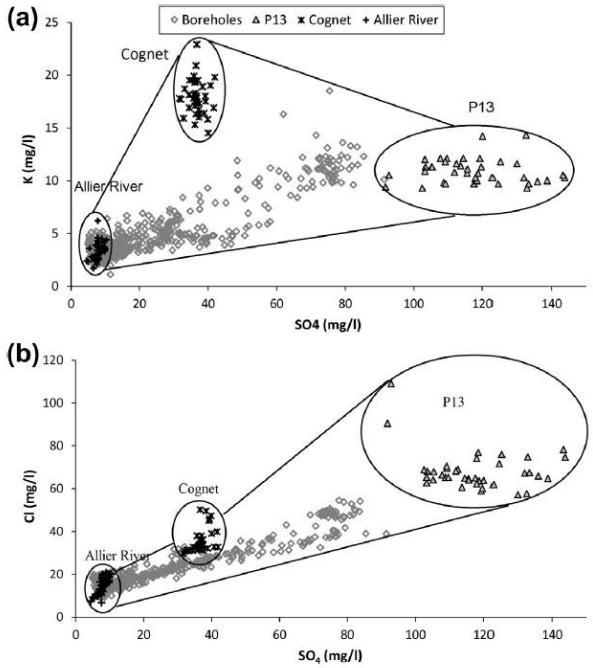

Fig. 14. (a) SO_4^{2-} vs K^+ and (b) SO_4^{2-} vs Cl^- plot.

supply from the southern part of the alluvial aquifer. This latter varies from 11% for B56 to 22% for B27 and is consistent with the location of the boreholes; the lower percentage corresponds to B56 closer to Allier River than B27. High contribution of southern aquifer for B65 (19%) may be due to the sealing of river bank during low flow period; the contribution of Allier River to B56 suggests that the bank is not sealed in this part of the river. Concerning boreholes B23 and B29, results of calculations involve the participation of the three possible origins. As these two boreholes are in the same distance from the hills (Fig. 2), the participation of the volcano-sedimentary aquifer seems to be the same and is evaluated to 27%. The participation of the southern part of aquifer versus Allier River evolved with the increasing distance from the river. Thus B29 presents a higher contribution of the southern part of the alluvial system (56%) whereas B23 displays higher income from the Allier River (37%).

Table 3
Contributions percentage of the 3 end-members.

Borehole ID	Recharge % by Allier River			Recharge % by Hills (Cognet)			Recharge % by South alluvial aquifer (P13)		
	K^+/SO_4^{2-}	K^+/Cl^-	Mean	K^+/SO_4^{2-}	K^+/Cl^-	Mean	K^+/SO_4^{2-}	K^+/Cl^-	mean
B10	87	82	84	0	0	0	13	18	16
B11	100	95	97	0	0	0	0	5	3
B18	100	95	97	0	0	0	0	5	3
B20	100	94	97	0	0	0	0	6	3
B23	33	41	37	23	32	27	44	27	36
B26	100	95	97	0	0	0	0	5	3
B27	79	76	77	0	0	0	21	24	23
B29	17	18	17	27	27	27	56	55	56
B33	100	94	96	0	0	1	0	6	3
B39	100	94	96	0	0	1	0	6	3
B56	90	85	87	2	0	1	8	15	12
B65	81	78	79	3	0	2	16	22	19
B66	98	91	94	0	0	0	2	9	6
B71	98	91	94	0	0	0	2	9	6

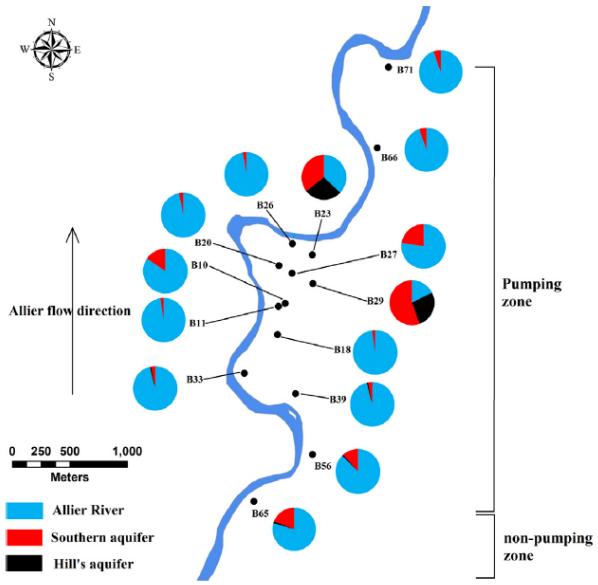

Fig. 15. Calculated percentage contribution of end-members to groundwater samples.

Overall, the contribution of Allier River recharge is significant in the majority of groundwater samples within the alluvial aquifer, contributing up to 100% in boreholes adjacent to it. As expected, the effect of Allier River recharge declines with distance from the river and thus the points far from the river are influenced by either incoming waters from the hills or from the southern part of the alluvial aquifer that modify both their chemical and isotopic signatures.

4.6. Conceptual model of the Allier alluvial aquifer

Groundwater circulates generally from south to north, with a natural alimentation from the hills in the non-pumped part of the alluvial aquifer. 4 end-members have been determined for the recharge of the alluvial groundwater: rainfall, Allier River, surrounding hills' aquifer and the southern part of the alluvial system. Isotopes of the water molecule show that water of the Allier Basin is recharged by rainwater with an evolution from a pole defined by the GMWL and the Allier River, which integrates the influence of the whole watershed to a more local pole defined by the LMWL ($\delta^2H = (7.6 \pm 0.2)\ \delta^{18}O + (1.3 \pm 1.1)$). However, autochthonous recharge by rainfall seems contributing a few to the geochemistry of the alluvial aquifer feeding as only 38% of the total precipitation infiltrate and that effective precipitation harbours major ion concentrations largely below the groundwater contents. Then the chemical content of the investigated boreholes of the alluvial system depends mainly on the contribution of the 3 other end-members. The main recharge is assumed by the Allier River, and then thanks to the water movement generated by the pumping, the water move towards east where the chemistry of boreholes is affected by water/rock interactions and evaporation. On the eastern and southern alluvial aquifer borders, a mixing with waters coming from the hills' aquifer or the southern non-pumped part of the system is shown, notably by the anthropogenic elements such as

nitrates, sulphates (associated with potassium) and chloride. The contribution of the 3 end-members to the boreholes' chemistry has been calculated and shows that Allier River could participate up to 100% in boreholes adjacent to it; this recharge declines with distance from the river (Fig. 15). Boreholes located on the eastern and southern borders are then affected by either incoming waters from the hills or from the southern part of the alluvial aquifer that modify their chemical and isotopic signatures. Locally a probable sealing of the river banks has been highlighted for B65.

5. Conclusions

Considering the fundamental role played by alluvial aquifer in the socio-economic context of a many regions of the world for their uses (drinking, industrial and agricultural purposes) and their ecological role in relation with their connection to surface water, the functioning of these systems has to be well understood. However, due to the interconnection of these systems to many water masses such as precipitation, rivers, pounds, alluvial aquifers, a simple model is not suitable. The complexity of the model increases with the exploitation of this shallow groundwater through large scale pumping what modify the general circulation of groundwater and then their quality. Simultaneous observation and interpretation of spatial and temporal variations in groundwater chemistry and isotope can support the assessment of groundwater recharge sources and contamination by human activities and allow establishing a solid conceptual model that includes water-rock interactions, influence of pumping, recharge and vulnerability. This achievement is fundamental to better understand the system and to elaborate further strategies for alluvial groundwater resource management. Our results supply fundamental results for the groundwater management of the alluvial aquifer of the Allier River. Thus, we highlight that even if rock-water interaction is an important process in the chemical acquisition of groundwater chemistry, anthropogenic activities may threat its quality. Then, contributions of end-members highlight the main issues for protecting groundwater from anthropogenic contamination. Southern and eastern parts of the aquifer suffer from the entrance of groundwater of a lower quality showing the importance of a better definition of the protection's area for drinking water supply. Close to the Allier River, attention should be paid to punctual pollution that may occur in such surface water but also to recurring contamination (due to discharge of waste water treatment plant for example). All this information has to be included in management strategies of groundwater in order to protect sustainability of this valuable resource.

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APPENDIX F

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‘’Evaluation of pharmaceuticals in surface water: reliability of PECs compared to MECs’’

Evaluation of pharmaceuticals in surface water: reliability of PECs compared to MECs.

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Abstract: Due to the current analytical processes that are not able to measure all the pharmaceutical molecules and to the high costs and the consumption of time to sample and analyse PhACs, models to calculate Predicted Environmental Concentrations (PECs) have been developed. However a comparison between MECs and PECs, taking into account the methods of calculations and peculiarly the parameters included in the calculation (consumption data, pharmacokinetic parameters, elimination rate in STPs and in the environment) is necessary to assess the validity of Predicted Concentrations. MECs variations of sixteen target PhACs [acetominophen (ACE), amlodipine (AML), atenolol (ATE), caffeine (CAF), carbamazepine (CAR), doxycycline (DOX), epoxycarbamazepine (EPO), fluvoxamine (FLU), furosemide (FUR), hydrochlorothiazide (HYD), ifosfamide (IFO), losartan (LOS), pravastatin (PRA), progesterone (PROG), ramipril (RAM), trimetazidine (TRI)] have been evaluated during one hydrological cycle, from October 2011 to October 2012 and compared to PECs calculated by using an adaptation of the models proposed by the Heberer and Feldmann (2005) and EMEA (2006). On annual basis, most of the PECs calculations are acceptable for they are comparable to the corresponding MECs. Concentrations within the environment could then be evaluated by using PECs. However, on a smaller timestep, PECs lead to some uncertainties. The seasonal evolution of PECS and MECS shows that PECs of ATE, HYD, PRA, FUR and CARB are in agreement with MECs; pharmacokinetics parameters included in the equation have to be adapted in order to obtain coherent values. PECs of DOX, EPO and ACE do not correspond to MECs and cannot then be used as a reliable estimation of concentrations.

Keywords: Pharmaceuticals compounds, Surface water, Measured Environmental Concentrations (MECs), Predicted Environmental Concentrations (PECs)

1. Introduction

The presence of pharmaceuticals in the aqueous environment is generally related to anthropogenic processes (Vystavna et al., 2012): industrial discharges, animal manure, wastewater treatment discharge, waste and runoff of unused drugs discharged in domestic waste landfill or in sewage water. Results of previous studies argue that wastewaters are the main sources of pharmaceuticals in the aquatic environment (Ternes, 1998; Hirsh et al., 1999; Heberer, 2002; Clara et al., 2004; Bendz et al., 2005; Lee et al., 2005; Lindqvist et al., 2005; Joss et al., 2006; Comeau et al., 2008); the most contaminated are hospital wastewaters

(Steger-Hartmann et al., 1997) as they content high concentrations of medicines. When administered to a human, a part of medicine drugs is excreted unchanged or metabolized in urine and feces and reaches the environment via sewage. A particular attention must be paid to the contamination of surface waters as they are partly used for drinking water supplies, or are in connection with alluvial systems that are used for these purposes, because they directly collect partially untreated wastewaters from Sewage Treatment Plants (STPs) and/or the leakage of septic tanks (Ternes et al., 1999). The concentrations of pharmaceuticals in surface water thus depend on various factors: consumption of medicines in the water catchment area of a water body, absorption and elimination rates of the pharmaceuticals from the organism, elimination rate in the STPs, the volume of surface water, and elimination rate in the environment (Ter Laak et al., 2010). In addition, the proportion of sewage treated before discharge in the environment and the disposal modes of unused drugs can be added (Ortiz de Garcia et al., 2013).

The presence of pharmaceutical products in the aquatic environment is known since the 70s. However, the interest of the scientific community on the pharmaceutical has really grown during the two last decades due to their continuous increased use (consumption in France has been multiplied by 200 since the 80s (Dulio et al., 2009)) and to the evolution of analytical techniques that enough improved to allow quantifying the presence of these substances in waters, even at really low concentrations. Then numerous publications deal with the Measured Environmental Concentrations (MECs) of pharmaceuticals that have been detected with levels which can go from ng/l to µg/l in surface waters of Austria (Clara et al., 2004), Canada (Comeau et al., 2008), Finland (Lindqvist et al., 2005), France (Togola and Budzinski, 2008; Vystavna et al., 2012), Germany (Ternes, 1998; Nödler et al., 2011), Greece (Arditsoglou and Voutsa, 2008), Italy (Zuccato et al., 2005), India (Larsson et al., 2007), Japan (Nakada et al., 2008), Korea (Choi et al., 2008), Norway (Grund et al., 2008), Romania (Moldovan, 2006), Spain (Joss et al., 2006), Sweden (Bendz et al., 2005), Switzerland (Tauxe-Wuersch et al., 2005), Ukraine (Vystavna et al., 2012), USA (MacLeod et al., 2007), Western Balkans (Terzic et al., 2008), ... in groundwater (Barnes et al., 2008; Vuillet et Cren-Olivé, 2011; Müller et al., 2011; Fram et al., 2011; Reh et al., 2013; Lopez-Serna et al., 2013, …), as well as in drinking and tap waters (Heberer, 2002; Kuster et al., 2008; Schwab et al., 2005; Vuillet et Cren-Olivé, 2011; Valcarcel et al., 2011; …). Nevertheless, due to the current analytical processes that are not able to measure all the pharmaceutical molecules, to the number and the variability of molecules that may enter the environment, to the high costs and the consumption of time to sample and analyse this molecules, and to the requirements of

Commission Directive 93/67/EEC, Commission Regulation 1488/94/EC and Commission Directive 98/8/EC, models to calculate Predicted Environmental Concentrations (PECs) have been developed (Henshel et al., 1997; Stuer-Lauridsen et al., 2000; Castiglioni et al., 2004). If PECs provide important information for the prioritization of pharmaceuticals products for environmental strategies, approximations introduced in the calculations lead to uncertainties (Coetsier et al., 2009). Then a comparison between MECs and PECs, taking into account the methods of calculations and peculiarly the parameters included in the calculation, is necessary to assess the validity of predicted concentrations. Most of the studies present a comparison between MECs and PECs calculated by using national consumption data (Heberer and Feldmann, 2005; Johnson et al., 2007; Besse et al., 2008; Coetsier et al., 2009; Ort et al., 2010; Ter Laak et al., 2010; Vystavna et al., 2012; Ortiz de Garcia et al., 2013), only few of them use local consumption (Oosterhuis et al., 2013) despite the fact that local patterns can highly modify the estimations. Our study is a new attempt to compare, for a local site localised on the stream of the Allier River, PECs and MECs of selected molecules, measured on a monthly basis during one year, in a site where patterns of consumption differ from the national ones and to evaluate the reliability of PECs.

2. Material and methods

2.1. Site Settings

This study was performed in central France, in the Allier River, located in the Allier basin covering a surface of 14 310 km^2 (Figure 1). In this region, the climate is subjected to high spatial variability due to altitude variations from 167 to 1423 m.a.s.l. and to the mixed influences of both oceanic and continental climate as well as Mediterranean incomes in the southern part. Rainfall presents an average of 800 mm/year and is often different from year to year and even from one location to another. These variations strongly influence the Allier River, the main tributary of the Loire River, which flows roughly South toward North with a total length of 410 km long and assumes a pluvial regime with high flow during autumn/spring and low flow during winter/summer. Concerning, land occupations, the upper Allier basin is poorly occupied in terms of inhabitants and activities and mainly comports grasslands and forestry zones whereas the basin's alluvial plain is used primarily for animal husbandry and agriculture (maize and cereal) which occupies about 71% of the land cover, forest and grassland (24%) and urban areas (5%). The sampling site (45°45'16.20'', 3°13'9.43'', z=320 m) is located on the Allier River, about 20 km from the east of the city

Clermont-Ferrand and is directly connected to an alluvial aquifer used for the drinking water supply of about 100 000 inhabitants. 378 STPs, but only 18 serving more than 2000 inhabitants, have been recognized in the Allier Watershed above the sampling site. The nearest STP is Cournon's one, 4.2 km upstream to the station, which is dedicated to the treatment of wasterwaters of 36 000 inhabitants living in the Auzon watershed. The treatment processes consist of an activated sludge with prolonged aeration and nitrification / denitrification added to phosphate removal. The STP's effluent discharges in the Auzon River 300 m upper the connection between Auzon River and Allier River. It is assumed that this station contributes for a great part to the concentrations measured in the sampling site.

2.2. Sampling methodology and analytical procedure of MECs

Fourteen campaigns have been achieved, every 4 weeks, at the sampling site of the Allier River from October 2011 to October 2012. Grab water samples have been collected in pre-rinsed bottles of green glass, kept cool in an ice-box and immediately transported to the EUROFINS laboratory where analyses have been performed. Each sample has been analysed for 47 pharmaceuticals according to the following analytical procedure: each sample is preconcentrated through a solid phase extraction, after pH adjustment according to the physico-chemical properties of molecules, then pharmaceuticals are adsorbed on a copolymer (styrene divinylbenzene) and eluted with methanol or a mixture of methanol/acetonitrile. After concentration, pharmaceuticals were analysed by LC-MS/MS (liquid-phase chromatography provided with a system of detection by mass spectrometry). For every dosage by mass spectrometry by tandem or MS / MS, the quantification is insured by means of two couples of characteristic ions of the molecule, the second couple serving to confirm the identification of the molecule. In total, 705 measurements have been achieved.

2.3. Selection of PhACs

Analyses of 47 PhACs have been achieved on the samples collected from the Allier River between October 2011 and October 2012. Among these, 16 have been selected (Table 1) for they belong to the priority list of the AFSSAPS (French Agency of Sanitary Safety of Food and Health Products, 2008): acetominophen (ACE), amlodipine (AML), atenolol (ATE), caffeine (CAF), carbamazepine (CAR), doxycycline (DOX), epoxycarbamazepine (EPO), fluvoxamine (FLU), furosemide (FUR), hydrochlorothiazide (HYD), ifosfamide (IFO), losartan (LOS), pravastatin (PRA), progesterone (PROG), ramipril (RAM), trimetazidine

(TRI). For Caffeine and Ifosfamide, only MECs are presented. PECs cannot be determined because no or poor information is available on the consumption on these two molecules: caffeine is mainly due to the consumption of coffee, tea and soft drinks instead of its pharmaceuticals compound (Camacho-Munoz et al., 2010) and ifosfamide is only consumed in hospitals.

3. Calculations of PECs

3.1. Consumption data:

The CPAM (social health care system of Puy-de-Dôme) provided monthly data on subsidised pharmaceuticals molecules in Auzon water catchment. This dataset concerns 91% of the total inhabitants of the Auzon basin (43 833 covered by the national social insurance over a total of 47 930 inhabitants). The dataset comprises the number of packages subsidised by the CPAM which have been bought from October 2011 to October 2012 (Table 1). Medicines dispensed in hospitals (ifosfamide) and over-the-counter drugs are not included in these dataset.

3.2. Determination of pharmacokinetic parameters:

When consumed, PhACs (Pharmaceuticals Active Compounds) can be absorbed by the digestive tract: a fraction will be eliminated directly by feces while the other will pass into the body. The absorption rate depends on the route of administration. The fraction which is not absorbed is eliminated unchanged. The fraction absorbed can then pass through several metabolisation processes that can be summarized into two steps: phase I and phase II reactions. Phase I reactions correspond to oxidations (hydroxylation, N or S-oxidation, etc) and give metabolites that are different from the parent compounds. These metabolites can show a pharmacological activity. Phase II reactions correspond to conjugations with functional groups which enhance elimination from the body and lower the pharmacological activity of the parent compounds. The main groups are glucuronide and sulfonide whose conjugated metabolites are susceptible to be cleaved in the sewage water and regenerate parent compounds (Heberer and Feldmann, 2005), even if sulfonide ones appears to be more stable (Johnson et al., 2007; Kumar et al., 2012). Glucuronide and sulfonide conjugates should then be considered together with the excreted unchanged parent compound in order to calculate excretion rate.

Pharmacokinetic parameters (absorption, excretion unchanged and glucuro- or sulfo-conjugated, Table 1) have been determined through a general review that includes

www.theriaque.org (official French summaries of products characteristics), www.drugs.com, www.drugbank.ca and literature review (Heberer and Feldmann, 2005; Besse and Garric, 2008; Carballa et al., 2008; Besse et al., 2012; Ortiz de Garcia et al., 2013; Oosterhuis et al., 2013). Injected products were logically set to an absorption rate of 1. When no data is available, the most conservative parameters are taken: absorption and excretion rates are set equal to 1. For some molecules, excretion rates include glucuro-conjugates but do not consider sulfo-conjugates, eventually leading to an underestimation of excretion.

3.3. Determination of Fstp (elimination rate in STPs) and environmental parameters:

The elimination rates of each PhAC for various type of STPs (Table 1) were reviewed in the literature (Heberer and Feldmann., 2005; Joss et al., 2006; Vieno et al., 2007; Carballa et al., 2008; Miege et al., 2009; Besse and Garric, 2008; Besse et al., 2012; Soulier et al., 2011; Ortiz de Garcia et al., 2013; Oosterhuis et al., 2013). When no data was available, the most conservative value was taken: the elimination rate was set equal to 0 (i.e. the molecule is not eliminated at all by STP).

The daily flow rates of the Allier and Auzon Rivers have been extracted from www.hydro.eaufrance database (French Ministry of Ecology and Sustainable Development).

3.4. Model used to calculate PECs:

The model used in this publication is adapted from the models proposed by Heberer and Feldmann (2005) and EMEA (2006).

It was assumed that the entire amount of each product subsidised was consumed and that the consumption profile of the 91% of Auzon basin inhabitants covered by national health insurance can be applied to the entire population. Amounts of each PhAC monthly excreted within the Auzon catchment are calculated by equation 1:

$$m_{Auzon,x} = \sum b_j \times u_j \times m_j \times [(1 - a_j) + a_j \times e] \text{ (Equation 1)}$$

where, m_{Auzon} is the total amount of the PhAC excreted during the month x in the Auzon catchment, b_j is the number of packages of formulation j subsidised during the month x in the Auzon catchment, u_j is the number of units per package of formulation j, m_j is the amount of PhAC per unit of formulation j, a_j is the absorption rate for formulation j which depends on the mode of administration, and e is the portion of the PhAC excreted unchanged or as

glucuro- and/or sulfo- conjugates after its absorption. For metabolites, $(1 - a_j)$ member has been suppressed from equation 1, since the part of the PhAC that is not absorbed is not metabolized, and m_j member has been divided by the molecular mass of the parent molecule and multiplied by the molecular mass of the metabolite.

The pharmacokinetic parameters may differ from one reference to another (Table 1). When more than one value is available for at least one pharmacokinetic, a range of predicted amounts excreted annually in the catchment area can be derived from minimum and maximum values by using the equations 2 and 3:

$$m_{Auzon,x,min} = \sum b_j \times u_j \times m_j \times [(1 - a_{j,max}) + a_{j,max} \times e_{min}] \text{ (Equation 2)}$$

$$m_{Auzon,x,max} = \sum b_j \times u_j \times m_j \times [(1 - a_{j,min}) + a_{j,min} \times e_{max}] \text{ (Equation 3)}$$

where, $m_{Auzon,x,min}$ and $m_{Auzon,x,max}$ are respectively the minimum and the maximum amounts of the PhAC excreted during the month x in the Auzon catchment by people covered by the national health insurance, $a_{j,min}$ and $a_{j,max}$ are respectively the minimum and the maximum absorption rate for the formulation j, and e_{min} and e_{max} are respectively the minimum and the maximum excretion rate of PhAC after its absorption.

STP of Cournon treats wastewater of 36000 inhabitants of the Auzon catchment, the amount of PhAC incoming into Cournon's STP is calculated by equations 4 and 5:

$$m_{inf,x,min} = m_{Auzon,x,min} \times \frac{pop.STP}{pop.Auzon} \text{ (Equation 4)}$$

$$m_{inf,x,max} = m_{Auzon,x,max} \times \frac{pop.STP}{pop.Auzon} \text{ (Equation 5)}$$

where pop. Auzon is the number of inhabitants of Auzon catchment covered by national health insurance and pop. STP is the number of habitants linked to the STP of Cournon. Amount of PhAC exiting the STP of Cournon is given by equations 6 and 7:

$$m_{eff,x,min} = m_{inf,x,min} \times (1 - Fstp_{max}) \text{ (Equation 6)}$$

$$m_{eff,x,max} = m_{inf,x,max} \times (1 - Fstp_{min}) \text{ (Equation 7)}$$

where, $Fstp_{min}$ and $Fstp_{max}$ are respectively the minimum and the maximum elimination rates (Table 1) for the same type of STPs as the one installed in Cournon city.

The minimal and maximal PECs for each PhAC incoming into the Allier River is finally calculated by using equations 8 and 9:

$$PEC_{min} = \frac{m_{eff,x,min}}{flow_{AUZON+ALLIER}} \text{ (Equation 8)}$$

$$PEC_{max} = \frac{m_{eff,x,max}}{flow_{AUZON+ALLIER}} \text{ (Equation 9)}$$

where, $flow_{AUZON+ALLIER}$ is the daily flow rates (m^3/s) of Allier and Auzon Rivers measured the day of the corresponding sample.

Environmental degradation and sorption are currently not included in the prediction. Moreover incoming concentrations from the upper Allier Basin is not taken into account. Upstream amounts of labile molecules, such as Acetaminophen, able to reach downstream part are extremely low (Buerge et al., 2003; Kasprzyk-Hordern et al., 2009; Vystavna et al., 2013). However, for conservative molecules, concentrations coming from the upper basin could enhance concentrations at the sampling site.

3- MECs

MECs variations of the sixteen target PhACs have been evaluated during one hydrological cycle, from October 2011 to October 2012. Statistical calculations are presented in Table 2. Vystavna et al. (2012) show that two river basins with similar hydrologic characteristics and water usage (wastewaters, discharge, irrigation, …) can however present different pollution status according to the different socio-economic characteristics in terms of population density, economic activities, incomes, lifestyles, etc. Then data collected during the present study have been compared in priority with concentrations measured in French watersheds similar to the Allier basin, when information is available. Nine among the sixteen PhACs selected have been positively detected in the Allier River with the concentrations in the following order: ACE > CAF > EPO > HYD > PRA > FUR-ATE > CAR > DOX. AML, FLU, IFO, LOS, PROG, RAM, TRI have never been measured during the one year sampling either because they are not present in the environment due to low consumption (AML, FLU, RAM, TRI) or due to the low persistence in the environment (FLU, PROG) or because the quantification limit imposed by the methodology is to high compare the concentrations of these molecules in the Allier River.

Atenolol, carbamazepine and caffeine are the most frequently detected molecules in the Allier River with 71%, 78% and 85% of occurrence.

3.1. Caffeine

Caffeine is the most widespread PhAC in the environment (Nikolaou et al., 2007) with the highest frequency reported in similar studies (Spongberg et al., 2011) and is often considered as a good anthropogenic waste marker. This molecule has a labile behaviour in the environment (Benotti and Brownawell, 2007); concentrations can then be lowered rapidly in the environment. In the Allier River, concentrations in caffeine vary from 11 $ng.L^{-1}$ to 81 $ng.L^{-1}$ with a mean value of 41.3 $ng.L^{-1}$. These values are consistent with the ones found in the Hérault River in France (13-107.2 $ng.L^{-1}$ in Togola and Budzinski, 2008) and in the Jalle River (40-75 $ng.L^{-1}$, Vystavna et al. 2012). They are lower than those measured in Costa Rica (max=1.12 $mg.L^{-1}$ in Sponberg et al., 2011) where a natural origin from plants could be invoked, South Korea (105 $ng.L^{-1}$, Kim et al., 2007), Spain (415.7 $ng.L^{-1}$, Fernandez et al., 2010), USA (med = 0.1 $\mu g.L^{-1}$, Koplin et al., 2002).

3.2. Carbamazepine

Along with caffeine, carbamazepine has been proposed as an anthropogenic waste marker as it is one of the most frequently detected drugs in aquatic environment and it is poorly degraded in STPs (Ternes, 1998; Heberer and Feldman, 2005). Literature provides then large information on concentrations of this molecule in surface waters. Carbamazepine in the Allier River presents concentrations between 1.2 to 5.8 $ng.L^{-1}$, with a mean value of 3.3 $ng.L^{-1}$. These values are generally lower than the concentrations available in France (13.9-56.3 $ng.L^{-1}$ in Rabiet et al., 2006; 0-56.3 $ng.L^{-1}$ in Togola and Budzinski, 2008; 105-675 $ng.L^{-1}$ in Coetsier et al., 2009; mean of 13.9 $ng.L^{-1}$ in Vuillet and Cren-Olivé, 2011; 17-27 $ng.L^{-1}$ in Vystavna et al., 2012) or in other countries like Canada (0.24-28 $ng.L^{-1}$, Lissemore et al., 2006), Germany (max = 1075 $ng.L^{-1}$ in Herberer, 2002), Italy (max = 175.3 $ng.L^{-1}$ in Zuccato et al., 2005), Serbia (6-130 $ng.L^{-1}$ in Grujic et al., 2009), South Korea (mean = 25 $ng.L^{-1}$ in Kim et al., 2007), South Wales (1-356 $ng.L^{-1}$ in Kaspryzk-Hodern et al., 2008), Spain (11-90 $ng.L^{-1}$ in Gros et al., 2006; 9-110 $ng.L^{-1}$ in Pedrouzo et al., 2007; nd-104 $ng.L^{-1}$ in Fernandez et al., 2010; 80-3090 $ng.L^{-1}$ in Ginebreda et al., 2010; 1.2-266.7 $ng.L^{-1}$ in Osorio et al., 2012), Switzerland (30-250 $ng.L^{-1}$ in Ollers et al., 2001), Ukraine (2-272 $ng.L^{-1}$, Vystavna et al., 2012). Small values comparable to the ones of our study have been reported by Togola (2006)

for the Gironde and Adour River estuaries and by Spongberg et al. (2011) in Costa Rica (1-3 $ng.L^{-1}$). As this carbamazepine is noted to be highly resistant to biodegradation and thus highly recalcitrant under standard biological wastewater treatment conditions (Clara et al., 2005; Kosjek et al., 2009; Donner et al., 2013), the consumption factor may be invoked to explain the differences observed between the different studies.

3.3. Atenolol

Information on Atenolol, a current β-blocker, is incomplete since only a few studies take this molecule into account. Atenolol has been detected in twelve samples among fourteen with concentrations varying from 1.3 to 13 $ng.L^{-1}$ and a mean value of 4.9 $ng.L^{-1}$, values in agreement with the mean of 4.7 $ng.L^{-1}$ reported by Vulliet and Cren-Olivé (2011) in Rhône-Alpes watersheds. Other data gathered from the literature review are systematically higher: 0-465 $ng.L^{-1}$ in Spain (Gros et al., 2007; Ginebreda et al., 2010; Fernandez et al., 2010, Osorio et al., 2012), median value of 17.2 for the Po River (Zuccato et al., 2005).

3.4. Acetaminophen

Among the nine compounds detected in the Allier River, Acetaminophen, one of the most prominent pain killer, presents the highest concentrations between 25 and 200 $ng.L^{-1}$, consistent with the data of Rabiet et al. (2006, max=211 $ng.L^{-1}$), but has been detected positively only three times. Togola and Budzinski (2008) and Vuillet and Cren-Olivé (2011) found lower values, comprised from 10.6 to 72.3 $ng.L^{-1}$, for the Hérault River, and from 0.4 to 71 $ng.L^{-1}$ for the Rhône-Alpes region, respectively. Concentrations in this molecule are highly variable: 78 to 610 $ng.L^{-1}$ in Serbia (Grujic et al., 2009), 30 $ng.L^{-1}$ (Pedrouzo et al., 2007) to 2420 $ng.L^{-1}$ (Ginebreda et al., 2010) in Spain, 4.1 to 73 $ng.L^{-1}$ in South Korea (Kim et al., 2007), not detected in U.K. (Roberts et al., 2006), 2.1 $ng.L^{-1}$ (Conley et al., 2008) to 10 $\mu g.L^{-1}$ in USA (Kolpin et al., 2002). These variations could be explained by the degradation and dilution factors that decrease the concentrations of this non-conservative molecule downstream the STPs (Vystavna et al., 2013). The low ratio of detection of 21% for Acetaminophen is also due to its labile behaviour.

3.5. Others positively detected PhACs

Five other PhACs, DOX, EPO, FUR, HYD and PRA have been detected with the following occurrence and concentrations: DOX 21% (1.1-1.8 $ng.L^{-1}$), EPO 7% (0-46 $ng.L^{-1}$), FUR 64% (1.6-17 $ng.L^{-1}$), HYD 57% (11-42 $ng.L^{-1}$), PRA 64% (1.8-18 $ng.L^{-1}$). Little information exists

on these molecules within the literature. EPO, one of the metabolite of carbamazepine, has been positively detected only one time at a concentration largely exceeding the CAR's one. The input and persistence of antibiotics, such as doxycycline into the environment is of major concern due to possible development of bacteria resistance to these compounds (Kachatourian, 1998). In our study, DOX has been detected only three times and with low concentrations. Most of the studies carried out on PhACs, show an absence of doxycycline (Hirsch et al., 1999; Kolpin et al., 2002; Focazio et al., 2008, Vulliet and Cren-Olivé, 2011; Wei et al., 2011). Concentration of 74 $ng.L^{-1}$ with an occurrence of 77% has been reported by Spongberg et al. (2011) in Costa Rica river waters. Tetracycline antibiotics have been shown to dissipate rapidly in the aqueous environment due notably to photocatalytic degradation (Makowski et al., 2009). The relatively high occurrence and concentration found by Spongberg et al. (2011) likely indicates high usage in Costa Rica compared to previously reported studies. Low concentration and occurrence in the Allier River is related to both factors of low consumption and photodegradation. FUR, HYD and PRA are prescribed for long-term treatments, that explains their high occurrence in Allier River; concentrations have to be relied to the consumption factor. FUR is a loop diuretic used in the treatment of congestive heart failure and oedema, determined as stable in the environment during 90 days (Kirit et al., 1980). Values found for the Allier River are in agreement with the measurements (median = 3.5 $ng.L^{-1}$, max = 67.2 $ng.L^{-1}$) achieved in the Po River by Zuccato et al. (2005). They are lower than concentrations of 254.7 $ng.L^{-1}$ reported by same author for Lambro River. HYD is a diuretic drug frequently used for the treatment of hypertension, congestive heart failure, symptomatic oedema, diabetes insipidus, renal tubular acidosis. Concentrations evaluated for the Allier River are lower than those been reported for Spain and Italy: Llobregat River presents concentration from 0 to 2435.5 $ng.L^{-1}$ (Osorio et al., 2012), Henares-Jarama-Tajo Rivers from 4.2 to 960.3 $ng.L^{-1}$ (Fernandez et al., 2010), mean for Lambro River is of 255.8 $ng.L^{-1}$, median value for Po River is of 4.6 $ng.L^{-1}$ (Zuccato et al., 2005). At least, PRA is primarily used for the treatment of dyslipidemia and the prevention of cardiovascular disease. Values measured in the Allier River are in agreement with the data reported for the Rhône-Alpes neighbouring region (1.6 $ng.L^{-1}$, Vulliet and Cren-Olivé, 2011).

3.6. Time-evolution

The observed variations within a sampling location can be due to varying consumption rate over time, such as ACE and DOX (Nödler et al., 2011), decreasing (bio)degradation in waste water treatment and the environment at low temperature (Daneshvar et al., 2010; Gardarsottir

et al., 2010; Suarez et al., 2010), varying the river's flow rate (Ter Laak et al., 2010) and dilution of surface water by rain water (Baker and Kasprzyk-Hordern, 2013).

Figure 2 shows the temporal evolution of the PhACs, flow rate of the Allier River, Rainfall height and temperature records from October 2011 to October 2012. Two peaks of concentrations can be seen in February 2012 and September 2012. Positive peak of February 2012 can be explained by low flow rate of the Allier River, small rainfall amount and low temperature. However, the peak registered in September 2012 seems not to be related to the temperature but most probably to the low flow rate of the Allier River or the dilution by rainwater.

Variation of consumption with time will be explored in the next paragraph.

4- Comparison between PECs and MECs

Annual averages of PEC and MECs have been used to calculate PEC/MEC ratios (Figure 3, Table 2) to see if PECs and MECs are in the same order of magnitude. An absence of values within the MECs dataset means an absence of PhACs within the Allier River or a concentration below the quantification limit. To evaluate the impact of these low values annual averages of MECs are calculated: 1) by considering that an absence of measurement corresponds to a concentration equal to 0 $ng.L^{-1}$) by considering that an absence of values corresponds to an absence of measurements (Ter Laak et al., 2010), 3) by attributing to the absent value, a concentration equal to LQ/2 (Choubert et al., 2011), 4) by attributing to the absent value, a concentration equal to LQ (Coetsier et al., 2009).

PEC/MEC ratios were used to assess the reliability of PEC calculation over a long period (14 months). This assessment was made on the basis described by Coetsier et al. in 2009:

-if PEC/MEC was in [0.2; 4]: PEC was acceptable.

-if PEC/MEC was less than 0.2: PEC was significantly underestimated.

-if PEC/MEC was more than 4: PEC was significantly overestimated.

-if PEC/MEC was higher than 8: PEC was strongly overestimated.

All the selected PhACs have been sorted by using this classification (Table 3). Most of them appear to be acceptable thanks the methodology of Coetsier et al. (2009).

4.1. Pravastatine

PEC/MEC ratios are comprised between 0.77 and 1.19 and show a good correspondence between PECs and MECs at an annual scale. Figure 3a presents the evolution of MEC, PEC and LQ (Limit of Quantification) of pravastatine for the October 2011-October 2012 period. The two curves are characterized by similar shapes, MECs presenting however bigger amplitudes. This marginal difference could be explained by calculations method that includes mass of PhAC rejected through the whole month and then attenuates daily variations of PECs whereas MECs consist of punctual measurements. As information on the PRA's (bio)degradability is not available, inputs of PRA from the upper Allier basin, before the connection between the Allier and the Auzon Rivers, can be implied and explain the slightly higher MECs.

4.2. Acetaminophen

PEC/MEC ratios indicate an acceptable correspondence between PECs and MECs with values comprised between 0.90 and 4.22 with a general overestimation. Figure 3b shows the evolution of MEC, PEC_{min}, PEC_{max} and LQ of ACE. Differences quoted between PEC_{min} and PEC_{max} can be explained by excretion parameter (Table 1) that varies from 0.06 to 0.85. MECs of ACE vary between PEC_{min} and PEC_{max} and present an evolution that differs significantly from the calculated concentrations. Only three positive measurements have been achieved for this molecule at the Allier sampling site. This could be explained by the behaviour of acetaminophen within the environment as this molecule is recognized as a non-persistent one (Lam et al., 2003; Loffler et al., 2005; Yamamoto et al., 2009) or most probably by an uncompleted consumption of sold medication.

4.3. Hydrochlorothiazide

PEC/MEC ratios dataset, varying from 0.33 to 0.59, is consistent whatever the method of calculations selected and shows a clear underestimation of PECs compare to MECs. Figure 3c highlights MEC, PEC_{min}, PEC_{max} and LQ of hydrochlorothiazide evolutions. Same peaks are observed on the three concentration curves, PECs presenting attenuated evolution. This underestimation could be explained by a wrong evaluation of the pharmacokinetic parameters. As no information about the persistence of hydrochlorothiazide in the environment is available, to our knowledge, supply by the upper part of the Allier basin could also be suspected and generate MECs above PECs.

4.4. Doxyxycline

PEC/MEC ratios of doxycycline vary from 1.26 to 5.9 and highlight the significant overestimation of PECs compare to MECs. Figure 3d presents the same trends, doxycycline has been measured only three times during the whole period of sampling and peaks do not correspond to PECs ones. This molecule is considerably affected by biodegradation (Kümmerer and Cunningham, 2006) and photoreaction (Kummerer, 2009) that could partly explain the difference observed.

4.5. Carbamazepine and epoxycarbamazepine

PEC/MEC ratios for carbamazepine show a good correspondence between PECs and MECs as the values vary between 0.83 and 1.05. Generally, PEC_{min} are slightly underestimated and PECmax are slightly overestimated (Table 2, Figure 3e). MECs evolve between PECmin and PEC_{max} curves and present the same shape. The model of calculation is then clearly adapted to evaluate PEC of carbamazepine, marginal difference could be corrected with a best fitting of excretion and elimination parameters. This molecule is well-known to be persistent in the environment; an input from the upper Allier basin should be taken into account. Nevertheless, as the consumption of carbamazepine is really low, it is probable that the concentration before the junction between Allier and Auzon Rivers is highly diluted by the Allier River.

Epoxycarbamazepine that is a metabolite of carbamazepine does not follow the same scheme. Only one positive measurement has been achieved during the sampling period and even does not match the PEC calculated for the same time (Table 2, Figure 3f). Evaluation of Epoxycarbamazepin through PEC calculations seems to be difficult.

4.6. Atenolol

This molecule presents the same behavior than the one of carbamazepine: good correspondence of PECs and MECs are shown both by PEC/MEC ratios that vary from 0.87 to 1.02 (Table 2) and by Figure 3g that presents the evolution of MEC of atenolol between PEC_{min} and PEC_{max}, concentrations curves evolving similarly. Moreover, literature on the persistence of this PhAC reports a half-life up to 166 days (Liu and Williams, 2007; Yamamoto et al., 2009), concentrations of atenolol measured at the investigated site should include incomes from the upper part of the Allier Basin, before the connection with Auzon River. The same conclusion can be achieved for this pharmaceutical with a possible best fitting by modifying excretion and elimination parameters thanks to observations.

4.7. Furosemide

PEC/MEC ratios give values comprised between 2.36 and 3.67 (Table 2). These values are close to the limit value of 4 imposed by Coetsier et al. (2009). MECs curve (Figure 3h) presents the same shape as PEC_{min} and PEC_{max} curves but is clearly below the two latters. This could imply either an uncompleted use of medicine prescribed either a degradation of FUR within the environment. According to the literature review achieved during this study, no data is available on elimination rate of this molecule in surface water, PBT profiler gives a DT50 equal to 60 days. This seems in accordance with an uncompleted used of this molecule after being sold. This conclusion should be verified and completed with further experimentation on this molecule.

4.8. Other molecules

AML, FLU, LOS, PROG, TRI have not been detected in the Allier River during the sampling campaign. PECs have been compared, for these five molecules, to LQ or LQ/2. For AML, FLU and TRI, PEC/MEC ratios are lower than 0.2 indicating that PECs are underestimated compare to the evaluate MECs. AML and FLU present low consumption patterns in the Auzon basin (Table 1) and concentrations in the Allier River are certainly lower than LQ or even LQ/2. Concentrations of RAM seem to be closer to LQ/2 (Table 3) as $PEC/MEC_{LQ/2}$ is comprised between 0.2 and 4. Quantification limit of TRI is high (100 $ng.L^{-1}$, Table 1), explaining the absence of detection of this molecule during the sampling campaign. Concentrations of this molecule should be lower than LQ. At last, estimation of MECs of LOS and PROG by LQ or LQ/2 seems to be in good agreement with PECs.

5. Conclusion

Sixteen PhACs have been selected for they belong to the priority list of the AFFSAPS and they are a part of the dataset acquired on the Allier River during one year measurements, from October-2011 to October-2012.

Nine among the sixteen targeted molecules have been positively detected in the surface waters of the Allier River. Atenolol, carbamazepine and caffeine are the most frequently measured PhACs in relation both with consumption and persistence in the STPs and the environment. Acetominophen and caffeine, despite their (bio)degradation facility in the STPs and environment, present the highest concentrations of the database due to the fact that these compounds are among the most used in France.

Comparison between MECs and PECs has been achieved by using an adaptation of the models proposed by Heberer and Feldmann (2005) and EMEA (2006). On annual basis, most of the PEC calculations are acceptable for they are comparable to the corresponding MECs. Concentrations within the environment could then be evaluated by using PECs. However, on a smaller timestep, PECs lead to some uncertainties. The seasonal evolution of PECS and MECS shows that PECs of ATE, HYD, PRA, FUR and CARB are in agreement with MECs but pharmacokinetics parameters included in the equation have to be adapted in order to obtain coherent values. However PECs of DOX, EPO and ACE do not correspond to MECs and cannot then be used as a reliable estimation of concentrations.

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Table 1: Pharmacokinetics parameters of the target PhACs

Name	Therapeutic class	Available whithout medical prescription	Administration route	Absorption rate a_j (min-max)	Excretion rate e_j (min-max)	Elimination rate in STP F_{step} (min-max)
Acetaminophen (ACE)	pain killer - antipyretic	yes	Oral	1[1,2,3] 0,95[5]	0,59-0,77[1] 0,06[5] 0,85[4]	0,97[5] >0,9[8] 0,99[10] 0,96[13]
			Parenteral	1		
			Rectal	1[1] 0,95[5]		
Amlodipine (AML)	Calcium chanel blocker	no	Oral	1[1,3] 0,64-0,9[2]	0,1[1,2,3,4]	-
Atenolol (ATE)	β blocker	no	Oral	0,50[1,2,3]	1[1,3,4]	0,61[6] 0-0,76[4] 0,58[11] 0,08[10]
			Parenteral	1		
Carbamazepine (CAR)	anti epileptic	yes*	Oral	1[1] 0,9[5] 0,85-0,9[12]	0,01-0,02[1] 0,03[2] 0,12[5] 0,01-0,03[12]	0[6] 0-0,53[4] 0,03-0,1[7] 0,29[5] 0-0,2[8] -1,21[11] 0,37[12] 0,09[10]
10,11-epoxycarbamazepine (EPO)	Pharmacologically active metabolite of carbamazepine	-	-	-	0,8[5]	0,0185[5]
Doxycycline (DOX)	tetracycline	no	Oral	1[1,2,3]	0,4-0,72[1] 0,72[4]	0,06[4]
			Parenteral	1		
Fluvoxamine (FLU)	selective serotonin reuptake inhibitor	no	Oral	1[1,3] 0,53[5]	0,02[2,3] 0,04[5]	0,63[5]
Furosemide (FUR)	loop diuretic	yes*	Oral	0,65[1] 0,6[2,3]	1[1,4]	0-0,62[4]
			Parenteral	1		
Hydrochlorothiazide (HYD)	thiazid diuretic	no	Oral	0,6-0,8[1] 0,5-0,6[3] 0,65-0,75[2]	0,95[1]	0,23-0,31[7]
Ifosfamide (IFO)	alkilating agent	no (hospital use only)	Parenteral	1	0,12-0,53[2,3] 0,5[9] 0,61[5]	0,03[5]
Losartan (LOS)	angitensin II receptor antagonist	no	Oral	1[1,2,3]	>0,04[1,3] 0,04-0,6[2]	0,88-0,89[7]
Pravastatine (PRA)	HMG CoA reductase inhibitor	no	Oral	0,34[1,3]	0,5[4]	-
Progesterone (PROG)	progestins	no**	Oral	0,99[5]	0,1[5]	0,245[5]
			Dermal	0,1[1]		
Ramipril (RAM)	ACE inhibitor	no	Oral	0,56[1] 0,5-0,6[2,3]	0,02[2,4]	-
Trimetazidine (TRI)	anti-anginal	yes*[n]	Oral	-	-	-

*First dispensation requires medical prescription and only prescribed amount is subsidised. **Except for one pharmaceutical form. [n] Reimbursement stopped since March 2012. [1] www.theriaque.fr, [2] www.drugs.com, [3] www.drugbank.ca, [4] Besse et al. (2008), [5] Ortiz de Garcia et al. (2013), [6] Soulier et al. (2011), [7] Oosterhuis et al. (2013), [8] Joss et al. (2006), [9] Besse et al. (2012), [10] Miège et al. (2009), [11] Vieno et al. (2007), [12] Heberer and Feldmann (2005), [13] Yamamoto et al. (2007).

Table 2: PECs, MECs (in ng.L^{-1}) and PEC/MEC ratios

PhACs	LQ (ng.L^{-1})	nb	Min (ng.L^{-1})	Max (ng.L^{-1})	Mean (ng.L^{-1})	Med (ng.L^{-1})	MEC without0	MEC with0	MEC LQ/2	MEC LQ	PEC_{min}	PEC_{max}	PEC	PEC/MEC with0	PEC/MEC without0	PEC/MEC LQ/2	PEC/MEC LQ
ACE	10	3	25.0	200.0	87.3	37.0	87,3	18,7	22,6	26,6	1,1	156,8	78,9	4,2	0,9	3,49	2,97
AML	10	0	-	-	-	-	0,0	0,0	5,0	10,0	0,1	0,3	0,2	-	-	0,03	0,02
ATE	1	12	1.3	13.0	4.9	4.2	4,9	4,2	4,3	4,4	1,7	6,8	4,3	1,0	0,9	1,00	0,98
CAF	10	10	11.0	81.0	41.3	37.5											
CAR	1	11	1.2	5.8	3.3	3.3	3,3	2,6	2,7	2,7	0,1	5,4	2,7	1,1	0,8	1,01	1,01
DOX	1	3	1.1	1.8	1.4	1.4	1,4	0,3	0,7	1,1	1,3	2,3	1,8	5,9	1,3	2,59	1,66
EPO	5	1	46.0	46.0	46.0	46.0	46,0	3,3	5,6	7,9	11,8	16,9	14,4	4,4	0,3	2,56	1,81
FLU	5	0	-	-	-	-	0,0	0,0	2,5	5,0	0,0	0,1	0,0	-	-	0,01	0,00
FUR	1	9	1.6	17.0	4.9	2.9	4,9	3,2	3,3	3,5	7,5	15,6	11, 6	3,7	2,4	3,47	3,30
HYD	5	8	11.0	42.0	22.4	18.0	22,3	12,8	13,9	14,9	7,0	8,0	7,5	0,6	0,3	0,54	0,50
IFO	1	0	-	-	-	-											
LOS	5	0	-	-	-	-	0,0	0,0	0,5	1,0	0,3	0,5	0,4	-	-	0,78	0,39
PRA	1	9	1.8	18.0	5.9	3.9	5,9	3,8	4,0	4,2	4,5	4,5	4,5	1,2	0,8	1,14	1,09
PROG	1	0	-	-	-	-	0,0	0,0	0,5	1,0	0,9	0,9	0,9	-	-	1,71	0,86
RAM	5	0	-	-	-	-	0,0	0,0	2,5	5,0	0,6	0,7	0,7	-	-	0,27	0,13
TRI	100	0	-	-	-	-	0,0	0,0	32,1	64,3	1,6	1,6	1,6	-	-	0,05	0,02

Table 3: Classification of PhACs according to PEC/MEC ratios

$PEC/MEC_{with0}<0.2$	$0.2<PEC/MEC_{with0}<4$	$4<PEC/MEC_{with0}<8$
	ATE, CAR, FUR, HYD PRA	ACE, DOX, EPO
$PEC/MECwithout0<0.2$	$0.2<PEC/MEC_{without0}<4$	$4<PEC/MEC_{without0}<8$
	ACE, ATE, CAR, DOX, EPO, FUR, HYD, PRA	
$PEC/MEC_{LQ/2}<0.2$	$0.2<PEC/MEC_{LQ/2}<4$	$4<PEC/MEC_{LQ/2}<8$
AML, FLU, TRI	ACE, ATE, CAR, DOX EPO, FUR, HYD, LOS PRA, PROG, RAM	
$PEC/MEC_{LQ}<0.2$	$0.2<PEC/MEC_{LQ}<4$	$4<PEC/MEC_{LQ}<8$
AML, FLU, RAM TRI	ACE, ATE, CAR, DOX EPO, FUR, HYD, LOS PRA, PROG	

Figure 1: location of the study site within the Allier Basin

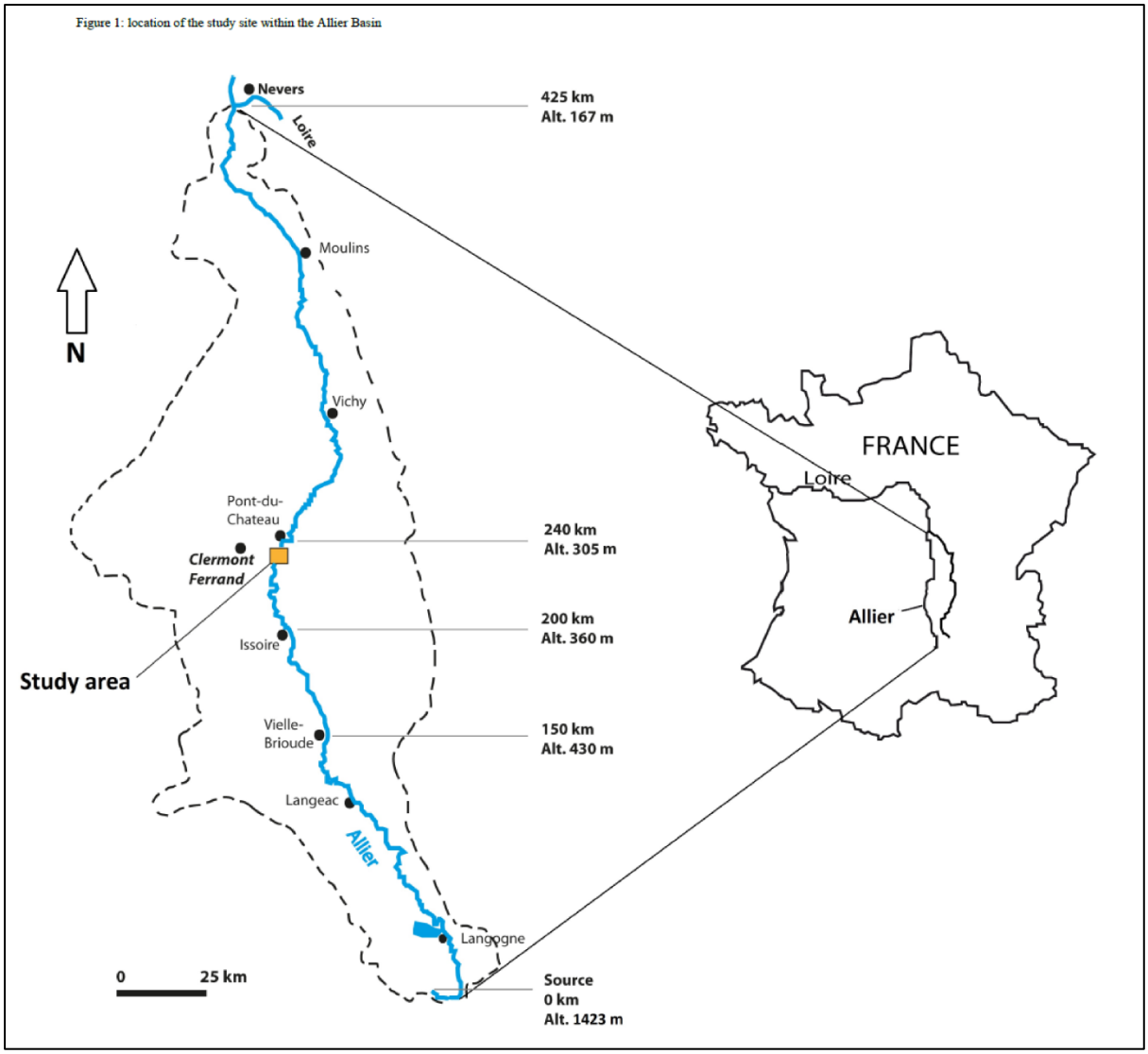

Figure 2: Temporal variations of Allier and Auzon flow rates, rainfall, temperature and PhACs concentrations ($ng.L^{-1}$)

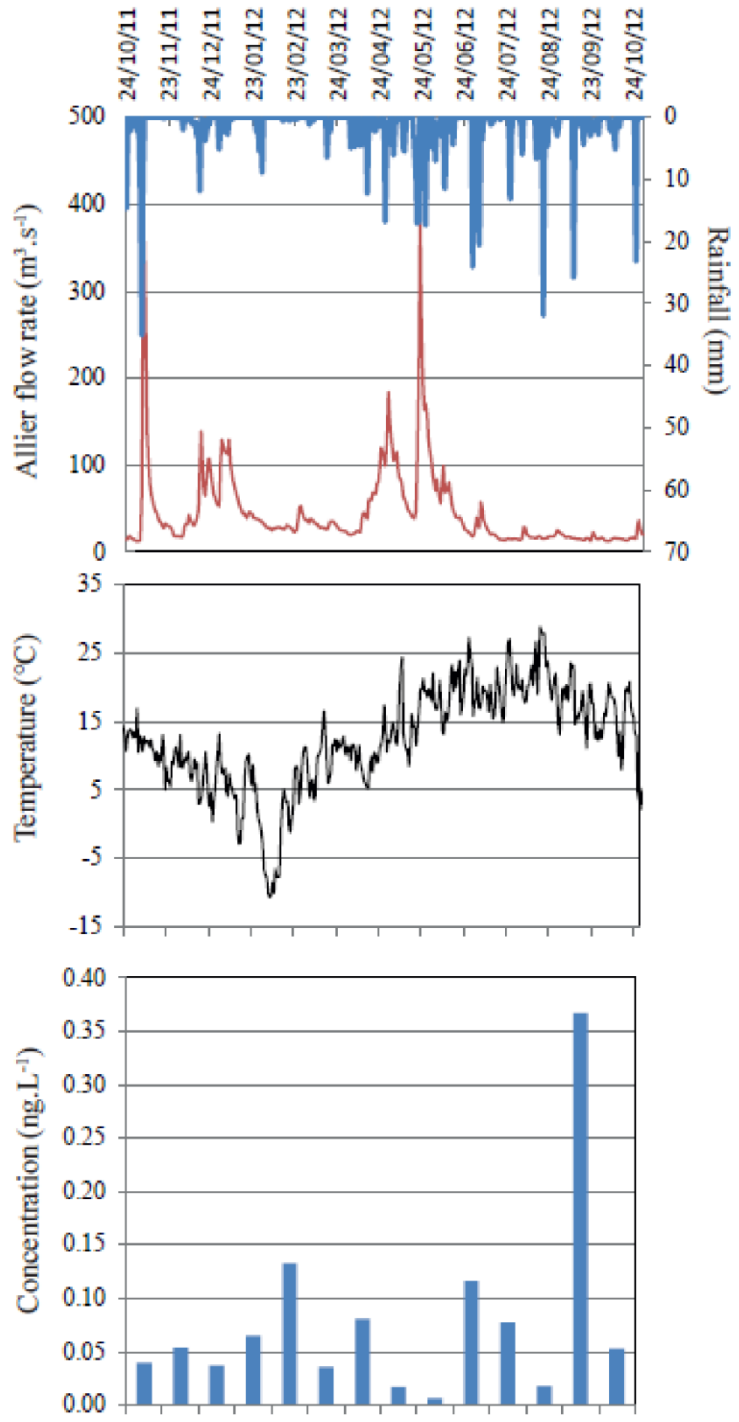

Figure 3: Temporal evolution of MECs (Measured Environmental Concentrations) and PECs (Predicted Environmental Concentrations). PECmax and PECmin are the maximum and minimum value of PECs when data and pharmacokinetic parameters are available, LQ is Limit of Quantification.