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## Suivi par capteurs passifs des polluants émergents dans les eaux de surface en contexte urbain

Jessica Denila Villanueva

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**Thèse de Doctorat**  
**L'UNIVERSITÉ BORDEAUX 1**

ECOLE DOCTORALE SCIENCES ET ENVIRONNEMENTS

Par

**Jessica Denila VILLANUEVA**

Pour obtenir le grade de docteur  
Spécialité : géoressources, patrimoines et environnements

**Suivi par capteurs passifs des polluants  
émergents dans les eaux de surface  
en contexte urbain**

**(Monitoring emerging pollutants in surface waters using  
in-situ sampling devices in an urban context)**

Soutenue le 8 juillet 2013

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## **RÉSUMÉ :**

L'étude a pour objectif de déterminer la qualité des eaux de surface sous différentes conditions climatiques et pratiques de gestion des eaux de surface. Trois sites ont été choisis pour: (1) la rivière Jalle de Blanquefort, (2) le lac de Bordeaux, France et (3) la rivière Pasig aux Philippines. Les sites français présentent des collecteurs d'eau qui se déversent directement dans les eaux de surface. La rivière Pasig sert de collecteur d'eaux usées en l'absence de stations de traitement des eaux usées et collectées. Au cours des campagnes de mesure, il a été possible de suivre l'impact de la variabilité climatique (pluviométrie) et d'évènements aléatoires sur la qualité chimique (éléments traces métalliques et polluants organiques) des eaux ; en combinant échantillonnage classique et par capteurs passifs. Les propriétés physico-chimiques de l'eau ainsi que les caractéristiques des particules et l'utilisation d'analyses statistiques permettent de préciser le comportement des molécules détectées et de décrire l'évolution hydrochimique des eaux de surface urbaines et estuariennes vis-à-vis d'aléas climatiques contrastés.

## **ABSTRACT:**

The study aimed to assess the water quality of the surface water in differing climate conditions and management practices. Three interesting sites were chosen, (1) Jalle River and (2) Bordeaux Lac both in France and the (3) Pasig River in the Philippines. The French sites have rainfall and run-off collectors that directly discharge water to the water bodies. Pasig River, on the other hand, becomes a waste collector as waste management and treatment plant are lacking. Trace metals and organics (pesticides, herbicides, pharmaceuticals and drugs) were measured. Conventional and passive sampling approaches were employed. The mass fluxes were obtained in order to calculate the pollution transport. Physico-chemical properties and the particle characteristics, integrating statistical analyses, facilitated in explaining the behavior of the measured molecules and describing the hydrological system in relation to climate variability.

**Keywords :** passive sampling techniques, hydrogeochemistry, trace elements, organic pollutants, run-off, urban collectors, urban hydrology, France, Philippines

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*Passion should be fed by tons of efforts and endless patience with deep sighs and Zen smiles,  
It should be welcomed by an open-mind but a critical thinking,  
It should overcome problems and convert it into challenges instead,  
It should be equipped with imaginations, creativity and resourcefulness,  
It ought to walk towards utility and essentials in life,*

*Lest, it has to also find time and means to put it into writing.*

- Jessica Denila Villanueva, 2013  
(For His Glory!)

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## **CHAPTER I Introduction**

## 1. Contexte

L'augmentation, tant de la production que des usages des différents éléments et composés chimiques de synthèse, couplés à l'urbanisation de plus en plus intense de terroitoires, génère des dégradations croissantes de l'environnement notamment des eaux continentales et estuariennes. À l'heure actuelle, un des débats scientifiques porte sur le degré de pollution des masses d'eaux suite aux rejets chroniques, avec ou sans traitement des eaux urbaines, par des contaminants organiques et inorganiques. De nombreux chercheurs qui quantifient les polluants émergents tels que les métaux traces, les produits de soins personnels, pharmaceutiques et autres molécules pour la santé, essaient de comprendre leurs devenir dans les eaux de surfaces et souterraines. La majorité des études ont montré que ces composés sont généralement détectés à l'état de trace. Néanmoins du fait de rejets continus et diffus, ces faibles quantités affectent le « bon état écologique » des plans d'eau. Si les usines de traitement existent, force est de constater qu'elles ne peuvent supprimer totalement les polluants émergents détectés. En l'absence d'usine de traitement, les doutes sur la qualité chimique des eaux de rejets sont pleinement justifiés. D'autre part, les gestionnaires des eaux collectées (eaux pluviales et de ruissellement) s'interrogent sur une amplification possible de la pollution par ces molécules lors de leur rejet directement dans les cours d'eau.

Partout dans le monde, les nations conscientes de ce problème se sont engagées à résoudre les problèmes concernant la pollution des masses d'eaux continentales et de leur évolution qualitative. En Europe, la Directive Cadre sur l'Eau (directive-cadre 2000/60/CE), et au niveau mondial via l'Organisation des Nations Unies (ONU) par l'adoption du chapitre 18 de l'AGENDA 21 ont défini un cadre administratif et des objectifs clairs quant à la protection de la ressource en eau. Ces deux cadres institutionnels définissent des stratégies de réponses aux préoccupations concernant l'état des masses d'eaux. L'objectif principal étant de préserver leur qualité intrinsèque et/ou de remettre en bon état environnemental la ressource. Dans ce but, les activités préliminaires portent sur l'évaluation de leurs qualités hydrochimiques (identification des polluants, quantification et détermination des flux, identification des sources et modalités de rejets et de traitements, etc.). Cette étape est fondamentale pour définir les caractéristiques et vulnérabilité des masses d'eaux vis-à-vis des activités anthropiques. Ainsi, la surveillance de la qualité de l'eau est une priorité mondiale et

la définition de stratégies pertinentes doivent être envisagée sur la base de résultats scientifiques objectifs et incontestables.

La littérature a montré combien l'évaluation des différentes fractions (totale, dissoute, labile) d'un élément ou d'un composé est importante. Ainsi, du point de vue chimique et écotoxicologique, les fractions dissoutes et labiles de l'ion libre sont les plus importantes du fait de leur mobilité et capacité à être adsorbées par le vivant. Cette phase de quantification (action de surveillance en continue), est délicate et nécessite des méthodes pertinentes pour assurer une quantification fiable de l'élément ou composé à mesurer.

Dans cette thèse, les avantages de l'échantillonnage passif in-situ sont discutés en tant qu'alternative aux méthodes classiques d'échantillonnage ponctuel. Les sondes qui ont été utilisées dans cette étude sont celles basés sur la diffusion graduelle dans des films minces (DGT), pour concentrer la fraction labile des métaux traces, et les échantillonneurs intégratifs d'espèces chimiques organiques polaires (POCIS) pour les composés organiques hydrophylles. Les résultats obtenus sont discutés en les comparants avec ceux obtenus par l'approche conventionnelle (échantillonnage direct ponctuel) de la fraction totale. Les paramètres physico-chimiques des eaux, l'hydrologie (débit, température, évènements ponctuels) et le climat (taux de précipitation) ont également été pris en considérations. Trois sites d'intérêts ont été choisis : la rivière de La Jalle et le Lac de Bordeaux en France et la rivière Pasig à Manille, Philippines. Les campagnes d'échantillonnage ont été menées pendant des régimes hydro-climatiques contrastés c'est-à-dire en période sèche et humide afin de préciser les tendances des éléments mesurés en fonction d'événements météorologiques variables.

## 2. Objectifs

L'objectif principal de cette étude est de fournir des approches simples et fiables pour caractériser et évaluer l'évolution de la qualité chimique d'eaux urbaines de surface. Les modalités opérationnelles pour la conduite de mesure sur le terrain ont été abordées du point de vue technique. Cette approche a pour but de pouvoir proposer des recommandations et approches en vue d'optimiser la gestion des ressources en eau. Parmi les résultats attendus :

- Définir les procédures d'évaluation de la qualité des eaux étudiées ;
- Evaluer la sensibilité et l'efficacité des échantillonneurs passifs in-situ dans différents contextes hydrodynamiques ;

- Produire des données de référence sur la quantification des éléments et composés chimiques présents dans les systèmes aquatiques étudiés ;
- Fournir des procédures analytiques en vue de déterminer les concentrations des différents éléments et composés ;
- Décrire et expliquer les variations spatio-temporelles observés lors des différents évènements qui se sont produits durant les différentes campagnes d'échantillonnage ;
- Définir les tendances globales des différents métaux traces suivis depuis l'amont vers l'aval des systèmes aquatiques étudiés ;
- Expliquer et mettre en perspectives les résultats obtenus sur le faible niveau de concentration observé dans la colonne d'eau.

### 3. Organisation du manuscrit

Ce manuscrit inclut une discussion à l'issue de chaque chapitre.

Le chapitre 2 fait le point sur l'état de l'art des échantillonneurs passifs in-situ en précisant les principes théoriques, les modalités de déploiement sur le terrain et leurs analyses en laboratoire, en précisant les avantages et limites.

Les chapitres 3 & 4 portent sur les sites d'études français (la Jalle et le lac de Bordeaux), les différents types de produits qui ont été détectés, et leurs concentrations respectives en fonction des variations spatiales (localisation) et temporelles (période humide et sèche). Les valeurs mesurées ont été obtenus à partir d'échantillonnages classiques (ponctuelles) et par capteurs passifs (enregistrement en continu sur plusieurs jours). Le chapitre 4 intègre le calcul des flux des contaminants détectés dans les eaux de ruissellement collectées, par approche en hydraulique urbaine en fonctions des surfaces actives du bassin collecteur.

Le chapitre 5 fait une synthèse de l'usage de capteurs passifs in-situ ttype DGT pour le suivi de la qualité chimique (métaux traces labiles) dans le contexte d'eaux de surfaces libre et collectées. Des recommandations sont proposées afin de permettre aux administrations en charge de la gestion de la qualité des ressources en eaux d'améliorer leur efficacité.

Le chapitre 6 porte sur l'évolution des métaux traces en contexte urbain et estuariens en fonction d'évènements climatiques contrastés. Une approche statistique par Analyse en

Composantes Principales (ACP) a permis de différencier les périodes entre elles et les résultats obtenus (données spatio-temporelles sur la physico-chimie des masses d'eaux étudiées). Les résultats obtenus permettent de valider l'approche technologique par capteurs passifs in-situ pour le suivi de masses d'eaux libres et collectées

Le chapitre 7 traite de la détection et la quantification de produits pharmaceutiques (Salbutamol, Atenolol, Carbamazepine, Cetirizine, Ibuprofen et Simvastatine) et des métabolites médicamenteux (Ecgonine, Methylester, Methamphetamine, Amphétamine, Extase (MDMA), Cocaïne, Benzoylécgonine et TetraHydroCannabilone) dans la rivière Pasig. A partir des doses prescrites, la quantité excrétée est comparée à la concentration mesurée et calculée. Les raisons des faibles traces mesurées (ng/L) sont fournies en intégrant les phénomènes d'absorption, pharmacocinétique, d'excrétion et modalité de mise à disposition (influence de la fraction biotique et inorganique dans la colonne d'eau) qui peuvent affecter les niveaux de concentration de ces composés organiques. La rivière Pasig étant dépourvue d'unités de traitement des eaux de rejets, les teneurs mesurées des composés pharmaceutiques et drogues sont comparées à d'autres études où les eaux sont traitées avant leur rejet en rivière.

La conclusion (chapitre 8) démontre que l'étude des polluants anthropiques détectés dans le contexte d'eau de surface en milieu urbain du point de vue hydrogéochimique est fondamentale pour définir des suggestions et recommandations en vue d'une gestion holistique des ressources en eau.

## **CHAPTER II Passive sampling technique: A REVIEW**

## 1. Introduction

Water bodies are, usually, the recipient of all the substances and compounds used, mostly, in different anthropogenic activities and alterations. Means can be from the discharges from treatments plants, storm-water, and surface run-off from urban and agricultural areas (Sliva and Williams 2001). This brought the degradation of the water quality. The quality of the water poses a lot of problems and concerns nowadays. Presently, there is growing interest on the importance of the water quality status and trends (Korol *et al.* 2005; Kerachian and Karamouz 2007; Chang 2008).

The Water Framework Directive (WFD) is renowned for the water policy. WFD is under EU environmental regulation of the water sector. This aims to have standards on the quality of waters that is intended for drinking, bathing, fish and shellfish harvesting (Kallis and Butler 2001). Among the specific objectives are (Borja 2005): (1) to prevent further deterioration, to protect and to enhance the status of water resources; (2) to promote sustainable water use; and (3) to enhance protection and improvement of the aquatic environment, through *specific measures* for the progressive reduction of discharges. This denotes that the water bodies should be in the level of good ecological status. Accordingly, in order to achieve the quality standards, this requires sound methods (Collins *et al.* 2012). Having standards, references, solution to monitor the quality of water for use as swimming, drinking and aquaculture activities are part of the goal of the Directives (Kallis and Butler, 2001).

Monitoring and assessments play crucial role in these aspects. These two (2) are being reinforced universally. The challenge to the scientists and to the environmental managers is to provide an effective technique on water sampling and monitoring. The emerging movement in water quality monitoring is the use of the passive sampling technique. There are a lot of commercial passive samplers available depending on the target elements or compounds of interest. The application is extensively documented. However, there is still reluctance in using this technique. Some of the probable reasons are:

1. It is, *even now*, new in the field of water quality monitoring?
2. The potency and capability is not yet fully understand?
3. Analytical protocols are more exigent?

## 2. Objectives

This paper discusses the functions and limitations of the emerging passive sampling technique. Although, the application of this technique is widely documented there are still some matters that needs more comprehension. The general principle of the passive sampling technique (*What is?*); the advantages and function (*Why use?*); the different available passive samplers (*What to use*) and the operation (*How to use?*).

## 3. General principle

The passive sampling device mimics the part of the organism but considers only the process of adsorption. The free analytes diffused and are adsorbed in the sorbent that explains the sequestering of the analytes. Generally, the water is filtered by the membrane then the solvent or resin captures the compound/analyte molecules; the housing secures the form and serves as the room for all the elements (Figure II.1). The membrane and sorbent acts as sink of the passively partitioned molecules (Prest and Jacobson 1997). Analytes are integrated over the time of sampling (Kot *et al.* 2000) then considers time weighted average (TWA). Since the free analytes are in small quantity, the passive sampling device is fabricated in such a way that it can detect even in trace amounts (Söderström *et al.* 2009).

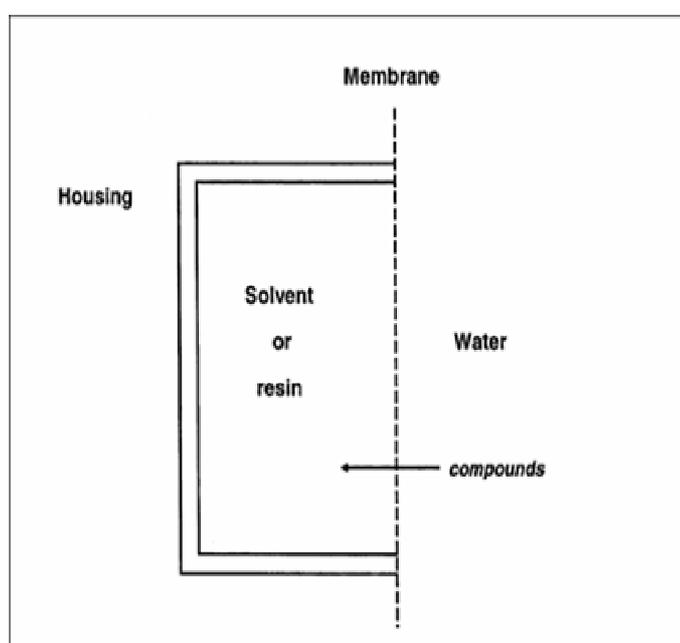


Figure II.1. Typical schematic diagram of a passive sampling device (Stuer-Lauridsen 2005)

The passive sampling devices reacts also to the environmental parameters such as temperature (Seethapathy *et al.* 2008), water flow and velocity, turbulence, biofouling, etc. (Alvarez *et al.* 2004; Li *et al.* 2010; Tang *et al.* 2012; Charlestra *et al.* 2012) as shown in Table II.1.

**Table II.1. Environmental effects on the uptake rates of different types of passive samplers (Seethapathy *et al.* 2008)**

Factors	Aqueous sampling
Effect if temperature on the sampling rate	Defined by permeability as a function of temperature based on Arrhenius-type relationships and diffusion coefficient changes with temperature in the boundary layer.
Effect if humidity on the sampler performance	Designed specifically to handle aqueous environments
Sampler response time	$R_p = \frac{L_m^2}{6D_m K_{mw}}$ <p> <math>R_p</math> - response time of the sampler  <math>D_m</math> - analyte diffusion coefficient in the membrane  <math>K_{mw}</math> - partition coefficient of the analyte between water and the membrane  <math>L_m</math> - thickness of the polymer membrane </p>
Effect of sorbent strength on the sampling rate	Weaker sorbents are used frequently with the sampler functioning under the kinetic or equilibrium regime, depending on the sorbent
Effect of analyte concentration on the sampling rate	Sorption and diffusion coefficient in the polymer may change at high analyte concentration levels resulting in variable uptake rates
Determination of uptake rates	Determines experimentally. Not easy to estimate uptake rate theoretically. Use of performance reference compounds (PRCs) is gaining importance
Effect of face velocity on uptake rates	Not a problem at moderate face velocity, but potentially significant at low face velocity and high membrane solubility

Passive sampler devices use diffusive and partitioning processes to continuously integrate contaminants (Harman *et al.* 2011). In terms of theory and modeling, a first-order, one compartment model describes the exchange process in between the passive sampler and water (Tang *et al.* 2012):

$$C_s = C_w \frac{k_u}{k_e(1 - e^{-k_e t})} \text{ and } \frac{k_u}{k_e} = K$$

Where :

- $C_s$  = the concentration of the analyte in the sampler at time  $t$
- $t$  = time of passive sampler exposure
- $C_w$  = the concentration of the analyte in the water
- $k_u$  = is the uptake rate constant
- $K$  = reference water phase coefficient
- $k_e$  = overall elimination rate constant

The passive sampling works in two (2) phases. The kinetic and the equilibrium phase (Figure II.2). The kinetic phase is at a linear uptake stage wherein the rate of diffusion of substances at the water boundary layer is proportional to the concentration in the bulk water phase (Greenwood *et al.* 2009).

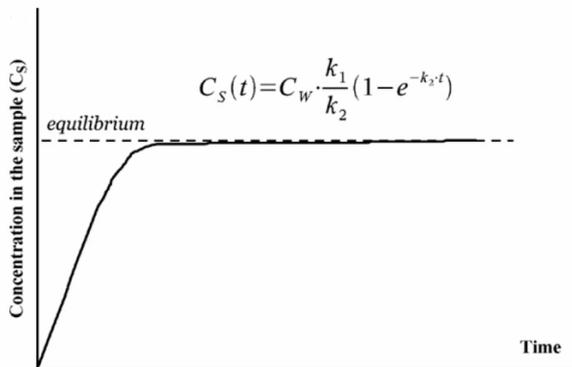


Figure II.2a. The Kinetic and Equilibrium Phases (Kot-Wasik *et al.* 2007)

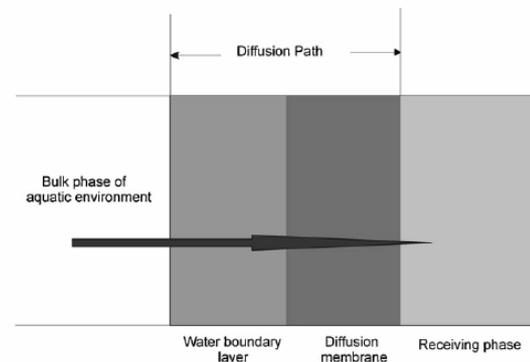


Figure II.2b. Passive sampler at kinetic mode (Greenwood *et al.* 2009)

Or the uptake is proportional to the chemical activity difference at the water and reference phases (Vrana *et al.* 2005). The initial uptake phase is linear or integrative that can be described as follows:

$$C_s = C_w k_u t$$

The 2<sup>nd</sup> phase is the equilibrium phase wherein sufficiency in terms of time is necessary (Figure II.2a). It should be long enough to allow the thermodynamic equilibrium in between the water and the reference phase to be established (Kot-Wasik *et al.* 2007).

## 4. Advantages and functions

The passive sampling technique is a very important approach, in terms of water quality assessments. The rationalization is due to the following considerations. These important factors were considered as basis why passive sampling should be included in the monitoring scheme:

### 4.1. In-situ (monitoring) reasons/advantages

Samples are subject to chemical changes such as contamination or physical changes such as perturbation during collection (Taillefert *et al.* 2000). Some of the limitations of the conventional water sampling methods are as follows (Alvarez *et al.* 2005):

1. Volume of water sampled may be insufficient to satisfy the detection limit required by the analytical method being used;
2. Represent contaminants that are only present at that instant time when water was collected;
3. Episodic events can over represent the true status of the system
4. Repetitive sampling can be costly and more tedious
5. Insufficiency of repetitive sampling can make the formulation of true time weighted average (TWA), which is fundamental in doing ecological risk assessment, impossible.

In situ sampling can bring about errors, perturbation, and contamination. Additionally, instantaneous measurements suffer from uncertainty of short-and long-term concentration variations (Liscio *et al.* 2009). Moreover, passive sampling is more appropriate, if, more thorough and continues recording of water quality is the objective (Vorwerk *et al.* 1996). This type of technique provides better quality information on important aquatic processes (Dunn *et al.* 2007). Furthermore, it allows examination of the behavior of the molecule in a natural process (Beeseley *et al.* 2010).

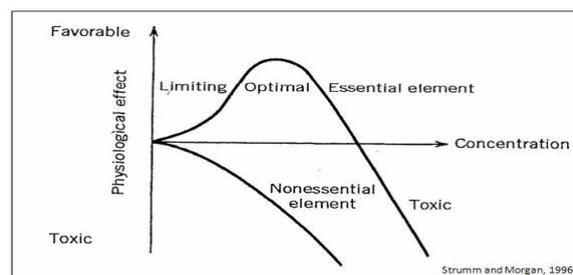
## 4.2. Bioavailability

The target fractions for bioavailability are the *labile or free metal ions* for trace metals and *freely dissolved fraction* for organics. These fractions can be extracted from the dissolved phase but laborious and technically more complicated when doing the analysis. In order to attain good quality results, bulk of water samples will be needed. Additionally, most of the analytes asks for longer time of measurement to be really captured.

These *free ions* have direct relationship to and are capable of responding to the physiological activity of the organisms. The interactions and end-processes will result to biological effects. Then depending on the reactions, it could or possibly give therapeutic effect (Torrado *et al.* 1997) or be beneficial to the organism (i.e. the essential elements), or on the other side, could lead to the level of toxicity. For instance, trace metal interaction to the enzyme proteins can cause damage to the biological system (Asano *et al.* 2010).

## 4.3. Ecotoxicological Principle

The elements in a high concentration can reach toxic level depending of course with the organism's reaction and resistance (physiological response). Lacking essential elements can lead to problems. To be able to reach an optimal uptake, a certain concentration is needed (Figure II.3). After the optimal stage, too much or higher concentration can bring the organism closer to the toxicity level. On the other hand, the uptake, in terms of concentration of the non-essential elements, has inverse relationship to giving a favorable condition. This only means that the higher the uptake is the higher the level of toxicity can be expected.



**Figure II.3. Physiological effect of the trace elements on the organism**

Water quality standards are, normally, based from ecotoxicology tests (USEPA 1986; Chèvre *et al.* 2008; Matsuzaki 2011). This then provides information on how to regulate and assess the water quality, mainly, to provide good water quality and protect both the resources

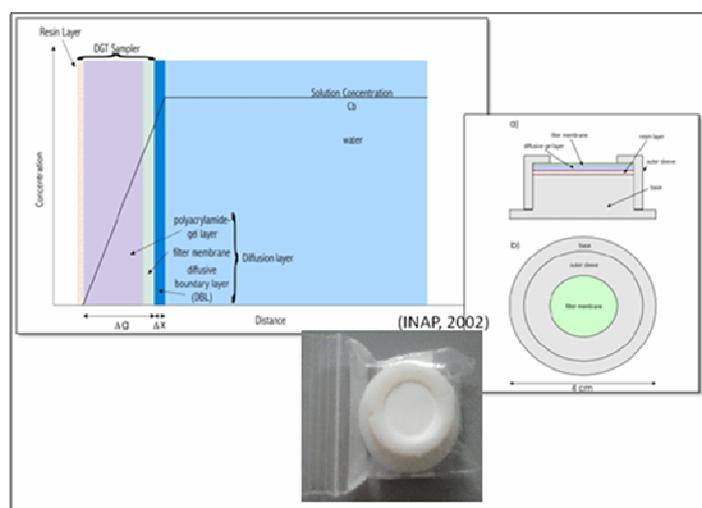
and the users. The table below from the USEPA gives the idea of the criteria, each falling in each specific definition that gives the details of the scope of what to check and expect.

## 5. The Passive Samplers and Use

There are a lot of existing passive samplers manufactured for monitoring the water quality and measuring different types of analyte molecules. These can be divided to three (3): inorganics (trace metals); hydrophobic organics; and hydrophilic organics. We would like to limit the scope of this paper to focus and discuss among many two (2) different kinds of passive samplers. These are the Diffusive Gradient in Thin Films (**DGT**) and the Polar Organic Chemical Integrative Sampler (**POCIS**). Each can be used based on the research objective or the target analyte molecules.

### 5.1. Diffusive Gradient in Thin-Films (DGT)

DGT (Figure II.4) is used to measure metal in a natural system (Meylan *et al.* 2003) and a technique for dynamic speciation in water, sediments and soils (Österlund *et al.* 2010).



**Figure II.4. DGT Schematic Cross-Section and Plan View (left)**

DGT is formed with layers of hydrogels (polyacrylamide gels). The topmost surface is covered by a membrane ( $0.45 \mu\text{m}$ ) that serves as filter. The next layer is the hydrogel that helps in diffusion. Actually, labile fractions are difficult to sequester due to its high mobility. To answer this difficulty, the last layer was added that functions as a binding layer which has the resin gel (Chelex-100 resin) that captures the selective metals. The whole membrane and

hydrogels are securely assembled in a plastic piston. Table II.2 presents the advantages and limitations of DGT. Time weighted average (TWA) concentration ( $C_{DGT}$ ) at the interface of the diffusive gel can be calculated by using the following formula (Zhang and Davison 1995; Roulier *et al.* 2008):

$$C_{DGT} = \frac{M \Delta g}{DtA}$$

Where:

<b><math>M</math></b>	=	Accumulated mass of the free metal ion (mg)
<b><math>\Delta g</math></b>	=	Diffusive layer thickness
<b><math>D</math></b>	=	Diffusion coefficient of the free metal ion
<b><math>t</math></b>	=	Deployment time (s)
<b><math>A</math></b>	=	Resin surface

And where M (Zhang *et al.* 2002; Bade *et al.* 2012):

$$M = \frac{C_e (V_{HNO_3} + V_{gel})}{f_e A}$$

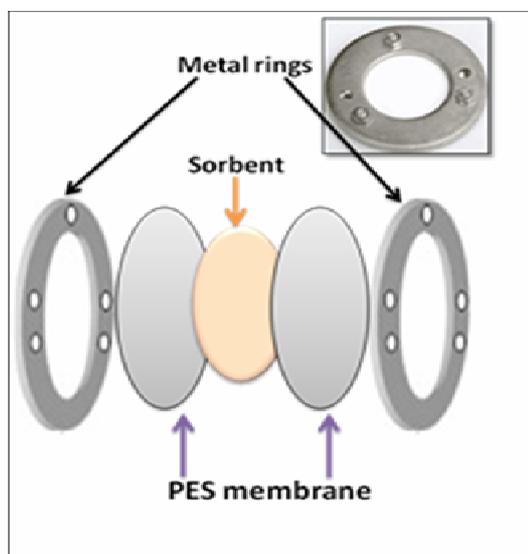
<b><math>C_e</math></b>	=	Concentration of the free metal ion in the 1M HNO <sub>3</sub> (µg/l)
<b><math>V_{HNO_3}</math></b>	=	Volume of the HNO <sub>3</sub> (ml)
<b><math>V_{gel}</math></b>	=	Volume of the resin gel (ml)
<b><math>f_e</math></b>	=	Elution factor for each metal
<b><math>A</math></b>	=	Exposure area (cm)

**Table II.2. Summary of DGT application in the aquatic systems (INAP 2002)**

<b>Advantages</b>	<b>Limitations/Considerations</b>
<p>Speciation: provides an in situ measure of labile metal species in solution. Allows inference of metal bioavailability and toxicity.</p>	<p>pH: limited in pH range if Chelex resin (pH 5 to 9, but ~2-11 for Cu)            Accuracy assayed concentrations depends on knowledge of diffusion coefficients in hydrogel. These may not be rigorously known.            Co diffusion can be a constraint in waters if very low cation concentrations (<math>&lt;2 \times 10^{-4} \text{M}</math>)</p>
<p>Sensitivity: pre-concentration of metals allows for ultra trace-level determinations.            Contamination: the potential for contamination associated with water collection and filtration is eliminated.</p>	<p>Capabilities have not been rigorously defined for some metals/metalloids (e.g. Mo, As, Se)            FIAM: subject to some of the limitations of the free-ion activity model.</p>
<p>Analytical Interference: obviates matrix effects associated with conventional analyses of high ionic-strength solutions</p>	<p>Metal Species Detected: requires more precise determination of the spectrum of species detected (e.g., kinetically-labile).</p>
<p>Time Integration: provides a time-integrated measure of labile-metal species over desired deployment interval            Multitude of Applications:</p> <ul style="list-style-type: none"> <li>• Metal speciation</li> <li>• Toxicity testing</li> <li>• Complexation kinetics of metal-ligand complexes</li> <li>• Complexation Capacity</li> <li>• Development of site-specific discharge criteria and assimilative capacity</li> </ul>	<p>Mining Impacted Systems: more work is required to validate the use of DGT in mining-impacted environments            DGT vs. toxicity: additional study is required to assess the relationship between DGT values and toxicity to aquatic biota.</p>
<p>User Friendly: deployment and retrieval do not require specialized equipment or highly trained personnel.</p>	
<p>Costs: costs are compatible with standard water quality analyses</p>	

## 5.2. The Polar Organic Chemical Integrative Sampler (POCIS)

**POCIS** is designed for polar organic substances that are more water soluble compounds ( $\text{Log } K_{ow} < 3$ ) in aqueous environment (Figure II.5).



**Figure II.5. POCIS structure**

It has a solid receiving phase (sorbent) that is sandwiched in two microporous polyethersulfone (PES) membranes. The latter serve as filter in order to exclude the particulates. The membrane is tightly secured by metal rings. POCIS has two (2) different configurations: 1. *Generic* for pesticides and hormones and 2. *Pharmaceutical*. Table II.3 presents the advantages and limitations of POCIS.

The target analytes sequestered by POCIS can be expressed by the below-mentioned first-order, one compartment model and the  $k_d$  is the desorption or elimination rate constant (L/d). At the integrative phase of uptake,  $k_d$  is negligible compared to  $k_u$ . So, equation can be simplified to (Alvarez 1999; Alvarez *et al.* 2007; Bailey *et al.* 2013):

$$C_w = \frac{C_{POCIS} \times M_{POCIS}}{R_s \times t}$$

Where:

$M_{POCIS}$  = Mass of the sorbent (g)  
 $R_s$  = Sampling rate (L/d)

And (Bartelt-Hunt *et al.* 2009):

$$R_s = \left( \frac{D_w}{L_w} \right) \times A$$

Where:

$D_w$	=	Aqueous diffusion coefficient of the compound
$L_w$	=	Thickness of the stagnant film layer
$A$	=	Surface area of the sampler

**Table II.3. Summary of POCIS application in the aquatic systems (Alvarez 2010)**

Advantages	Limitations/Considerations
Speciation: for water soluble organic chemicals	Only for those with log $K_{OWS}$ less than 3
Sorbents have strong sorptive properties acting as sink enabling to measure pharmaceuticals, illicit drugs, polar pesticides, phosphate flame retardants, surfactants, metabolites and degradation products	Configuration depends on the sorbent use: 1. Pesticide POCIS or generic (use a triphasic admixture: Isolute® ENV+ and Ambersorb® 1500 or 572 carbon dispersed on S-X3 BioBeads®) 2. Pharmaceutical POCIS (uses Oasis-HLB)
Sensitivity: designed to sample low levels of organic contaminants	
Contamination: suggest s the use of performance reference compounds (PRCs) to answer bio-fouling problems	Prone to build-up of bio-film on the membrane Contaminants are subject to photo degradation
The PES membrane somehow helps in avoiding the photo degradation problems.	
Allows background correction.	
Analytical Interference: Matrix specific interferences are well defined	Check the requirements specific to the laboratory where the analysis will be done.  Requires: knowledge on the sampling rate for each chemical measured  Clean-up and processing methods are not well defined. These methods will depend on the each laboratory for each specific chemical class determination.
Time Integration: works as a time-integrated measure depending on the selected duration of deployment	
Multitude of Applications:	
<ul style="list-style-type: none"> <li>• Chemical analysis</li> <li>• Toxicity test</li> <li>• Bio-indicator Tests</li> </ul>	
Screening tool	

## 6. Field and operation

Passive sampling technique can be described as passive and active, in terms of its function. Passive because the devices are pre-fabricated with controlled parts and substances and they work still and in a subtle way. At the same time, active as there is a continuous activity going on inside the sampler once they are out of their package. They react to its environment. At the same time, they capture and sequester analyte molecules that have affinity to the sorbents or gel.

The passive sampling technique starts with the objective. Figure II.6 illustrates how the technique is being carried out. Site inspection follows. The local site describes the water system and site physical characteristics. The sources of the target analyte molecules should be identified and noted. Other elements and compounds and the sources that might cause interference must be recorded as well. Common protocols for field operations are identified in *Boxes 1-4*. Security and accessibility are essentials for deploying the passive samplers. Since the period of deployment account for certain duration of time, theft and vandalism are among the risks.

The sampling points where deployment of the passive samplers will be done should be representatives of the site. The time of retrieval is defined by the sampling interest. The samplers need to be kept at the required temperature (4°C for DGT and 0°C for the POCIS). Thermo coolers and ice packs can help. It might need time before the analysis can be done. So, in the meantime, samplers can be kept at the cold compartments. Unlike, the samples taken from the conventional method, passive samplers have longer shelf life. In the laboratory, extraction is a requisite before performing the analysis. In between, clean-up and other preparation methods are applied. These depend on the protocol of the laboratory.

Results are firstly given in mass. Then calculations are performed in order to get the concentration each element. The value of the concentration is of time weighted-average (TWA). If there is contamination, it is easier to trace. Blanks can help in this aspect. In addition, the duplicates and triplicates can give information and help verify which among the values are considered outliers. After the values are validated data treatments can be applied (e.g. statistics). Data interpretation could be complicated. Like other sampling techniques, the results need supplementary information which goes back to the site background and

environmental parameters. Table II.4 provides a summary on the differences in employing the conventional vs. the passive sampling technique.

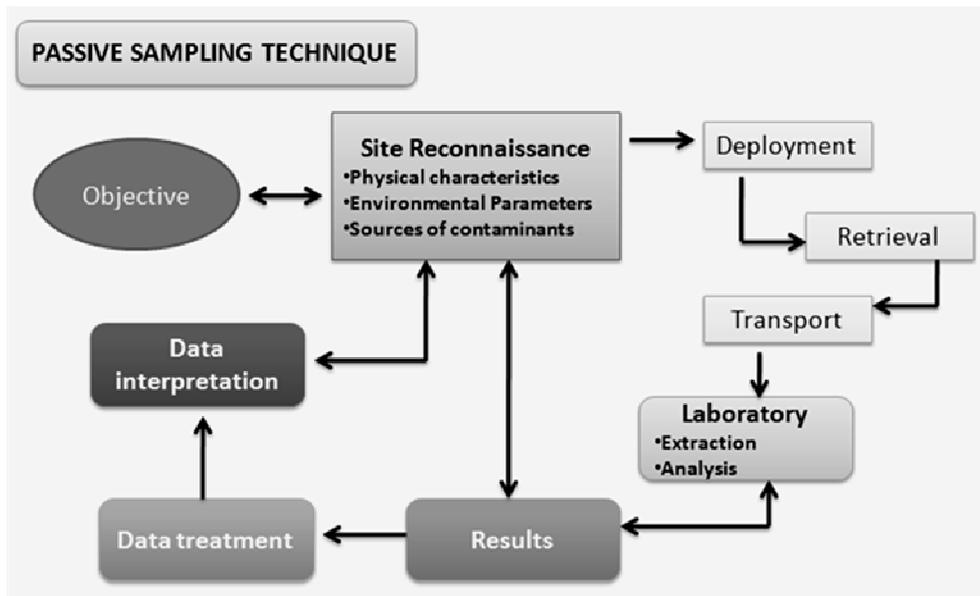


Figure II.6. The passive sampling schematic diagram from the research objective to data interpretation (cited from Chapter II).

## On-site operation: Field protocols

### Box 1. Site Reconnaissance:

#### Ocular site visits

1. Inspect the sites by conducting visits before installing the samplers.
2. Environmental factors such as turbulence, possible biofouling, ambient and water temperature and water pH should be checked.
3. Identify and locate the possible contributor of contaminants including the vapor-phase sources.
4. Select the sites that can best represent the system needed to be monitored.
5. Make sure that the selected sites are accessible and secure.
6. Conduct a water quality test and system examination (in the selected sites) by considering the following environmental parameters "at the very least" (additional parameters will depend on the system and the objectives):
  - pH (DGT works for pH 5-9)
  - water flow and depth
  - organic carbon (total and dissolved)
  - ionic strength
  - suspended matter
  - conductivity
  - chlorophyll concentration
  - dissolve oxygen (DO)
  - partition coefficient (e.g. POCIS works with  $\log k_{ow,s} < 3$ )
  - biological oxygen demand (BOD)

The abovementioned parameters *should be monitored also in parallel* to the passive samplers deployed.

7. If possible, particle size and characterization in the system is highly advised.
8. Consider the following:
  - a. Keep away in areas with high suspended solid discharge. If not, make sure to make or put possible obstruction.
  - b. Consider what type of canisters to be use for deployment. As samplers are so sensitive, consider using materials that will not contribute to the samplers.
  - c. For the canisters to stay immersed in the water, weights such as blocks are encouraged.

**Box 2. Pre-deployment****Before deployment**

1. Record the following data:
  - a. GPS coordinates: in decimal degrees and with at least four decimal places
  - b. Elevation
  - a. Accurate time and date
  - b. DO
  - c. BOD
  - d. Water temperature
  - e. Ambient temperature
  - f. Salinity
  - g. pH
  - h. Conductivity
  - i. Wind direction
  - j. Turbidity
  - k. Alkalinity
  - l. TSS
2. Some other observations could be noted down. Take some photos of the site specially if there are notable observations.
3. When transporting, make sure that each passive sampler is in an air-tight container.
4. Make sure that the samplers are in cold compartments. This is before deployment, upon retrieval and when transporting.
5. Samplers should be kept sealed prior to deployment. DO NOT remove from the sealed plastic bag unless is the time for deployment.

**Box 3. Immersing the passive samplers****Deployment**

1. The one who will deploy and collect the samplers should not smoke!
2. Hands should be clean.
3. Do not use hand lotion, perfume, colognes and other chemicals that might affect the samplers.
4. Use powder-free hand gloves.
5. White filter or the membrane (at the face of the unit) SHOULD NOT be touched. No contact on anything should be allowed.
6. Make sure that deployment of samplers is in duplicate (n=2) or triplicate (n=3) per target time and objective.
7. Do not forget the blank samplers (the same recordings should be done as well). This should be opened (i.e. opening the plastic or the case), once the 1<sup>st</sup> sampler to be immersed was open. The time that the sampler is immersed, put the blank back to its original container.
8. Samplers should be deployed immediately (minutes) right after it was removed from the plastic seal. So secure and place them in the canister as quick as possible.
9. Full immersion of the canister is needed to make sure that the water reaches the samplers.
10. If using samplers for organics, make sure that they are protected from sunlight all the time.

**Box 4. Retrieving the passive samplers****Retrieval**

1. Make sure that all the materials are all prepared.
2. The person who will get the samplers should follow again the protocol of deployment no. 1-5.
3. Immediately, remove the samplers from the canister.
4. Carefully, rinsed them with de-ionized water. Remove the surface water but do not dry them.
5. Put them in the allotted and properly labeled plastics or wrapper.
6. Place each in an air-tight plastic.
7. Put them in the cooler and keep them in the proper storage area.
8. Should be kept in the cold compartment until the time of extraction.

Table II.4. Conventional method vs. passive sampling technique

Factor	Conventional sampling	Passive sampling
1. Site (system)- site characteristics and environmental parameters	Site reconnaissance	Site reconnaissance  Secure from bio-film, high turbidity, suspended solids  Depending on the passive sampler to be use check the limitations (e.g. DGT is not advisable for water that has low-ionic force and works on pH 5-9 only).
2. Sampling (Operation)- Deployment	Grab: instantaneous Needs to do it more than once Tedious	Continuous (deployment) Needs security Non-laborious
Transport	Needs to be kept in cold compartments Bottles should be properly and securely sealed	Needs to be kept in cold compartments Should be kept in an air tight container
Conservation	Limited time: Analysis should be done in less than a week.	Has longer shelf-life
3. Sampling time consideration	Depends on the duration specified by the objective but the collection will be intermittent	Inorganics- days to months Organics- a week to months
4. Laboratory Analysis (Analytical Procedure)	If the target is the free-ions (which is very challenging in the case of trace metals): Needs bulk of water Needs preliminary method and analysis to take out the said fraction	Needs extraction and Clean-up  Depends on the methods and processes indicated in the specific laboratory
5. Results	The result of each sample provides a concentration of the sampling point at the instant (exact) time of collection.	Time-weighted average (TWA)  Values are directly the mass/concentrations of <i>free-ions</i> (as this is the target)
6. Interpretation	Information about the site, sources of contaminants, environmental parameters should be known hand-In-hand	

## 7. Synthesis

The passive sampling devices offered a lot of advantages in water quality monitoring and assessment. Sampling procedure in the local site is not as laborious and more practical than the conventional method. Operationally, this is valuable even to the unskilled people who usually are the ones that go to the field to do sampling, if properly trained with the protocols. Figure II.7 demonstrates the existing different water quality sampling methods and how they work in the system. Limitations are shown also in this figure.

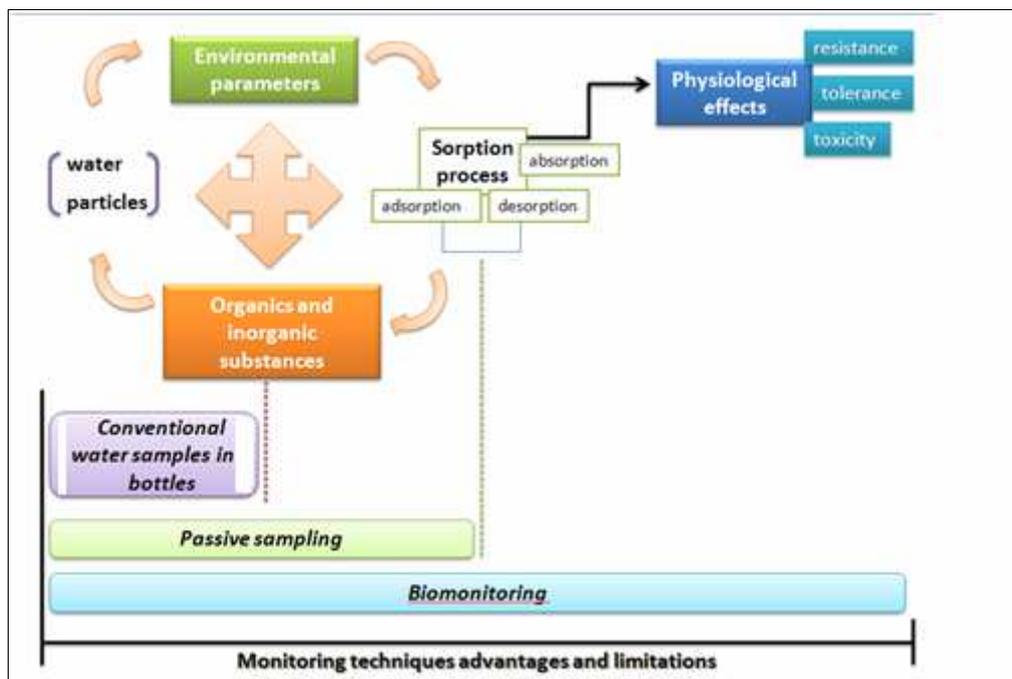


Figure II.7. Simple diagram describing the advantages and limitations of different monitoring technique with regards to the function to the water body

Passive sampling captures the important fraction (*free-ions*) that can influence the composition of bio-organisms and the aquatic system. But, with respect to analytical reasoning, passive sampler does not function fully or cannot be equated to bio-monitoring. The former limits to adsorption, while, the latter considers absorption and the biological processes necessary to evaluate the full biological effects of a certain contaminant.

The degree of contaminant accumulation in an organism processed through uptake, distribution and elimination (Björk 1995). However, passive samplers are not capable of processing or doing neither the physiological regulation nor the biotransformation within the organism. Thus, the passive samplers are only capable of determining the trend and

distribution of these molecules in the water. The “potential or possible” level that could or might cause danger or toxicity in the organisms due to the exposure to that particular contaminant in the system needs additional measurements. Therefore, in using the passive sampling devices make sure that the objective corresponds to the use.

## 8. Conclusion

- The pertinence of the passive sampling technique in the field of water quality monitoring and assessment is valuable.
- This method can detect the presence of the analyte molecules to the ultra-trace level.
- The in-situ process and the capability to capture the *free-ions* give more edge to the passive sampling technique than the conventional (e.g. spot and grab) sampling approach for aquaculture system and environmental concerns.
- The operation of passive sampling deployment is more practical and straightforward than the conventional sampling method. It lessens the collection time and quantity of samples.
- In the laboratory, in using the conventional sampling, there is a subsequent step in order to take out the free-ion fractions and bulks of water samples are necessary. The passive samplers collect directly the free-ions then analysis includes extraction and cleaning. Apart from this method, the analytical processes follow the same as the conventional way.
- The results offer the distribution of the molecules in the water. These molecules are important due to their *potential risks* or damage to the aquatic system that *might* eventually lead to the level of toxicity (depending on the biological reaction).
- Passive sampling *does not* equates bio-monitoring.
- Interpretation of the passive sampling results requires the knowledge of the environmental parameters and site characteristics. This is the same also when doing the interpretation for the conventional and bio-monitoring processes.

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**CHAPTER III State of the water quality of Jalle River and  
Bordeaux Lac in France: An assessment and  
documentation of the field and laboratory experiences**

## 1. Introduction

Water contaminants come from direct and indirect discharges of different substances and components to the water bodies. Rainfall and surface run-off serve also as media for pollution transport to the water column (Schüssler and Nitschke 1999). The apparent effects of human-induced activities produced growing awareness and concern on the environmental issues vis-à-vis the water quality (Barba-Brioso *et al.* 2010; Zulin and Liangliang 2007; Goldar and Banerjee 2004; García-Barcina *et al.* 2006; Dowd *et al.* 2008; Garcier 2010). The distress is on the potential risks of the contaminants to the ecosystem, biological community and public health.

Regulation is an imperative matter of interest. The Water Framework Directives was created aiming to have safe and clean water resources. Among the objectives of the WFD are to (Strobl and Robillard 2008; WFD 2003): classify the status of all water bodies or groups of water bodies, support risk assessment procedures; design future monitoring programs, and appraise long-term changes whose causes are both natural and anthropogenic. In the WFD legislation, it requires monitoring of the “water quality elements” such as (Madrid and Zayas 2007): physicochemical properties (temperature, density, color, turbidity, pH value, redox potential, conductivity, suspended solids, total/dissolved organic carbon); and chemical monitoring (with particular emphasis on the contaminants in the list of priority pollutants). These means that having effective water quality monitoring and assessments is necessary. However, water monitoring and sampling approaches are crucial issues in terms of measuring different contaminants in the aquatic environment (Budka *et al.* 2010).

There are short-comings of doing grab sampling as identified by Söderström *et al.* (2009). In order to arrive to adequate concentrations, large volume of water is necessary to be collected. There are preliminary steps needed (like pre-treatment) to minimize the alterations of the analyte concentrations. Samples represents only levels at a specific time and place (in that particular site where the samples were grabbed at the exact/instant time of the collection).

In this case the in-situ passive sampling technique provides a lot of advantages. They represent the freely dissolved fractions of an analyte molecule (Monteyne *et al.* 2013). This technique is less sensitive to accidental extremes (Kot *et al.* 2000). Samplers have good affinity to the target analyte; allows detection of the compounds at very low concentration

(Monteyne *et al.* 2013). Analyte concentration is integrated over the exposure time (Vrana *et al.* 2006).

The passive sampling technique involves probes/samplers that are capable of sequestering the freely dissolved aqueous contaminants of water (Emelogu *et al.* 2013). The phase of collection allows the analyte molecules in the water to diffuse around the boundary layer then to enter to the membrane through filtration and kinetic law. The receiving phase allows sorption followed by a sink of the analytes.

In this study, there are two (2) interesting sites located in Bordeaux, France. These are the Jalle River and the Bordeaux Lac. Each exhibits different interesting system characteristic. The former is one of the tributaries of the Garonne River. The stream passes to the Marais Natural Reserve which serves as habitat for some important aquaculture species. The latter is a (semi-)close, man-made system built on the 1960s (around 160 Ha). Both sites have a channel which serves as a waterway for the rainwater and surface run-off. The research objectives are: (1) to develop an effective sampling approach appropriate to the sites that will incorporate passive sampling (using the Diffusive Gradient in Thin Films (DGT) for the trace metals and the Polar Organics Chemical Integrative Sampler or POCIS for organic compounds) as a technique for water quality monitoring; (2) to assess the water quality of the sites (spatio-temporal trend); (3) to provide a baseline water quality data by measuring different kinds of molecules and substances (trace metals and organics); and (4) to document the experiences in employing the passive sampling technique in the field.

## 2. Materials and Methods

### 2.1. Sampling sites

As mentioned, both chosen sites in Bordeaux have a channel that collects the rainwater and surfacewater that directly discharge to the water system (Jalle River and Bordeaux Lac). Each exhibits two different kinds of systems. The former having a flowing and open system while the latter is a semi-closed one.

1. Jalle River that discharge to Garonne River. Within the chosen site, contribution of fluxes comes from the upstream. Sampling points are described in Figure III.1. Sampling point 1 (**JRrd**) is near the departmental road (Rocade Nord). Sampling point 2 (**JRC**) is at the collector where the rainwater and surface run-off pass and the discharge immediately reach the river. Sampling point 3 (**JRvf**) is at the railway (2 to 4 trains pass daily). Sampling point 4 (**JRrn**) is at the Marais Bruge Natural Reserve where it serves as a habitat for aquaculture species.

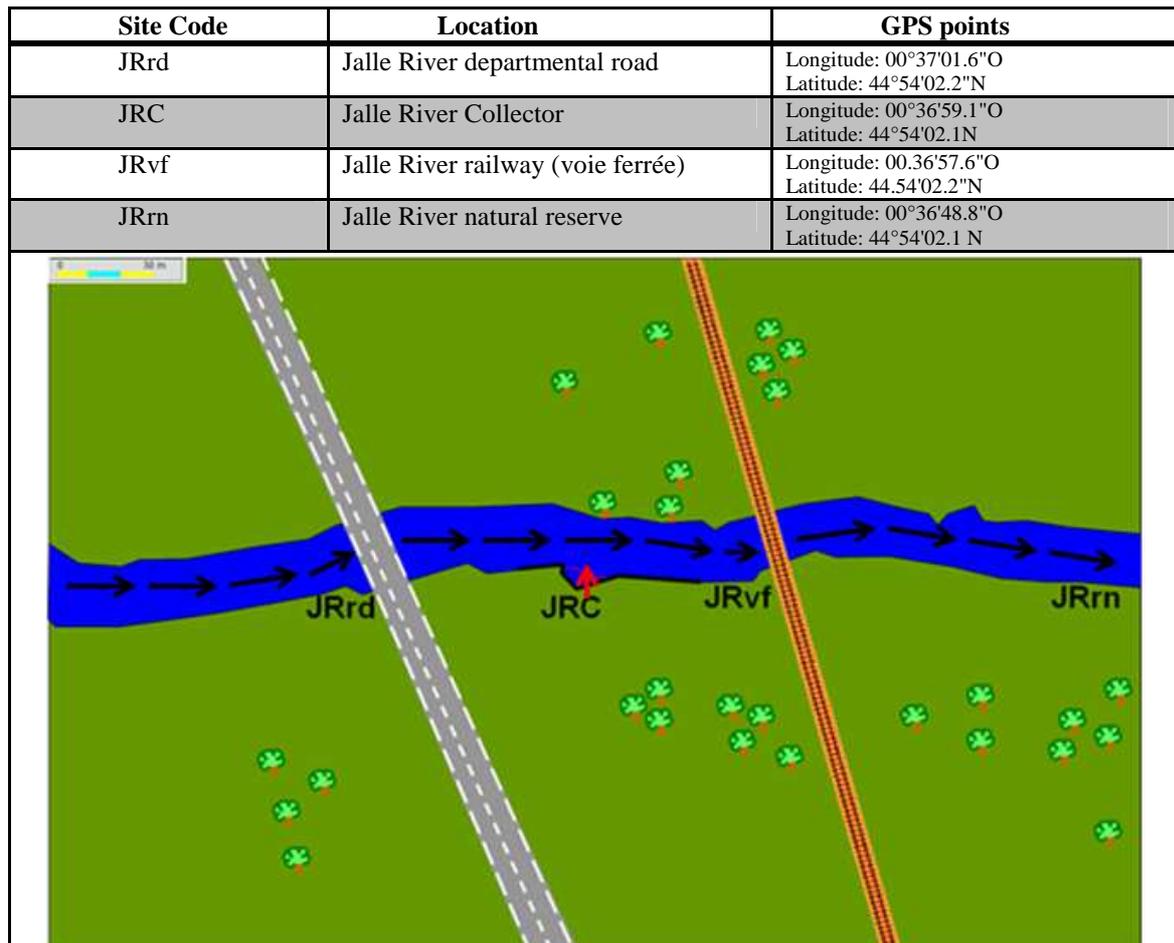


Figure III.1. Sampling points of the Jalle River site

2. Bordeaux Lac is a man-made lake. Four (4) sampling points are also chosen (Figure III.2). Sampling point 1 (**BLC**) is at the collector which also serves as the channel for both the rainwater and the surface run-off to directly allow discharge to the lake. Sampling point 2 (**BLbn**) is at the sailing school (Basse Nautic) at the pontoon. This area functions as a recreational spot. Sampling points 3 (**BL1m**) and 4 (**BL6m**) are placed roughly at the center at different depths (1meter and 6 meters, respectively).

Site Code	Location	GPS points
BLbn	Bordeaux Lac pontoon (Basse Nautique)	Longitude: 00°34'50.7" O Latitude: 44°52'51.23N
BLC	Bordeaux Lac Collector	Longitude: 00°34'38.2"O Latitude: 44°52'41.63N
BL1m	Bordeaux Lac 1 meter deep	Longitude: 00°34'44.1"O Latitude: 44°53'11.13N
BL6m	Bordeaux Lac 6 meter deep	Longitude: 00°34'44.1"O Latitude: 44°53'11.13N

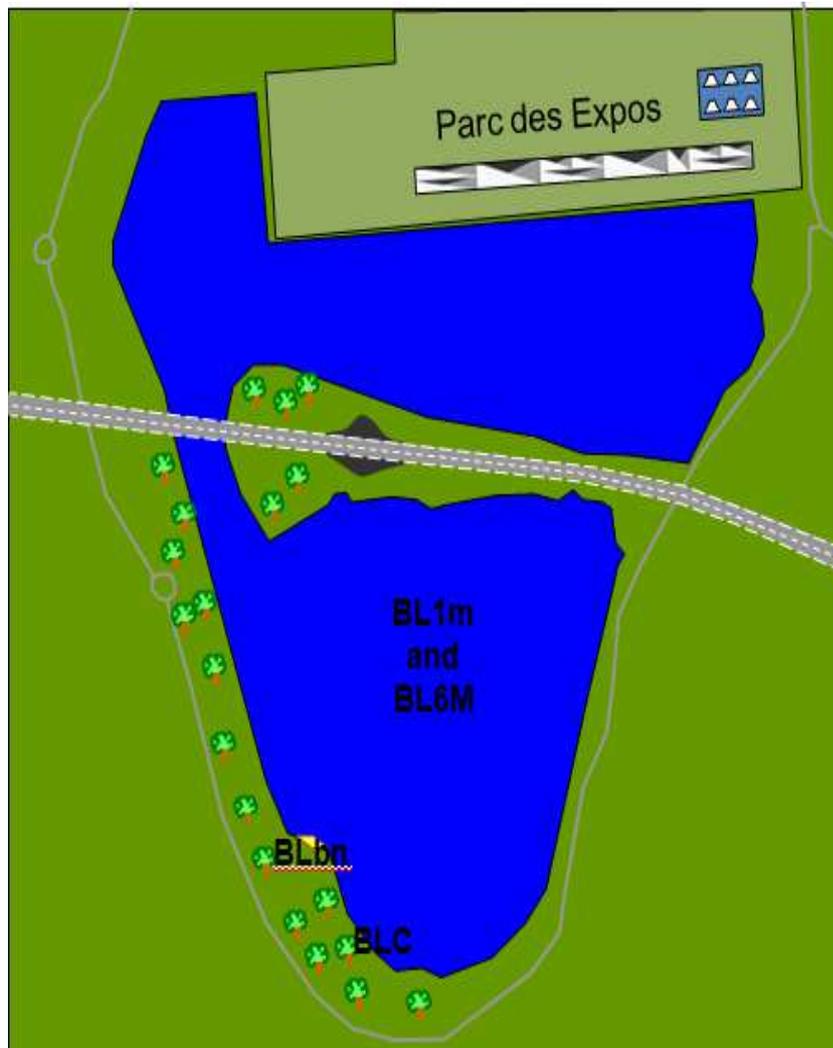


Figure III.2. Sampling points of the Bordeaux Lac site

## 2.2. Climate Background (Precipitation for the year 2011)

### 2.2.1. France

The year 2011 is considered as the warmest (Figure III.3) and driest (Figure III.4) year of the 20<sup>th</sup> century. During winter, deficits in rainfall were observed during January and February. The spring was so distinct and exceptional with very low rainfall and high temperature in France. La Météo France noted that the spring in this year was the driest of the last fifty years. The months March, April and May were gave remarkable rainfall shortage.

Summer was humid. This season experienced frequent rainfall. The temperature in June was higher than normal (1971-2000). Whereas, July's temperature was lower than normal. This month was rainy. The decrease in temperature continued in August. The rainfall condition varies among regions.

Autumn was also warm and dry this year. The rainfall varied differently as there were parts that had excess rainfall at the same time there were parts (like in the SW) that experienced substantial rainfall deficits. September was warm and very dry. This condition was prolonged to the months of October and November.

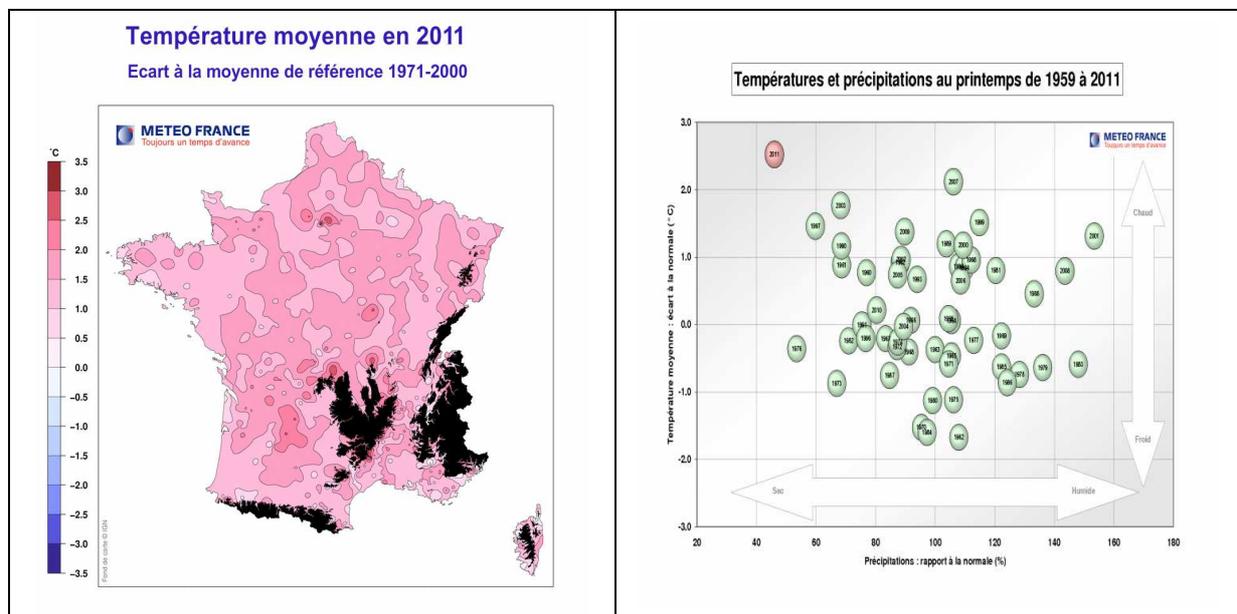


Figure III.3. Average temperature (Meteo France)

Figure III.4. Precipitation vs. Temperature accentuating year 2011 as an exceptional year (Meteo France)

## 2.2.2. Bordeaux (Cantinole 2011)

In Bordeaux, the year 2011 is considered exceptional as this is when it got the least rainfall since the 1970s. The total amount of rainfall (Figure III.5) for the whole year was 654.3 mm which is far from the normal annual total (1980-2010) rainfall (902.9 mm). Bordeaux received only around 72% of the normal annual total rainfall rate of the years 1980 to 2010. From all the months, only February, July, August and December exceeded the normal monthly average rainfall. Other months received only 20%-53% of the expected/normal monthly rainfall.

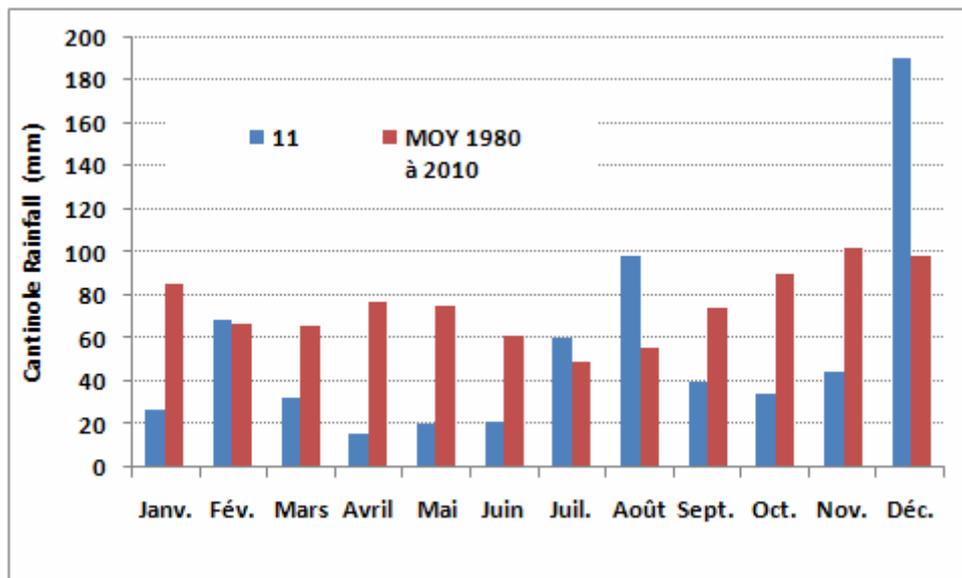


Figure III.5. Year 2011 vs. the average rainfall rate from 1980-2010

April is the month when least rainfall amount was received. It received 15.7 mm which is very far from the monthly average rainfall which is 77.2mm. This is only 20% from the monthly average. May has only 20.6 mm lesser than the normal monthly rainfall (which is 75.3mm); only 27% of the normal. June received only 21.2 mm from the expected approximate of 75.3mm (normal monthly average) that is only 28% from the normal. July is contrary to most of the months. It received 60.6 mm of rainfall which is which is 22% higher than the normal. August is like the previous month, it received higher amount of rainfall (98.3mm) compared to the normal month average (55.6). It received 43% higher than the normal.

### 2.2.3. Rainfall behavior during sampling

Sampling campaigns occurs in May for the first and August for the second (Figure III.6)

#### 1st sampling campaign

Two months before the sampling for the 1st period was done, the months of March and April did not receive the expected rainfall (66mm and 77mm respectively). March had 32.4 mm while April had 15.7mm. The scarcity of the rainfall continued while the 1st sampling period was conducted (Bordeaux Lac June until 4th of July; Jalle River: May). This season is considered as a dry period.

#### Accumulated rainfall within the sampling dates

Jalle River

May 7 - 2.8 mm

May 7-14 - 3.2mm

May 7-21 - 3.4 mm

Bordeaux Lac

June 20 - 0 mm

June 20-21 - 0mm

June 21-27 - 1mm

June 21-July 4 - 1.2 mm

Amount of rainfall 10 days before sampling: JR: 5.4 mm; BL: 7.0 mm

Amount of rainfall 20 days before sampling: JR: 6.6 mm; BL: 20.0 mm

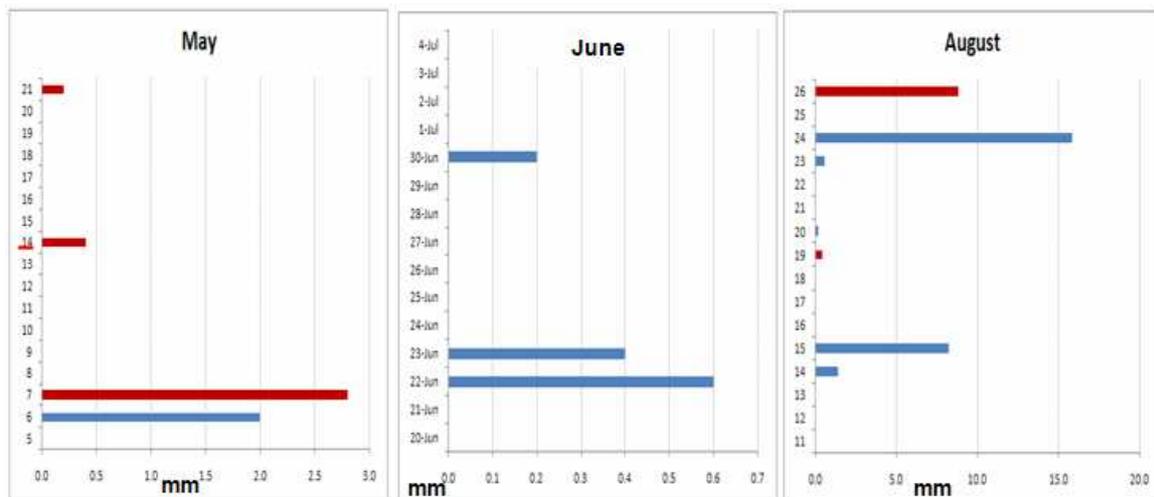


Figure III.6. Rainfall rate (in mm) during the sampling campaign

## 2nd sampling campaign

On July, the rainfall started on the 7th. The months of July and August gave rainfall records that are higher than the monthly normal average. Although, the year 2011, was considered a very dry year, these months succeeded in having rainfall above the normal monthly average. Thus, this season can be considered the wet period.

Accumulated rainfall within the sampling dates:

- August 12 - 0 mm
- August 12-19 - 10 mm
- August 12-26 - 35.4 mm

Amount of rainfall 10 days before sampling: 61.8 mm

Amount of rainfall 20 days before sampling: 71.8 mm

## 2.3. Sampling approach

The sampling scheme (Figure III.7) used in this research was applied for the selected two (2) periods. As mentioned before, Period 1 corresponds to the dry season while Period 2 was a wet one. Grab water samples were collected intermittently starting with Day 1 then after seven (7) days corresponding to the Day 7 (the 1<sup>st</sup> week) until Day 14 (the 2<sup>nd</sup> week), in parallel to the passive sampling. The molecules measured using the conventional sampling represent the total fraction.

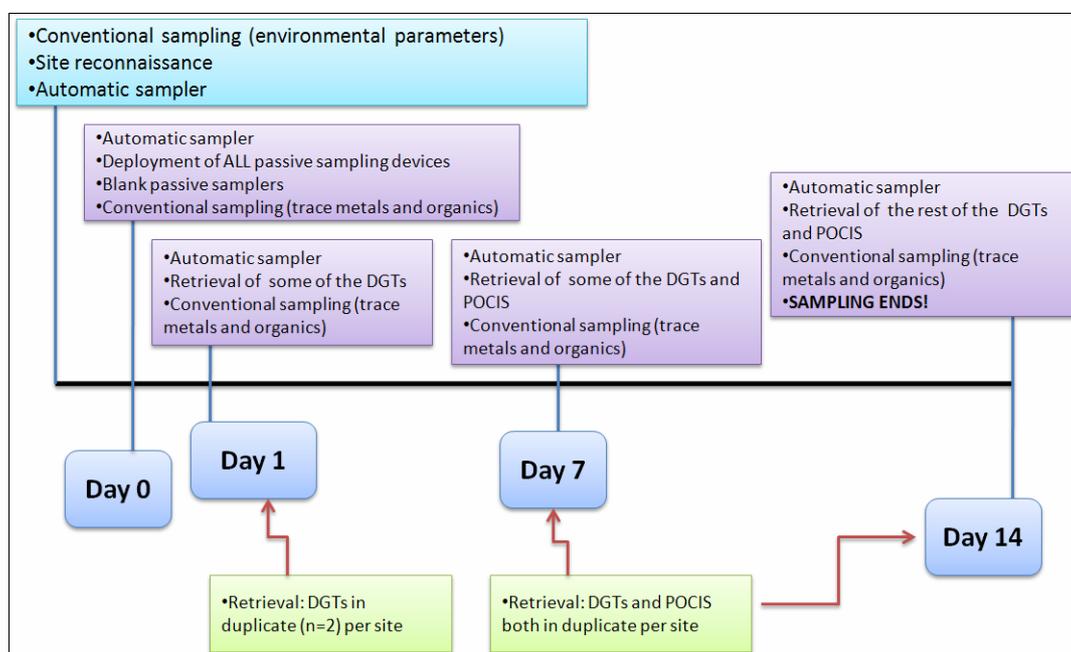


Figure III.7. The sampling scheme for the Jalle River and Bordeaux Lac sites

DGT samplers were immersed considering: 1 day (24h), 7days and 14 days. This means that in each sampling point, the samplers were retrieved at the target duration, otherwise, left immersed (i.e. 6 DGTs were immersed then each time 2 DGTs were retrieved and others were left immersed until the right time). For POCIS, 7 and 14 days were considered. They were immersed in duplicates (n=2) also in each site and each time collected at the target time (i.e. 2POCIS x Day 7 and Day 14 = 4POCIS immersed).

Passive samplers (6 DGTs and 4 POCIS) are deployed in each of the site for each period. All the passive samplers were carefully put inside a specially woven basket made from all natural raw materials. Typically it is use as a duck trap (*piège à ponte de canard*). This was chosen because the size can accommodate all the passive samplers. At the very least, the materials used is expected not contribute in any of the target compounds. The materials used are neither non-metal, nor pharmaceutical nor pesticides based. Each of the samplers was tied properly so that floating and bumping into each other can be prevented. This could bring damage or could hurt a membrane of a sampler. After making sure that all the passive samplers are in the right position, the basket type container was covered by a nylon fishnet with fine mesh.

In point of fact, planning on when to start was a great challenge. This is since the rainfall behavior during the sampling periods was very erratic (as previously discussed) due to precipitation and temperature rates. This then caused difficulties to have the exact request in terms of the access and use of the automatic samplers. Normally, the automatic samplers are not readily available anytime, unless, request was made. That resulted to incomplete information about the environmental parameters such as water conductivity and dissolved oxygen.

Nevertheless, baseline information can be provided in this research. Prior to the sampling campaign, a screening process was made that can describe temperature, pH, conductivity, ionic strength, hardness, total organic carbon (TOC), Zeta Potential and mean particle size. This was conducted on the 20<sup>th</sup> of April 2011.

The range is as follows for the Jalle River (Figure III.8): air temperature - 25-27 °C; water temperature - 17-20 °C; pH - 7.6-8.3; conductivity - 335-449 µS/cm; hardness - 102-117 mg eq CaCO<sub>3</sub>/L; TOC - 4.52-4.84 mg/L; Zeta Potential - (-12.07) to (-10.97) mV; and mean particle size - 147-217 nm. Here, it shows that the conductivity is relatively high.

And for Bordeaux Lac is as follows (Figure 9): air temperature - 24-27 °C; water temperature - 12-18 °C; pH - 8.3-9.1; conductivity - 382-392 µS/cm; ionic strength - 0.0061-

0.0063 M; hardness - 102-117 mg eq CaCO<sub>3</sub>/L; TOC - 7.84-8.46 mg/L; Zeta Potential - (-13.33) to (-9.09) mV; and mean particle size - 83-354 nm. The minimum temperature of the water recorded is at 5 meter deep.

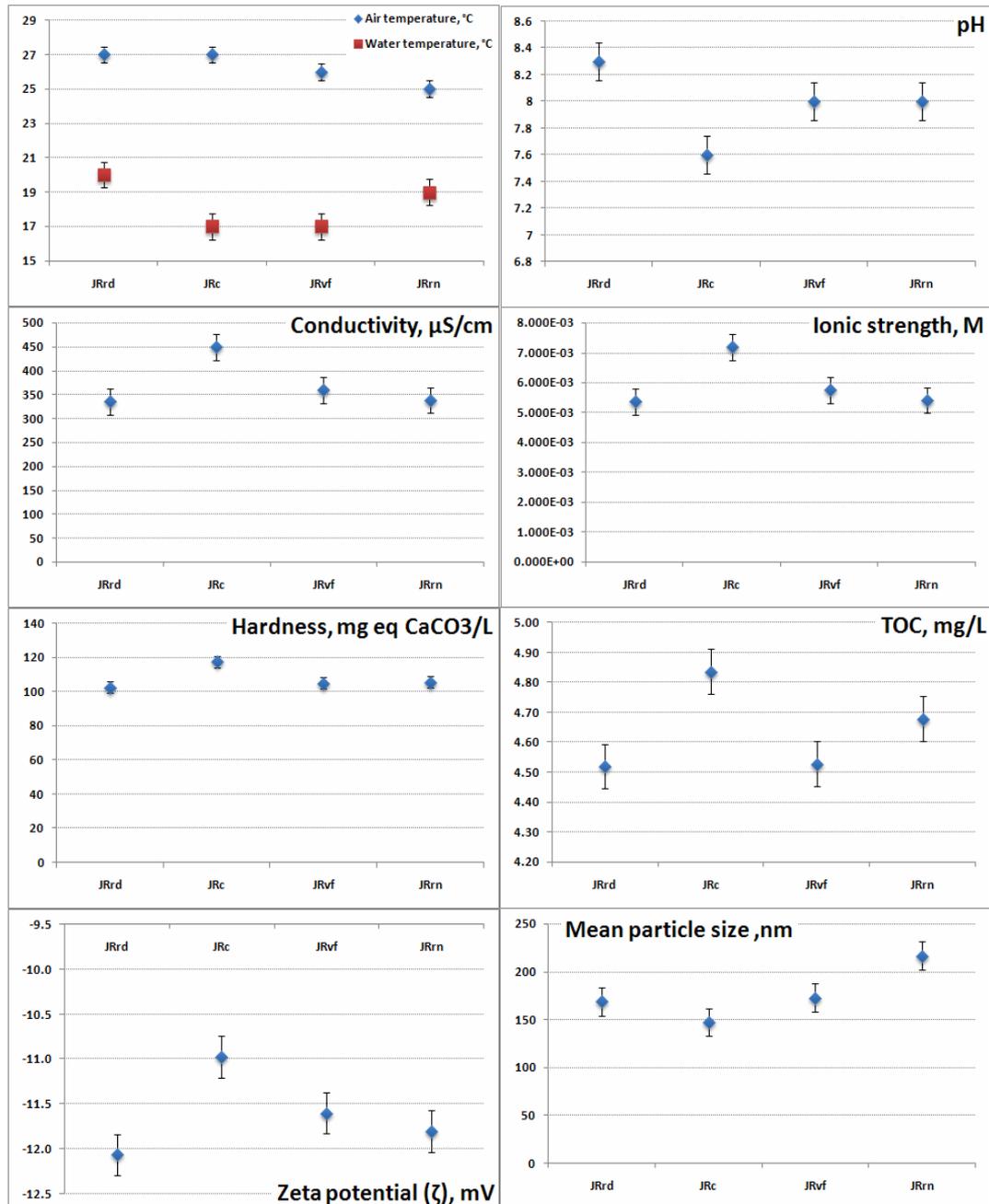


Figure III.8. Measured environmental parameters for the Jalle River

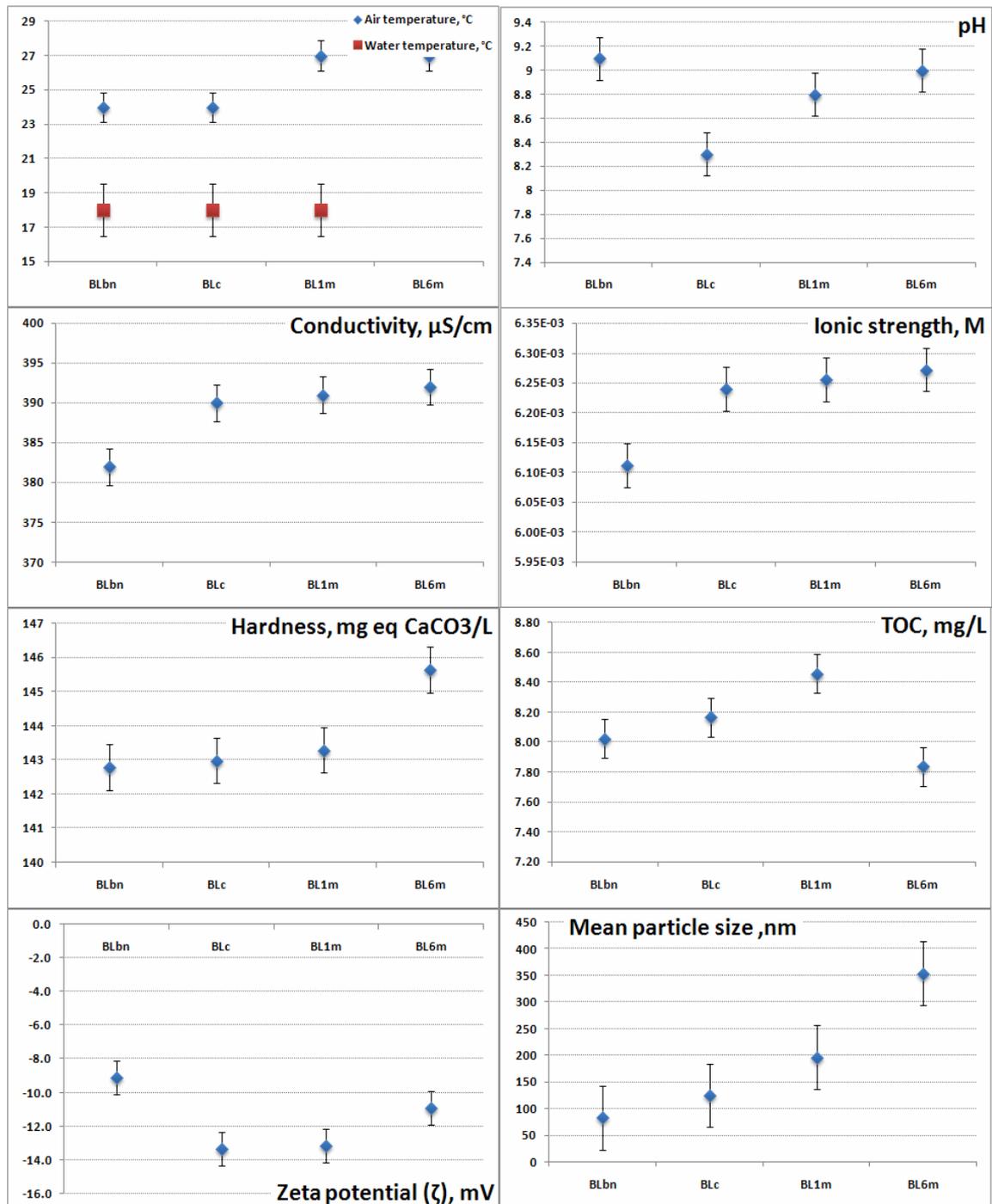


Figure III.9. Measured environmental parameters for the Bordeaux Lac

Using the conventional method, collecting water samples was done manually. Each bottle was immersed to the water and then immediately covered with a cap (to avoid airborne contaminants). There should be no air bubbles so it has to be checked. If there is, the procedure should be repeated. Make sure to collect water for trace metals at the last. For collecting waters with specific depth at the Bordeaux Lac (1 and 6 meters), Van Dorn water sampler is used (Figure III.10).



Figure III.10. Van Dorn water sampler (source of the picture on the right: Ecoenvironmental)

## 2.4. Materials and Quality control

Ultrapure Milli-Q water, Type 1, 18.2 M $\Omega$ ·cm was used for de-ionized water. Blank passive samplers were provided for each site for each sampling period.

### 2.4.1. Trace metals

Pre-washed (with nitric acid) 250 mL PTFE plastic bottles were used to collect the water samples for the trace metals. DGTs were purchased at DGT Research Ltd., Lancaster, UK. The Nitric acid used is Analar grade and ICP-MS grade Fortification Standard.

### 2.4.2. Organics

Amber/Brown 1L glass bottles were used for organic water sample collection. These bottles were pre-cleaned in the lab. For the POCIS, stainless metal rings were avoided; instead, aluminum metal rings and Teflon nuts and bolts were used to encase the POCIS sorbents and membrane.

## 2.5. Laboratory Analyses

Water samples in the bottles and POCIS were analyzed at LDAR 24 - PERIGUEUX. For trace metals most of the elements followed the NF EN ISO 17294-2 protocol of Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Elements such as Total Fe, Total Mn, Cu, Ti and Zn followed NF EN ISO 11885.

Organics such as Alkylphenols, Anilines, Chlorobenzenes, Chloronitrobenzenes, volatile and semi-volatile organic compounds, divers micropollutants, polycyclic aromatic hydrocarbon, some of the carbamates pesticides (Carbofuran, Chlorpropham, Propam), pesticide divers (Aclonifen, Benoxacor, Bromoxynil octanoate, Butralin, Clomazone, Cyprodinil, Dicofol, Diméthénamid-P, Ethofumesate, Procymidone, Quinoxylène, Trifuraline, Anthraquinone, and Crimidine), alcohol and nitrophenol pesticide (Ioxynil octanoate), organochlorepesticides (except Dimetachlore), organophosphore pesticides (Vamidotion, Bromophos éthyl, Bromophos méthyl, Carbophénotion, Chlorfenvinphos, Chlormephos, Chlorpyriphos éthyl, Chlorpyriphos méthyl, Diazinon, Dichlorvos, Fenitrothion, Fenthion, Malathion, Parathion éthyl, Parathion méthyl, Phosalone, and Terbufos), pyrethrinoides pesticides, triazine pesticide (Pendimethaline), and plastifiants followed the PS n°215 protocol of A highly sensitive and accurate multiplex gas chromatography–tandem mass spectrometry (GC-MS/MS). While amide pesticides, Aryloxyacid pesticides, other carbamates (Carbaryl, Carbendazime, Carbosulfan, Fénoxycarbe, Pyrimicarbe, Prosulfocarbe, Triazamate, and Aldicarb), pesticide divers (Fénoxaprop-éthyl, Fenpropidine, Fenpropimorphe, Flurtamone, Imidaclopride, Krésoxym-méthyl, Métalaxyl, Métazachlore, Norflurazon, Oxadixyl, Prochloraze, Phoxim, Méthomyl, Prétalachlore, Isoxaflutole, Metsulfuron méthyl, Bromacil (in salt form), Chlorothalonil, Fludioxonil (in salt form), and Fluroxypyr (in salt form)), Bromoxynil and Ioxynil in salt form, Dimetachlore, Oxydéméton-méthyl, strobilurine pesticides, sulfonyleureas, triazines (except Pendimethaline), triazoles pesticides, and urea substitute pesticides followed PS 13/14/11 protocol of the Liquid chromatography-tandem mass spectrometry (LC-MS/MS).

In each of the water quality parameters considered, laboratory procedural blanks were done and detection limit of DGT samples were determined by getting the standard deviation of the blank solution multiplied by three. For DGT, the resin layers were carefully removed using Teflon tweezers. Each resin was placed in a Teflon centrifuge tube with 1mL of 1M of

HNO<sub>3</sub>. To allow elution, the solutions were kept for 24h. Then dilution of the eluent using de-ionized water was applied. The solutions were analyzed using ICP-MS.

## 2.6. Molecules measured

From all the molecules considered (Appendix 1 and Appendix 2), below is the list of molecules measured within the Water Framework Directive or DCE (La directive-cadre sur l'eau) 2000 (reviewed 2008). - In bold, are in the Priority List; with asterisk (\*) are in the Priority Dangerous List; and in Italics are proposed to be included in the Priority List.

- |                                  |  |
|----------------------------------|--|
| 1. *Nonylphenols                 | 2. *4-n-Nonyphénol                             |
| 3. <b>Octyphénol - 4ter</b>      | 4. <b>Benzène</b>                              |
| 5. *Pentachlorobenzène           | 6. <b>1,2,3,5 + 1,2,4,5-Tétrachlorobenzène</b> |
| 7. <b>1,2,3-Trichlorobenzène</b> | 8. <b>1,2,4-Trichlorobenzène</b>               |
| 9. <b>1,3,5-Trichlorobenzène</b> | 10. *Hexachlorobenzène                         |
| 11. *Hexachlorobutadiène         | 12. *HAP                                       |
| 13. *Anthracène                  | 14. <b>Benzo(a)pyrène</b>                      |
| 15. *Benzo(b)fluoranthène ~      | 16. *Benzo(g,h,i)pérylène ~                    |
| 17. *Benzo(k)fluoranthène ~      | 18. <b>Fluoranthène</b>                        |
| 19. *Indéno(1,2,3-c,d)pyrène ~   | 20. <b>Alachlore</b>                           |
| 21. <b>Aldrine</b>               | 22. <b>Total DDT</b>                           |
| 23. <b>Dieldrine</b>             | 24. *Endosulfan                                |
| 25. <b>Endrine</b>               | 26. <b>Isodrine</b>                            |
| 27. <b>Chlorfenvinphos</b>       | 28. <b>Atrazine</b>                            |
| 29. <b>Simazine</b>              | 30. <b>Diuron</b>                              |
| 31. <b>Isoproturon</b>           | 32. *Cadmium                                   |
| 33. <b>Lead</b>                  | 34. <b>Nickel</b>                              |
| 35. <i>Xylène musk</i>           | 36. <i>Mécoprop (sous forme de sels)</i>       |
| 37. <i>Dicofol</i>               | 38. <i>Bentazone (sous forme de sels)</i>      |

Using DGT, trace metals measured are Cd, Co, Cr, Cu, Ni, Pb and Zn. The following pharmaceuticals are measured using the POCIS: Ofloxacin, Sulfaméthoxazole, Bézafibrate, Kétopofène, Diclofénac, Aténolol, Caffeine, Triméthoprime, Epoxycarbamazépine, Erythromycine, Propranolol, Bromazépan, Carbamazépine, Clarythromycine, Oxazépan, and Lorazépan.

### 3. Results and Discussion

#### 3.1. Trace metals

##### 3.1.1. Conventional sampling (grab samples)

##### A] Jalle River

Spatio-temporal trend can be highly observed on the measured concentrations. At Period 1, during Day 1 the following were observed: Fe and Mn, Co, Sn, Sr increased from JRrd to JRC; As, Ni, Zn decreased from JRrd to JRC; below detection at this time of Sb, Cr total, Cu, Pb and U; As and Zn increased from JRC to JRvf; and Fe and Mn, Co, Sn and Sr are highest in JRC. After 7 days, highest values of Fe, Co (JRvf), Mo, Ni, Zn and Sr were at JRC; highest values of Mn, As, Pb were at the JRrn and Sr was highest at JRrd. For the 14<sup>th</sup> Day, Fe, Co, Mo, Ni, Zn were highest at JRC but Sr was found least; Pb was highest at JRvf and Mn was highest at JRrn. The order of trace metals with respect to concentration is shown in Table III.1. Variations of concentrations of trace metals are presented in Figure III.11 to Figure III.14 .

During the 2nd period, as expected, most of the concentrations of the trace elements were found highest at the collector due to rainfall which induced high mass transport and water run-off.

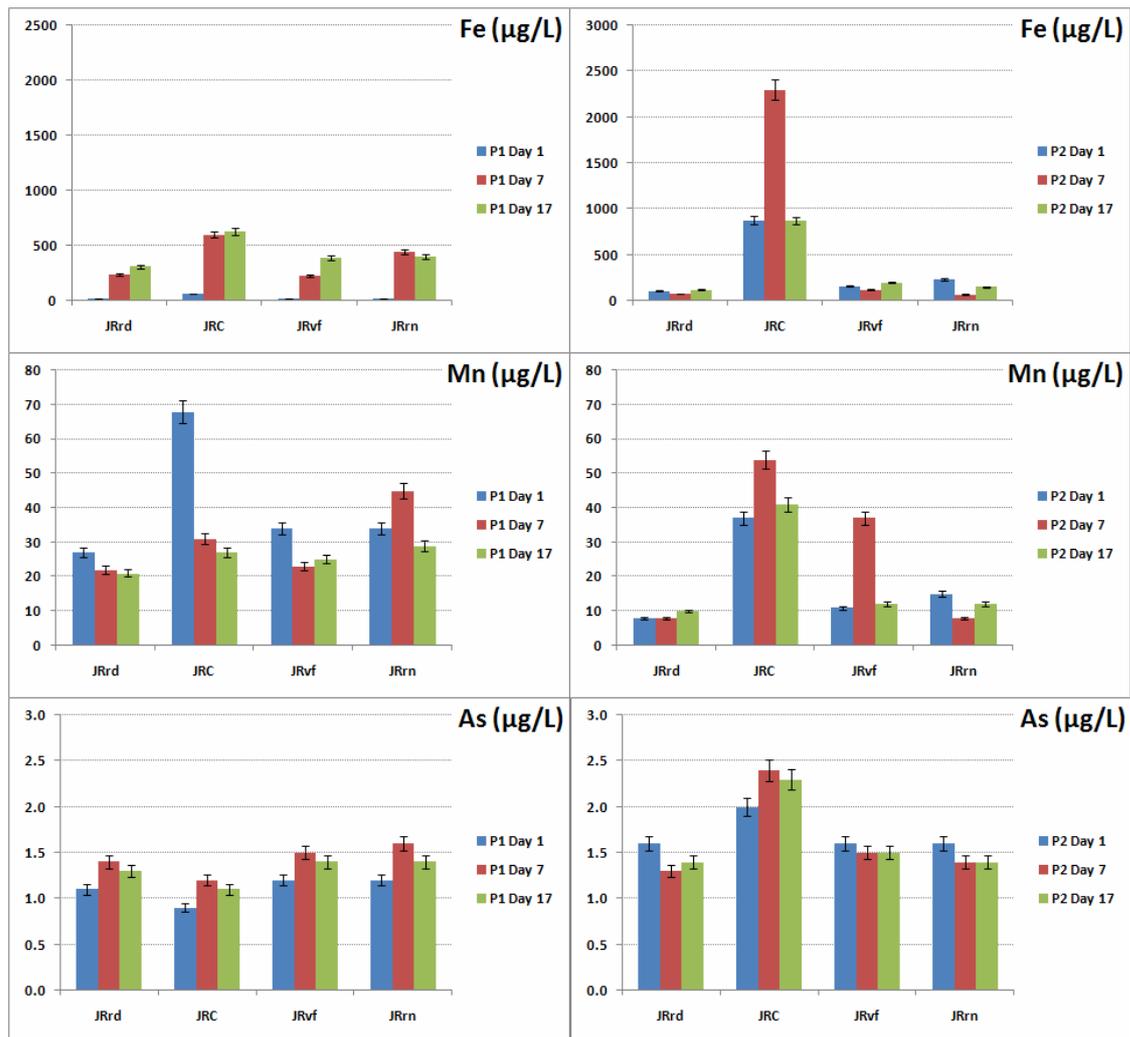


Figure III.11. Measured total trace metals (Fe, Mn and As) for the Jalle River for Period 1 (P1) and Period 2 (P2)

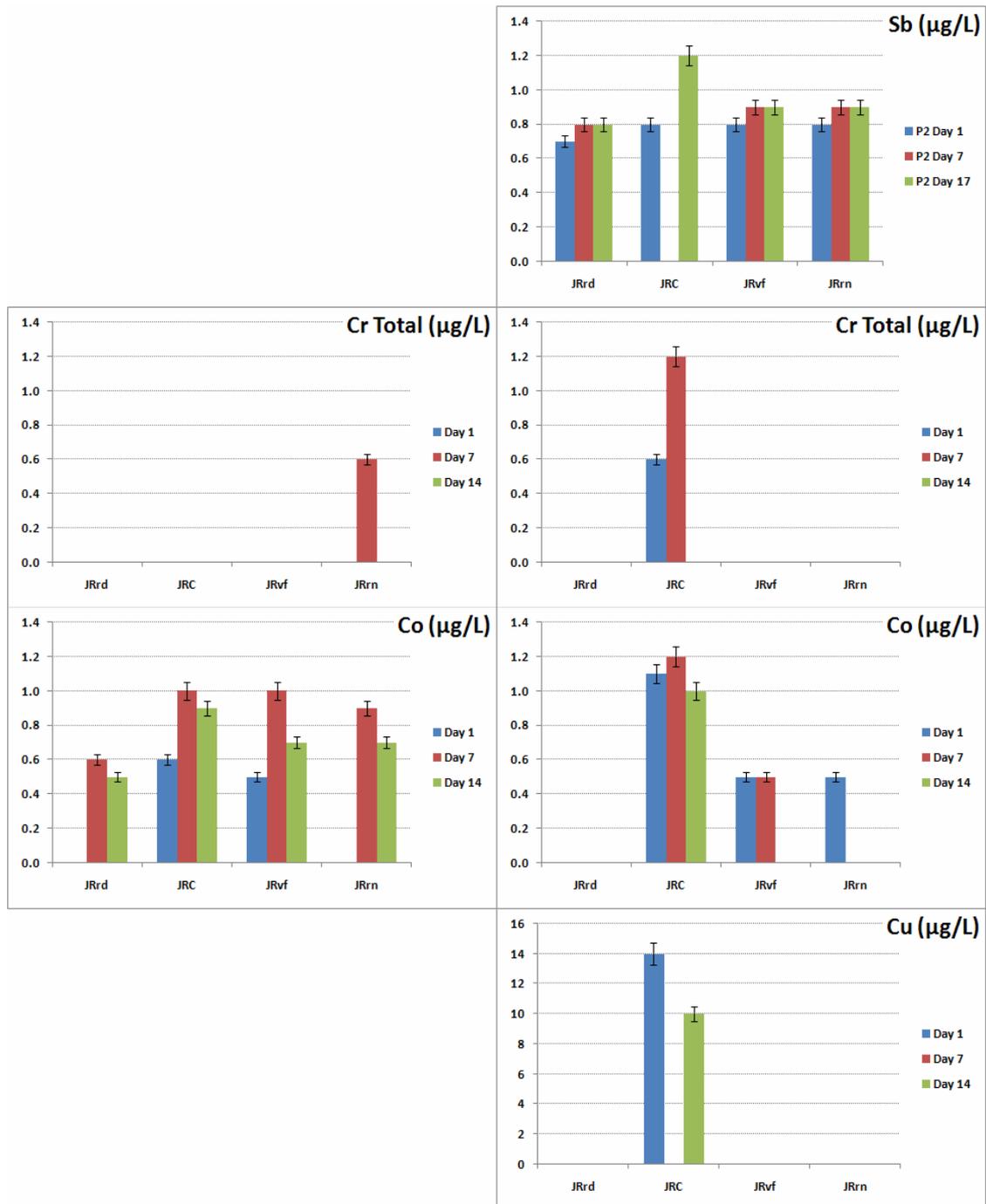


Figure III.12. Measured total trace metals (Sb, Cr total, Co and Cu) for the Jalle River for Period 1 (P1) and Period 2 (P2)

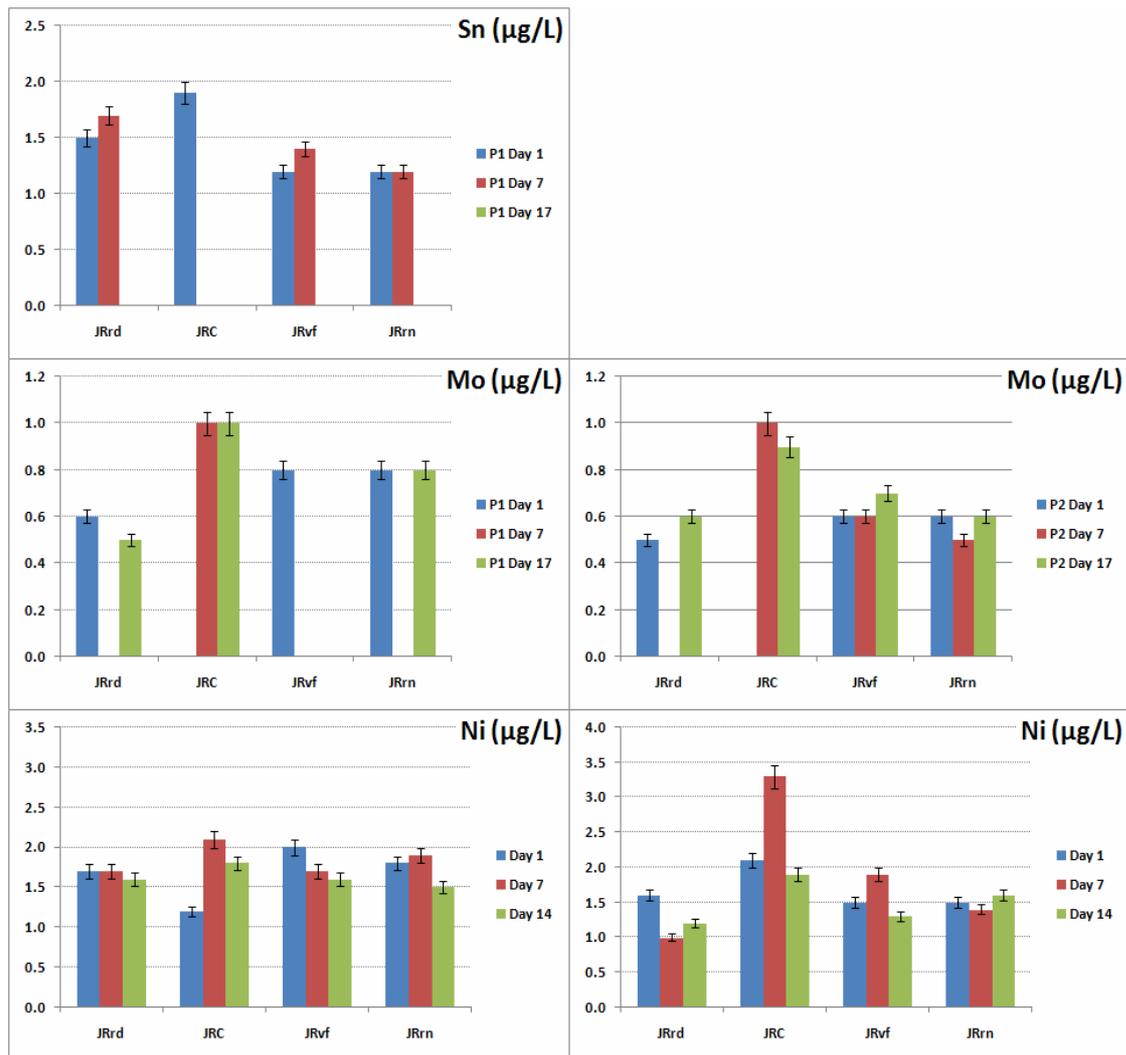


Figure III.13. Measured total trace metals (Sn, Mo and Ni) for the Jalle River for Period 1 (P1) and Period 2 (P2)

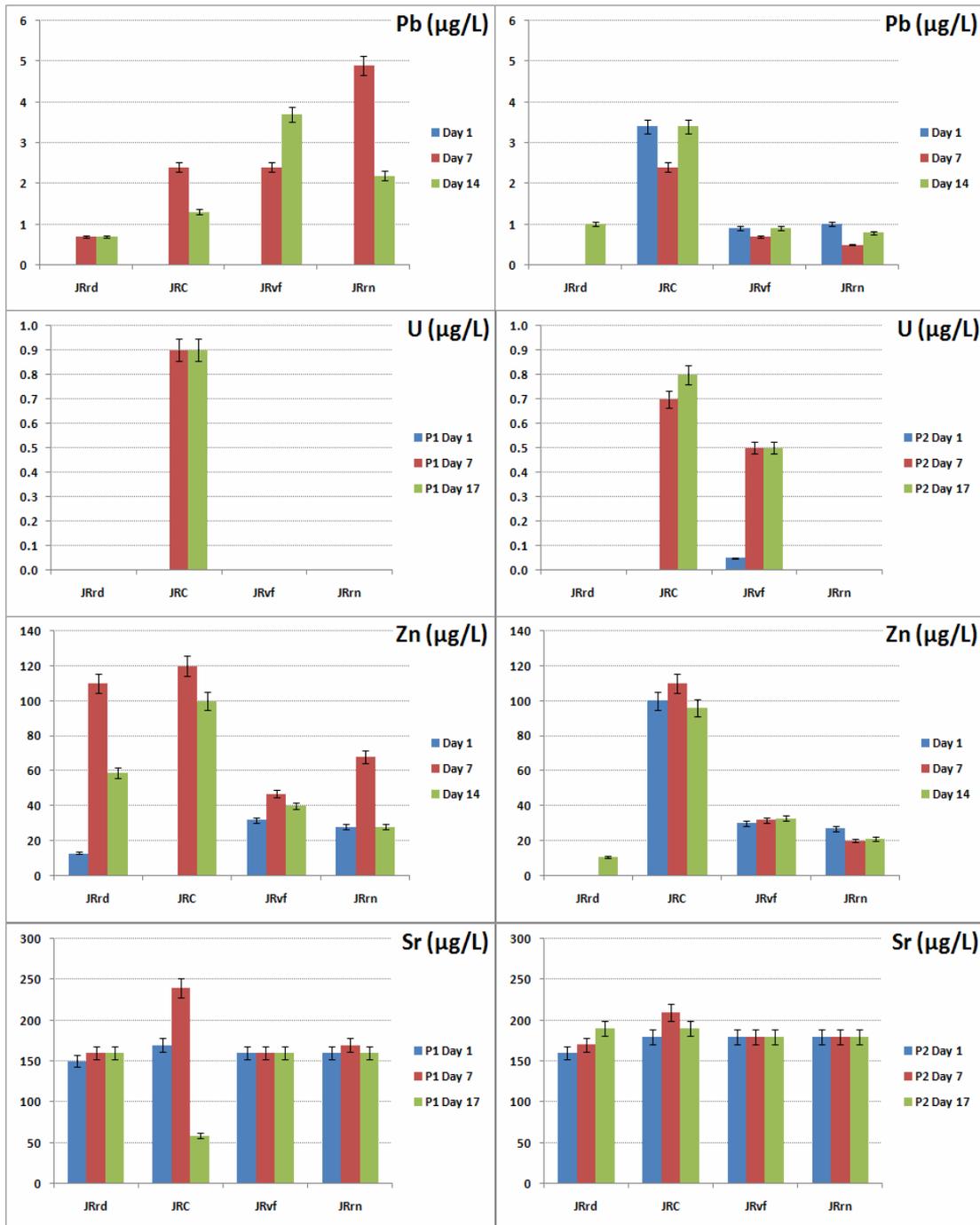


Figure III.14. Measured total trace metals (Pb, U, Zn and Sr) for the Jalle River for Period 1 (P1) and Period 2 (P2)

Table III.1. Order of trace metal concentration

Site	Period 1 Day 1	Day 7	Day 14
JRrd	Sr>Mn>Fe>Zn>Ni>Sn>As>Mo	Fe>Sr>Zn>Mn>Sn>Ni>As>Pb>Co	Fe>Sr>Zn>Mn>Ni>As>Co>Mo
JRC	Sr>Mn>Fe>Ni>Sn>Ni>As>Co	Fe>Sr>Zn>Mn>Pb>Ni>As>Co>Mo>U	Fe>Zn>Sr>Mn>Ni>Pb>As>Mo>Co>U
JRvf	Sr>Mn>Zn>Fe>Ni>As>Sn>Mo>Co	Fe>Sr>Zn>Mn>Pb>Ni>As>Sn>Co	Fe>Sr>Zn>Mn>Pb>Ni>As>Co
JRrn	Sr>Mn>Zn>Fe>Ni>As>Sn>Mo	Fe>Sr>Zn>Mn>Pb>Ni>As>Co>Cr	Fe>Sr>Mn>Zn>Pb>Ni>As>Mo>Co
	Period 2 Day 1	Day 7	Day 14
JRrd	Sr>Fe>Mn>As>Ni>Sb>Mo	Sr>Fe>Mn>As>Ni>Sb	Sr>Fe>Zn>Mn>As>Ni>Pb>Sb>Mo
JRC	Fe>Sr>Zn>Mn>Cu>Pb>Ni>As>Sb>Cr	Fe>Sr>Zn>Mn>Ni>As>Pb>Cr>Co>Mo>U	Fe>Sr>Zn>Mn>Cu>Pb>As>Ni>Sb>Co>Mo>U
JRvf	Sr>Fe>Zn>Mn>As>Ni>Pb>As>Mo>Co>U	Sr>Fe>Mn>Zn>Ni>As>Sb>Pb>Mo>Co>U	Fe>Sr>Zn>Mn>As>Ni>Sb>Pb>Mo>U
JRrn	Fe>Sr>Zn>Mn>As>Ni>Pb>Sb>Mo>Co	Sr>Fe>Zn>Mn>As>Ni>Sb>Mo>Pb	Sr>Fe>Zn>Mn>Ni>As>Pb>Mo

**Fe.** 1st period, increasing trend in all sites (except on the 14th May at JRrn)  
2nd period, the 7th day gave the lowest values except for JRC.

**Mn.** 1st period, JRrd, JRC and JRrn gave a decreasing trend through time, while, at JRvf, from the 7th day, an increase was found at the last day.  
2nd Period, JRC and JRvf gave the same trend as they increased in the 7th day.

**As.** 1st period, the trend was the concentrations slightly increased during the 7th day then slight decreased on the 14th day.  
2nd period, JRC followed the same trend as in the 1st period having concentrations double. For the rest sites, concentrations decreased on the 7th day.

**Sb.** The 1st period gave under the limit of detection concentrations.  
The 2nd period, close values were obtained ranging from 0.7µg/L to 1.2 µg/L.

**Cr Total.** The periods gave under the limit of detection concentrations except for at JRC on the 2nd period.

**Co.** 1st period, concentrations increased on the 7th day then decreased on the 14th day.  
2nd period, JRrd is under the limit of detection. Only JRC gave a complete detection through time.

**Sn.** For the 1st period, the concentrations at JRrd and JRvf increased at the 7th day. At the 14th day, the concentrations in all the sites dropped to under the limit of detection that continued until the 2nd period.

**Mo.** On the 1st Period of the 7th day, the concentration was detected only at JRC.  
At 2nd Period,

**Ni.** 1<sup>st</sup> period, JRrd slightly decreased at the 14<sup>th</sup> day; JRC and JRrn increased on the 7<sup>th</sup> day; and JRvf gave a descending concentration.

2<sup>nd</sup> period, JRC and JRvf increased on the 7<sup>th</sup> day, while, JRrd and JRrn decreased on the same day.

**Pb.** 1<sup>st</sup> Period, the 1<sup>st</sup> day gave under the limit of detections for all the sites. Concentration at JRC and JRrn decreased on the 14<sup>th</sup> day but not for JRvf.

Period 2, Pb was only detected at JRrd on the 14<sup>th</sup> day; the rest of the sites showed decrease in concentration on the 7<sup>th</sup> day.

**U.** 1<sup>st</sup> Period, U was only detected at JRC.

2<sup>nd</sup> period, complete detection was only found at JRvf. At the 7<sup>th</sup> and 14<sup>th</sup> day U was detected at JRC.

**Zn.** 1<sup>st</sup> period, Zn concentrations were found highest at the 7<sup>th</sup> day.

2<sup>nd</sup> period, at JRrd Zn was detected on the 14<sup>th</sup> day. JRC and JRvf both increased on the 7<sup>th</sup> day.

**Sr.** 1<sup>st</sup> Period, at JRC it increased on the 7<sup>th</sup> day then a sudden dropped was observed on the 14<sup>th</sup> day. JRvf gave same values through time while JRrd and JRrn increased on the 7<sup>th</sup> day.

2<sup>nd</sup> Period, JRrd and JRC both increased on the 7<sup>th</sup> day while JRvf and JRrn gave same values through time.

**B] Bordeaux Lac**

Trace elements such as Cr, Cu, Sn and Mo were above the detection limits only on the 1st Period. Whereas, Sb was above the detection limit during the 2nd Period with the exception on the 1st day at BL6m. Zn were above the detection limit on the 1st Period and at BLC and BL1m on the 1st Day of Period 2. Samples were lost during Period 2 at BLC. Due to this reason no further information can be given.

The following are below detection limit: Cr (except at BLC on Period 1 Days 0, 1 and 7); Cu (except at BLC Day 0, Period 1); and Sn (except Day0, Period 1 at BLbn). Variations of concentrations of trace metals are presented in Figure III.15 to Figure III.18.

**Fe.** Period 1- The concentration at the BLC during Period, Day 7 is exceptionally high. Except on Day 1 (where highest concentration was found at BL1m), BLC gave the highest concentration for this period. Least values were at the BL6m except on the 7th day wherein the least value was at BL1m.

Period 2- concentrations are lower in this period than Period 1. At BLbn, Days 1 and 7 are below the detection limit. The 14th day is higher than Day 1 for BLC and BL1m. At BL6m, detection was on Day 7.

**Mn.** Period 1- High concentrations were found at BL6m (Days 0 and 14) and BLC (Day7). The concentrations declined from Day0 to Day1 then increased on the 7th day. On the 14th day, the concentration increased except at BLC.

Period 2-has lower concentration than Period 1 except on Day 7 at the BLC

**As.** Period 1- The concentration ranges from 2.1 to 2.9 $\mu\text{g/L}$  with the exceptions at the BLC (giving 3.4 $\mu\text{g/L}$  and 8.1 $\mu\text{g/L}$ ).

Period 2- The range is from 2.5 $\mu\text{g/L}$  to 2.6 with the exception at BLC (giving until 4.8 $\mu\text{g/L}$ ).

**Sb.** The range in Period 2 is 0.9 $\mu\text{g/L}$  to 1.1 $\mu\text{g/L}$ .

**Mo.** The range is from 0.5 $\mu\text{g/L}$  to 0.9 $\mu\text{g/L}$  with under detections at BLC and BL6m on Day 0 and the latter on Day 1 of Period 1 then on the 14th Day of Period 2 (BL6m).

**Ni.** Period 1- The range starts from 0.8 $\mu\text{g/L}$  to 1.4 $\mu\text{g/L}$ .

Period 2- The range is from 0.6 $\mu\text{g/L}$  with a maximum value of 1.0 $\mu\text{g/L}$ .

**Pb.** Period 1- present at BLbn and BLC (except Day1) and on Day 14 (except at BL6m).

Period 2- detection was only on Day1 at BL1m and Day 1 at BLC.

**U.** The range is 0.5 $\mu\text{g/L}$  to 1 $\mu\text{g/L}$ . For Period 1, under detections were at BLC and BL6m (Day0) and BL1m (Day1).

**Zn.** Period 1- Highest concentrations were at BL6m except on Day1 (where the highest was at BLC). Significant increase from Day7 to Day 14 was found in all sites.

Period 2-detections were only on Day1 (BLC and BL1m).

**Sr.** The concentration ranges from 160 $\mu\text{g/L}$  to 180 $\mu\text{g/L}$  with exception at the BLC on Period 2 Day14 (giving 200 $\mu\text{g/L}$ ).

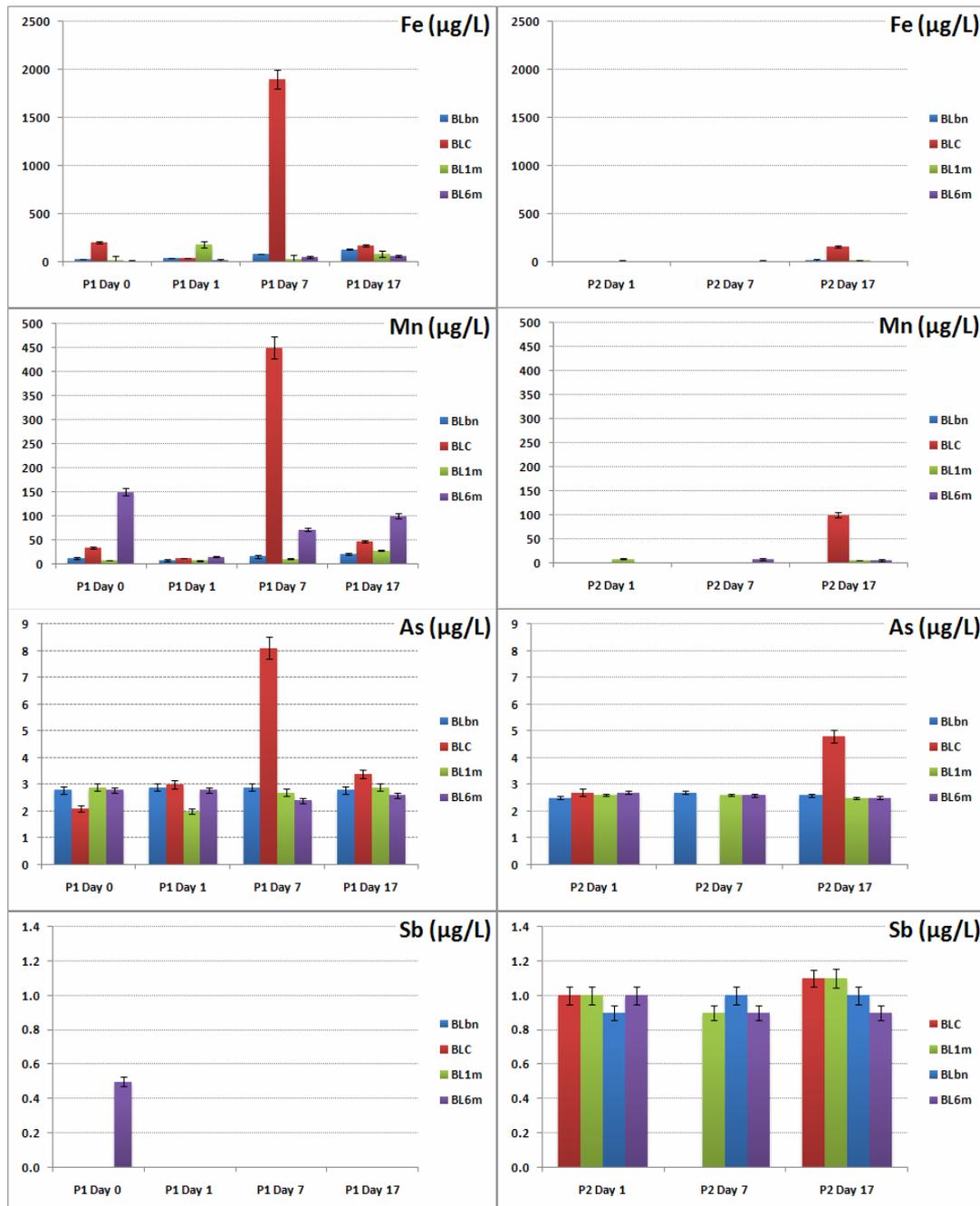


Figure III.15. Measured total trace metals (Fe, Mn, As, and Sb) for Bordeaux Lac for Period 1 (P1) and Period 2 (P2)

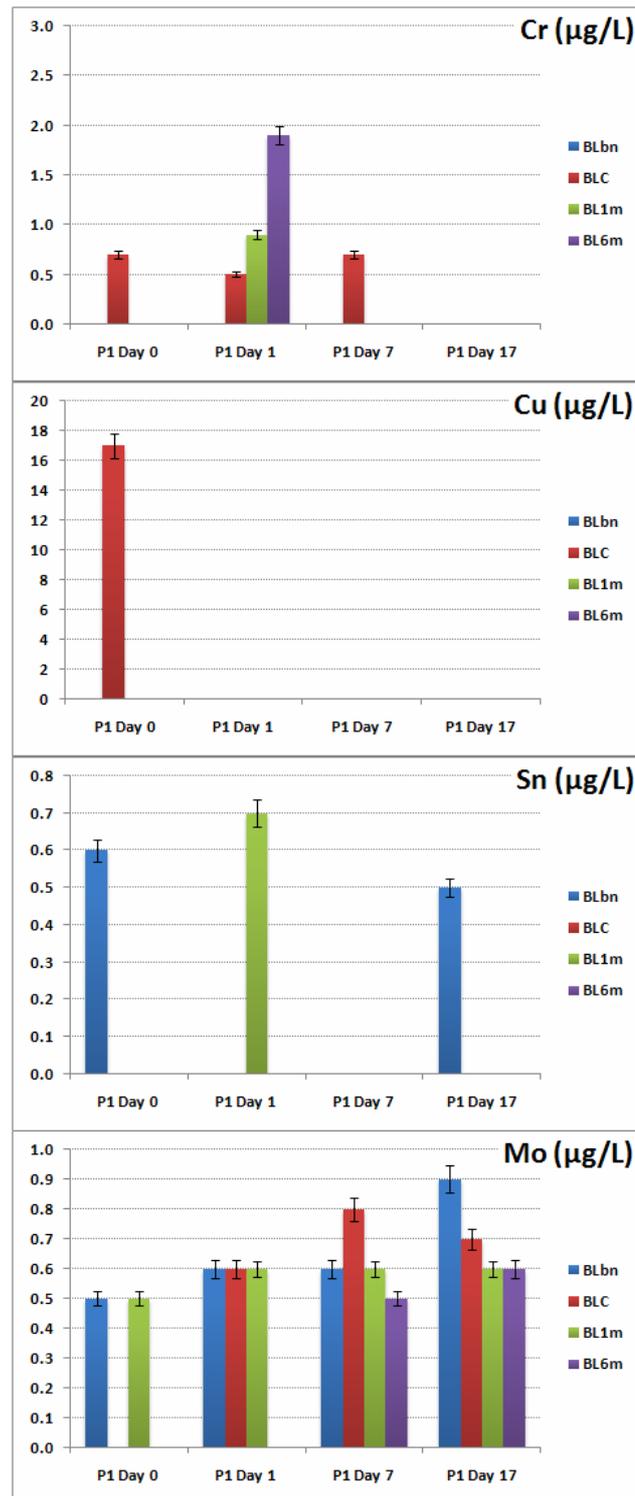


Figure III.16. Measured total trace metals (Cr, Cu, Sn, and Mo)for Bordeaux Lac for Period 1 (P1) and Period 2 (P2)

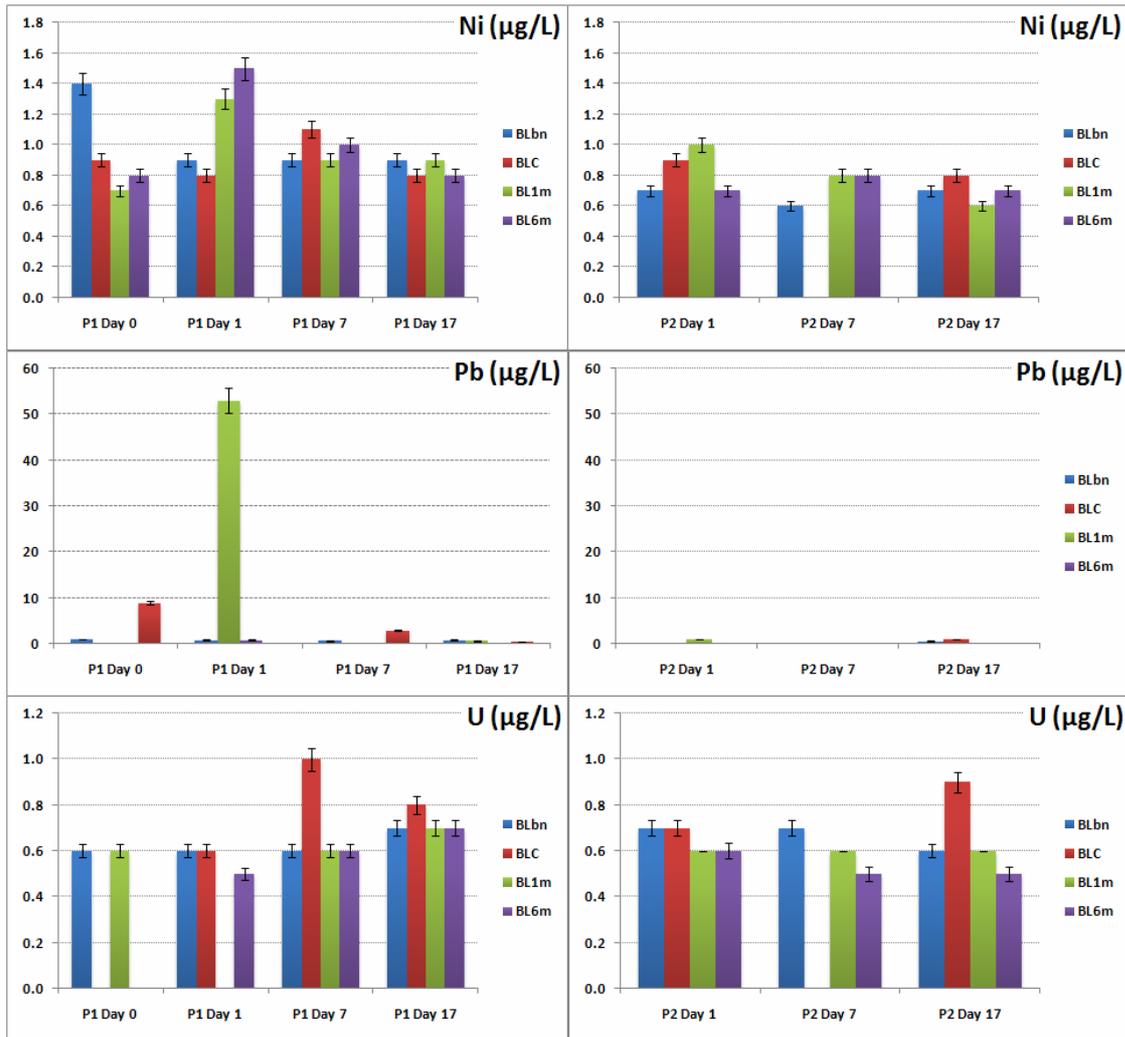


Figure III.17. Measured total trace metals (Ni, Pb, and U)for Bordeaux Lac for Period 1 (P1) and Period 2 (P2)

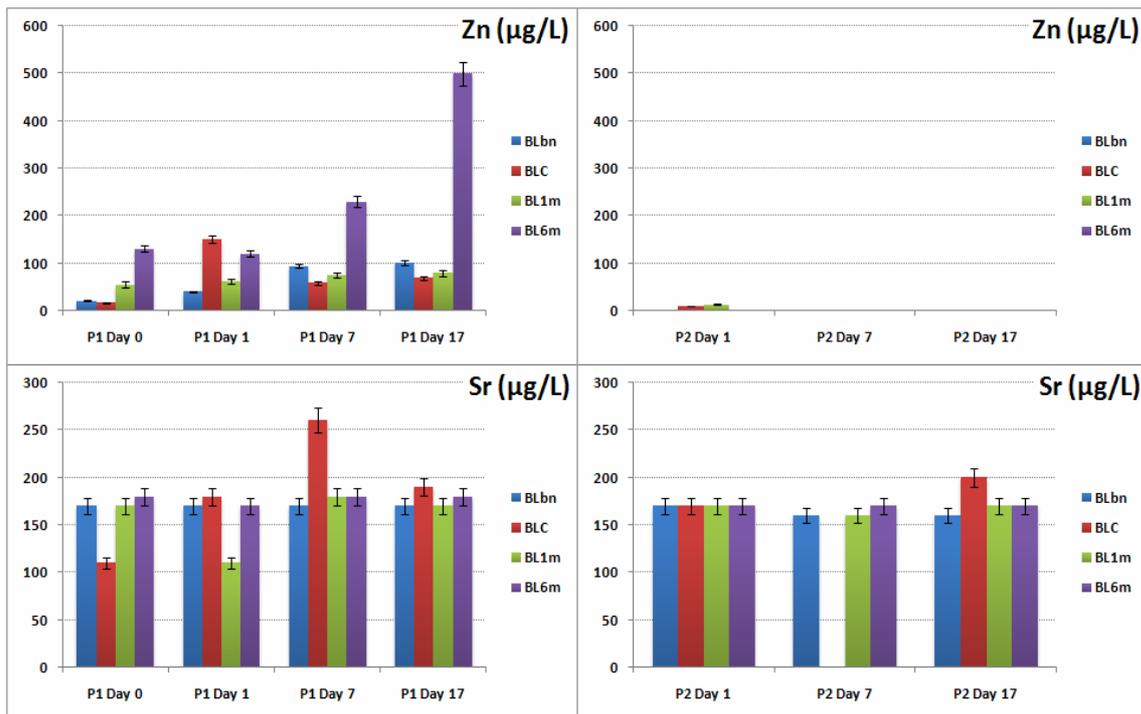


Figure III.18. Measured total trace metals (Zn and Sr)for Bordeaux Lac for Period 1 (P1) and Period 2 (P2)

### 3.1.2. DGT-labile trace metals

#### A] Jalle River

The results highly showed a temporal variability (Figure III.19 and Figure III.20). The general trend of the DGT labile trace metals starts with high concentration during the 1st day. On the 7th day the concentrations decreased and continue to dropped until the 14th day except for: Co (at JRrd, Period 2), Ni (at JRC, Period 1), Cu (at JRC and JRvf, Period 2), Zn (at JRC, Periods 1 and 2), Cd (at JRC, Period 2), and Pb (at JRrn, Period 2). The concentration difference in between the 7th and the 14th day is as high as the difference in between the 1st and the 7th day.

Notable, highest Zn and Cd concentrations where found at the JRC during Periods 1 and 2 (except on the 1st day of Period 2 where Cd is highest at the JRrd). Zn and Cd values increased as it reached the collector then continue to decrease until it reached the JRrn. It was only during Period 2, Day 1 when Zn and Cd increased at JRrn.

Co and Ni both have similar spatial trends (in terms of highest concentration) except during the 14<sup>th</sup> day of Period 1. This is as the highest concentration of Co was found at the JRvf while Ni was highest at the JRC during this particular time. During Period 1, 1<sup>st</sup> day both have the highest concentration at JRC and at the JRvf on the 7<sup>th</sup> day. For the 2<sup>nd</sup> period, Co and Ni concentrations were found highest at the JRrn. For the 7<sup>th</sup> and 14<sup>th</sup> day, JRvf gave the highest value.

Co increased as it reached JRC (except on Day 1 of Period 2) the concentration continued to increase going to the JRvf (except on Day 1 of Period 1) then decreased as it approached JRrn (except on Day 1 of Period 1). Whereas, from JRrd, the increase of Ni concentration was only during the 1<sup>st</sup> and 14<sup>th</sup> day of Period 1 and the 14<sup>th</sup> day of Period 2. At the JRvf, the decrease of concentration was experienced during the 1<sup>st</sup> and 14<sup>th</sup> day of Period 1. During the 1<sup>st</sup> day of both Periods 1 and 2, from JRvf, the concentrations decreased.

For Cr concentrations, the value decreased at JRC during the 1<sup>st</sup> and 14<sup>th</sup> day of Period 1 and the 7<sup>th</sup> day of Period 2. The increase of concentrations at JRvf was during the 14<sup>th</sup> day of Period 1 and 7<sup>th</sup> day of Period 2. Highest concentrations at Period 1 were found at JRrd during the 1<sup>st</sup> day; JRC at the 7<sup>th</sup> day; and JRrn on the 14<sup>th</sup> day. For Period 2, highest concentrations where found at JRC for both 1<sup>st</sup> and 14<sup>th</sup> day and at JRrn on the 7<sup>th</sup> day.

Cu concentrations were found highest at JRC during the 14<sup>th</sup> day of Periods 1 and 2 and the 1<sup>st</sup> day of Period 1. At JRrd, Cu concentration was highest during the 1<sup>st</sup> day of Period 1. During the 7<sup>th</sup> day of Periods 1 and 2, JRrn has the highest Cu concentration.

Pb concentrations were found highest at JRC during the 1<sup>st</sup> and 7<sup>th</sup> day of Period 1 and 7<sup>th</sup> day of Period 2. JRvf gave the highest concentrations during the 14<sup>th</sup> day of Periods 1 and 2. JRrn has the highest Pb concentration during the 1<sup>st</sup> day of Period 2. From JRrd the increase in concentration as Pb reached JRC was found during the 1<sup>st</sup> and 7<sup>th</sup> day of Period 1 and 7<sup>th</sup> day of Period 2. Then at JRvf, concentrations increased during the 14<sup>th</sup> day of Period 1 and the 1<sup>st</sup> and 14<sup>th</sup> day of Period 2.

Increase of concentrations was found only from Day 7 to Day 14 during Period 1 at JRC for Ni and Zn. From Day 1 to Day 7 of Period 2, the increase of concentration was at JRvf for Ni. Still in Period 2, from Day 7 to Day 14, the increase of concentrations were at JRrd for Co; JRC and JRvf for Cu; JRC and JRrn for Zn; and JRrn for Pb.

The concentration of Period 1 is high mostly higher than Period 2 on Day 1 except for Ni (JRrd and JRrn); Zn (JRrd and JRrn); and Cd (JRrd). During the 7<sup>th</sup> day, the concentrations are also higher in Period 1 than Period 2 except for Cr (JRvf and JRrn); Ni (JRrd, JRC and JRvf); and Zn (JRC and JRvf). On the 14<sup>th</sup> day, trace metals: Cr (at JRrd); Co (at JRrd and JRC); Cu (at JRrd and JRrn); Zn (at JRrd) and Cd at (JRrd) were higher on Period 1. Ni in all the sites was higher in Period 2.

At the 14<sup>th</sup> day, accumulation of the trace metals was higher during the 2<sup>nd</sup> Period compared to Period 1. The percent increase was as follows: Cr : 30.77% at JRC, 10.23% at JRvf and 4.97% at JRrn; Co: 20.42% at JRvf and 2.33% at JRrn; Ni : 14.91% at JRrd, 7.98% at JRC, 41.83% at JRvf and 46.78% at JRrn; Cu: less than 1% at JRC: 8.94% at JRvf; Zn: 12.89% at JRC, 27.29% at JRvf and 31.73% at JRrn; Cd: 51.35% at JRC, 6.01% at JRvf and 17.68% at JRrn ; and Pb : 31.57% at JRC.

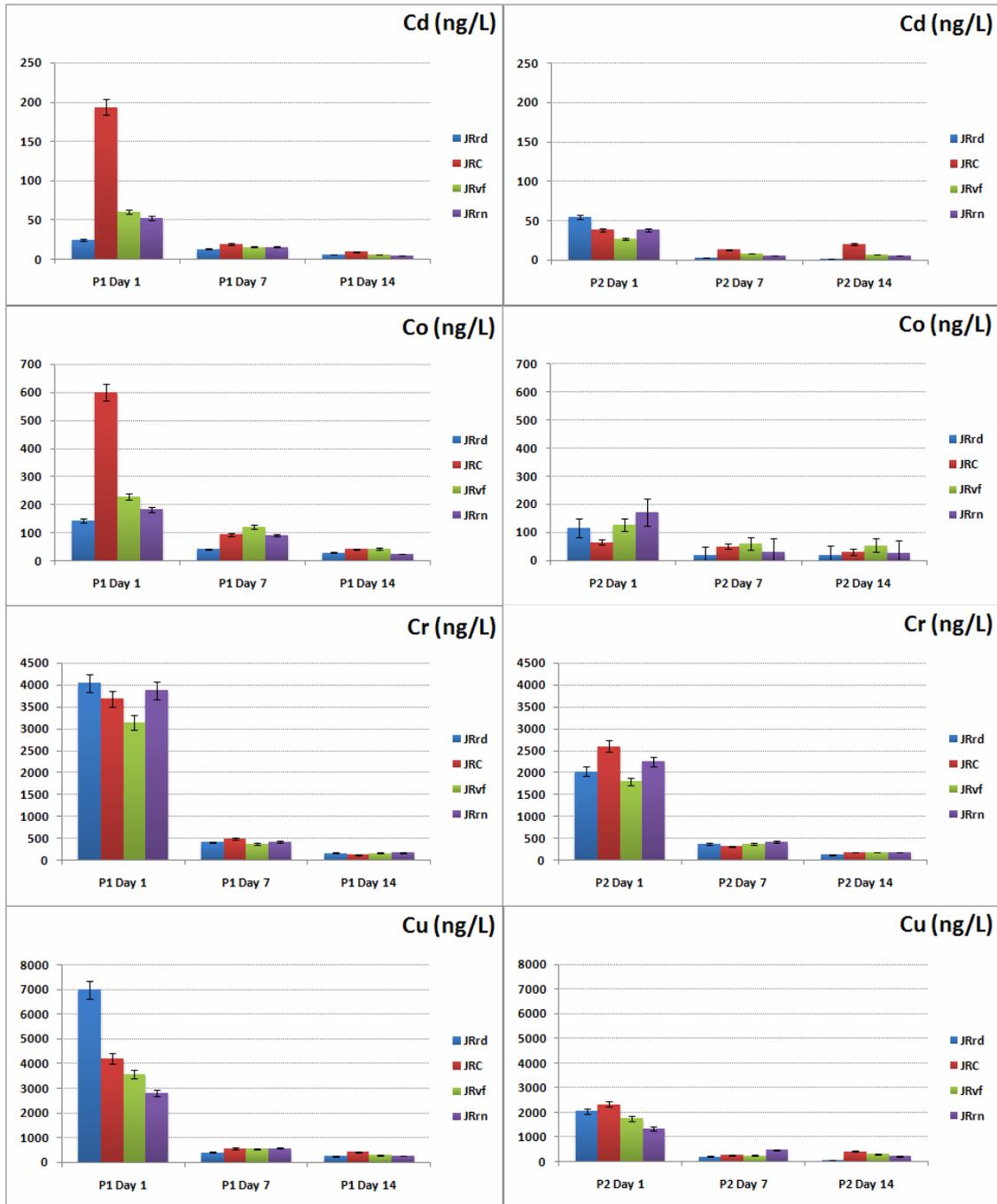


Figure III.19. Measured DGT labile-trace metals (Cd, Co, Cr and Cu)for Jalle River for Period 1 (P1) and Period 2 (P2)

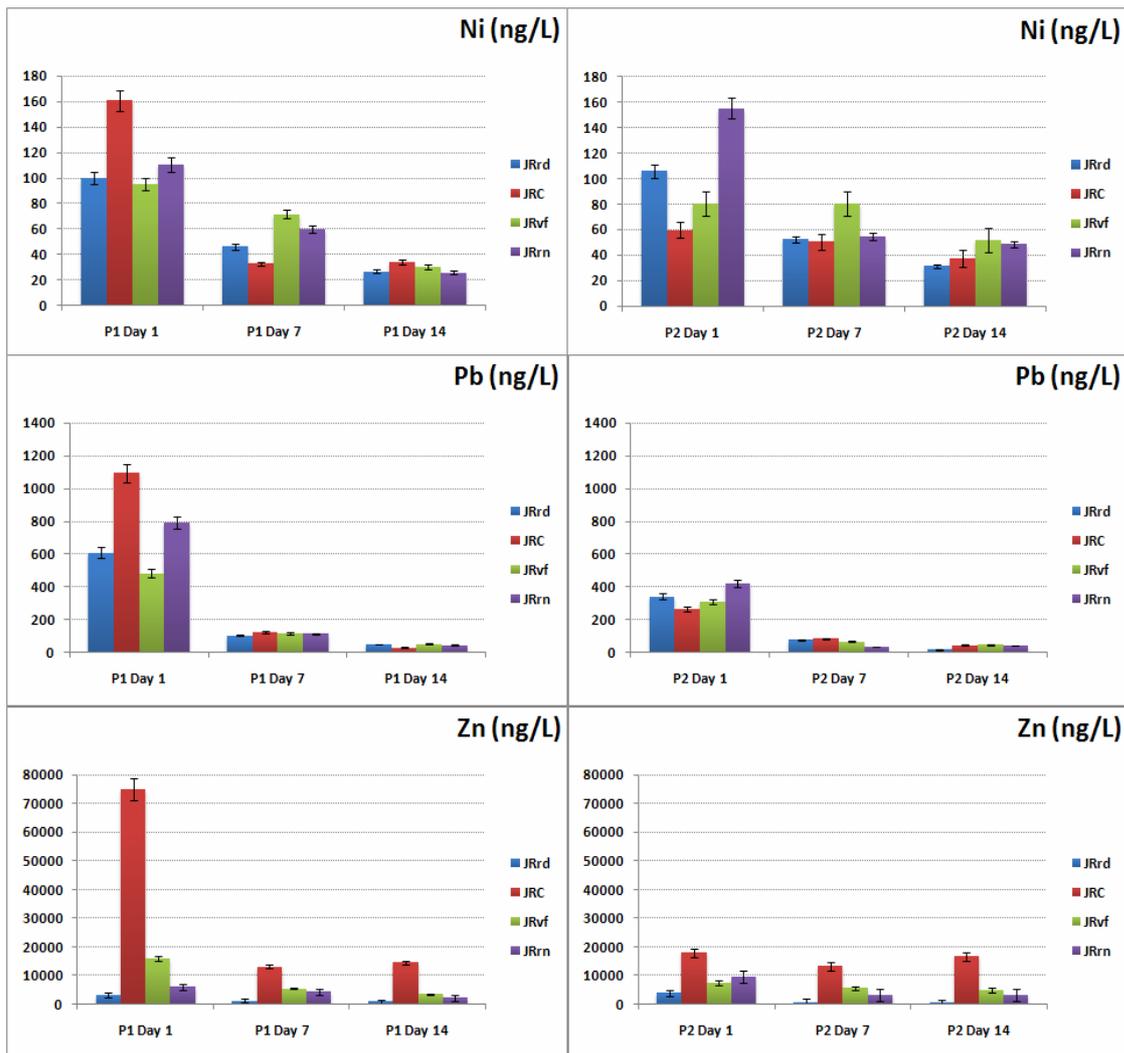


Figure III.20. Measured DGT labile-trace metals (Ni, Pb, and Zn)for Jalle River for Period 1 (P1) and Period 2 (P2)

**B] Bordeaux Lac**

In each of the trace metals in each period, Day 1 got the highest concentration as it is still in its kinetic phase. Unfortunately, the passive samplers were lost at the BLC site during the 2<sup>nd</sup> Period. For the 1st Period, the values decreased on the 7<sup>th</sup> day. On the 14<sup>th</sup> day the decrease continued for the DGT-labile trace metals Cr, Cd and Pb. At the BLbn site, per period, the concentration exhibited descending values through time. The concentrations at the BL1m site shows that for both periods there were descending order except for Ni and Cd on Period 2 Day 14. Whereas, at 6m deep (BL6m), the concentration decreased through time in both periods. Table III.2 presents which period has higher concentration per trace metal per site. Period 1 (Pd1) represents dry event and Period 2 (Pd2) has higher precipitation rate.

**Table III.2. Comparison of trace metal concentration (Period 1 vs. Period 2) per site**

Trace metal	Site	Day 1	Day 7	Day 14
<b>Cr</b>	BLbn	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &gt; Pd2</i>
	BL1m	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &gt; Pd2</i>	<i>Pd1 &lt; Pd2</i>
	BL6m	<i>Pd1 &gt; Pd2</i>	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &lt; Pd2</i>
<b>Co</b>	BLbn	<i>Pd1 &gt; Pd2</i>	<i>Pd1 &gt; Pd2</i>	<i>Pd1 &lt; Pd2</i>
	BL1m	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &lt; Pd2</i>
	BL6m	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &lt; Pd2</i>
<b>Ni</b>	BLbn	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &lt; Pd2</i>
	BL1m	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &gt; Pd2</i>	<i>Pd1 &lt; Pd2</i>
	BL6m	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &lt; Pd2</i>
<b>Cu</b>	BLbn	<i>Pd1 &gt; Pd2</i>	<i>Pd1 &gt; Pd2</i>	<i>Pd1 &gt; Pd2</i>
	BL1m	<i>Pd1 &gt; Pd2</i>	<i>Pd1 &gt; Pd2</i>	<i>Pd1 &gt; Pd2</i>
	BL6m	<i>Pd1 &gt; Pd2</i>	<i>Pd1 &gt; Pd2</i>	<i>Pd1 &gt; Pd2</i>
<b>Zn</b>	BLbn	<i>Pd1 &gt; Pd2</i>	<i>Pd1 &gt; Pd2</i>	<i>Pd1 &gt; Pd2</i>
	BL1m	<i>Pd1 &gt; Pd2</i>	<i>Pd1 &gt; Pd2</i>	<i>Pd1 &gt; Pd2</i>
	BL6m	<i>Pd1 &gt; Pd2</i>	<i>Pd1 &gt; Pd2</i>	<i>Pd1 &gt; Pd2</i>
<b>Cd</b>	BLbn	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &gt; Pd2</i>
	BL1m	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &gt; Pd2</i>	<i>Pd1 &lt; Pd2</i>
	BL6m	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &lt; Pd2</i>
<b>Pb</b>	BLbn	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &lt; Pd2</i>
	BL1m	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &lt; Pd2</i>
	BL6m	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &lt; Pd2</i>	<i>Pd1 &lt; Pd2</i>

The Table III.2 shows that concentrations are higher in Period 1 for Cu, Zn, Cr (Day 14 at BLbn and Day 7 at BL1m), Co (Days 1 and 7 at BLbn) and Cd (Day 7 at BL1m). The rest shows that Period 2 is higher than Period 2. Variations of trace metals are presented in Figure III.21 and Figure III.22.

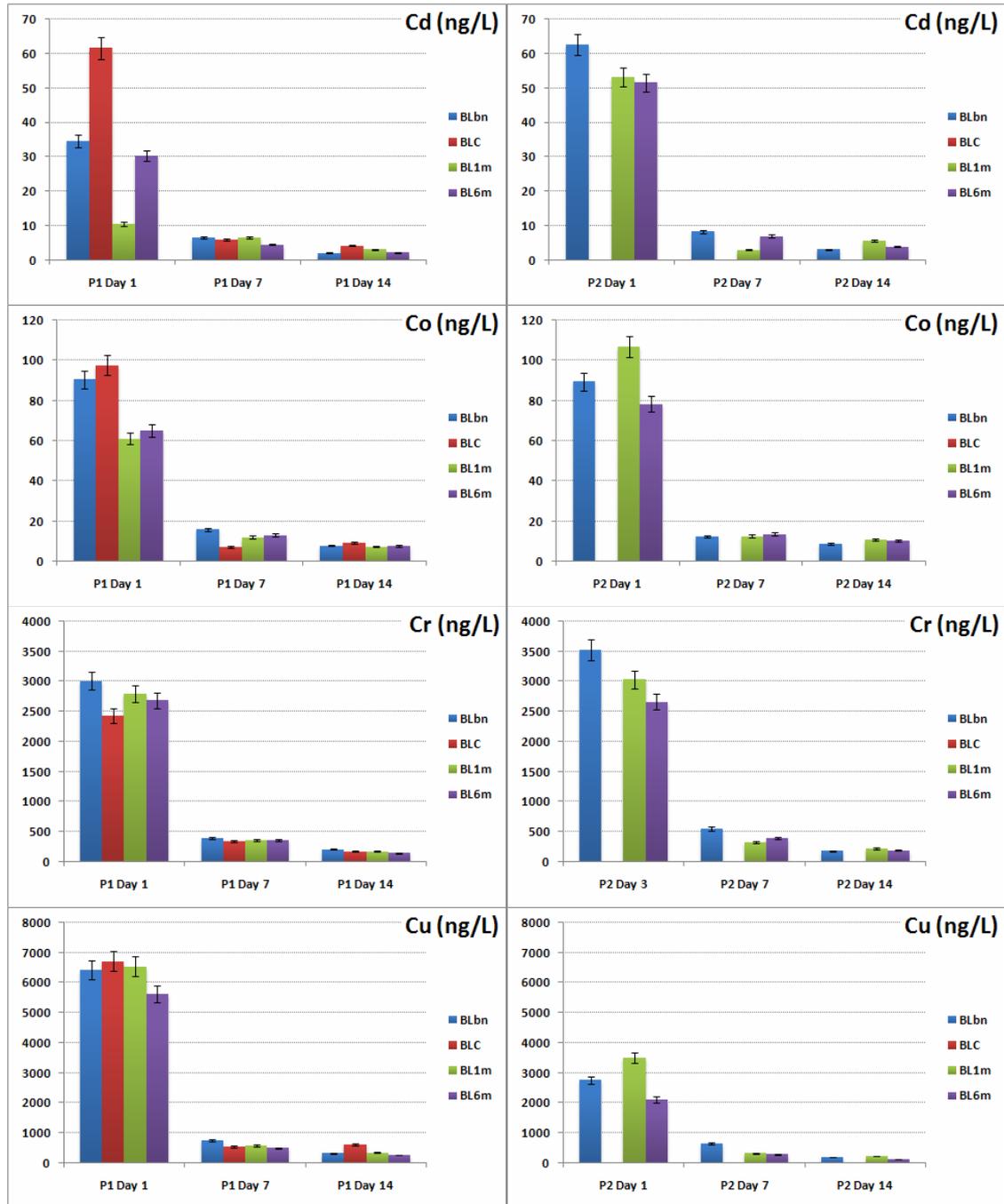


Figure III.21. Measured DGT labile-trace metals (Cd, Co, Cr, and Cu) for Bordeaux Lac for Period 1 (P1) and Period 2 (P2)

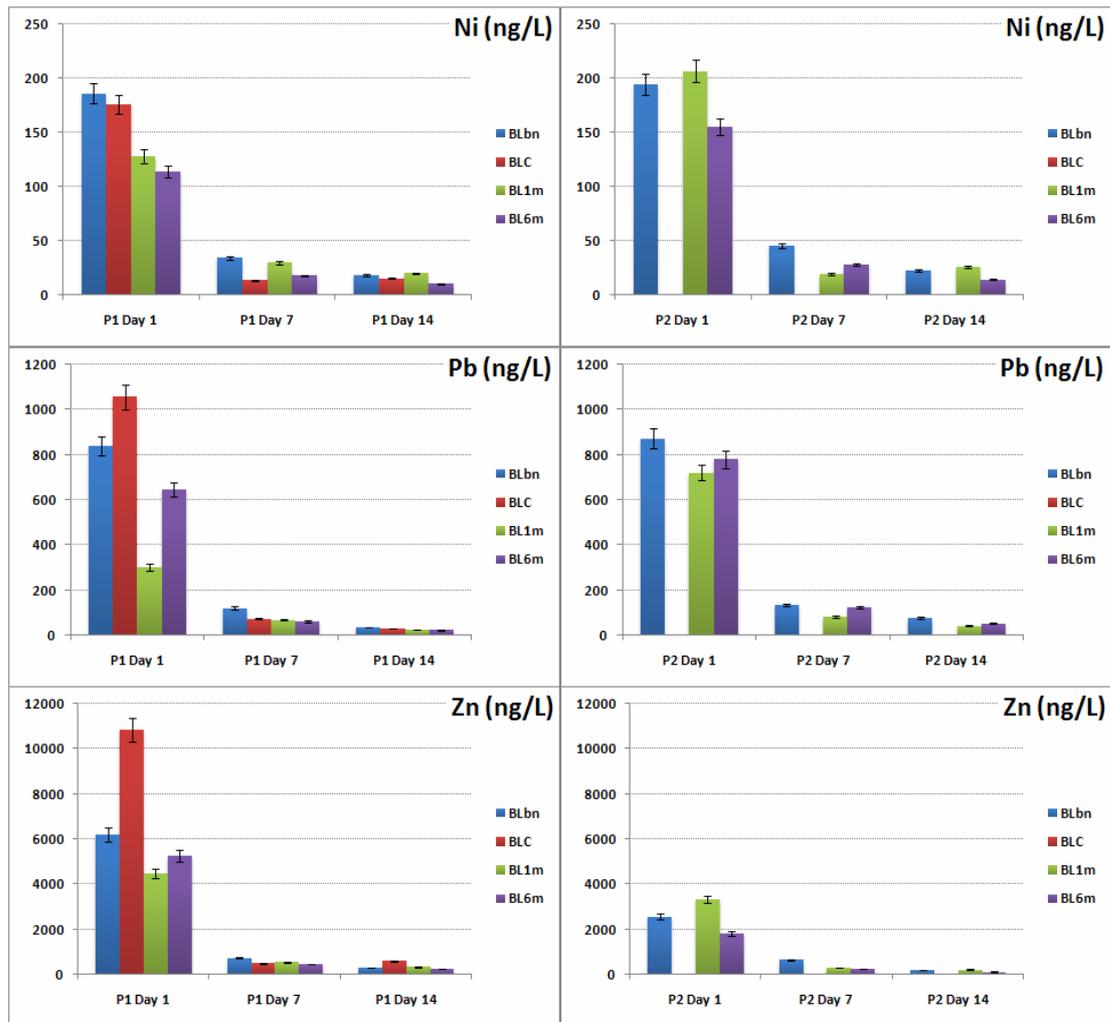


Figure III.22. Measured DGT labile-trace metals (Ni, Pb and Zn) for Bordeaux Lac for Period 1 (P1) and Period 2 (P2)

## 3.2. Organics

### 3.2.1. Conventional sampling (grab samples)

The measured organics using the conventional approach that are  $\geq$  the detection limit are showed in Figure III.23 and Figure III.24. These are: Nonylphenol, Octylphenol-4ter, 2,4-Dichloroaniline, 1,2,4-Trichlorobenzene, 1,3,5-Trichlorobenzene, Fluazifops, Mecoprop, Imidaclopride, HCH gamma, Oxadiazon, Diazinon, Diuron, and Polycyclic aromatic hydrocarbon (PAH) such as: Benzo(a)pyrène, Benzo(b)fluoranthène, Benzo(g,h,i)pérylène, Benzo(k)fluorantène, Chrysène, Fluoranthène, Indénol(1,2,3-c,d)pyrène, Phénanthrène, and Pyrène for the Jalle River.

For the Bordeaux Lac, there are: Nonylophenols, 2,4-Dichloroaniline, 1,2,4-Trichlorobenzene, Fluazifop, Oxadiazon, Oxydémétin-méthyl, Hydroxyterbutylazine, Diuron, Fenuron; pesticide divers: Imidaclopride Oxadixyl, Metsulfuron méthyl, Crimidine, Anthraquinone; and PAHs: Naphthalene and Phenanthrene.

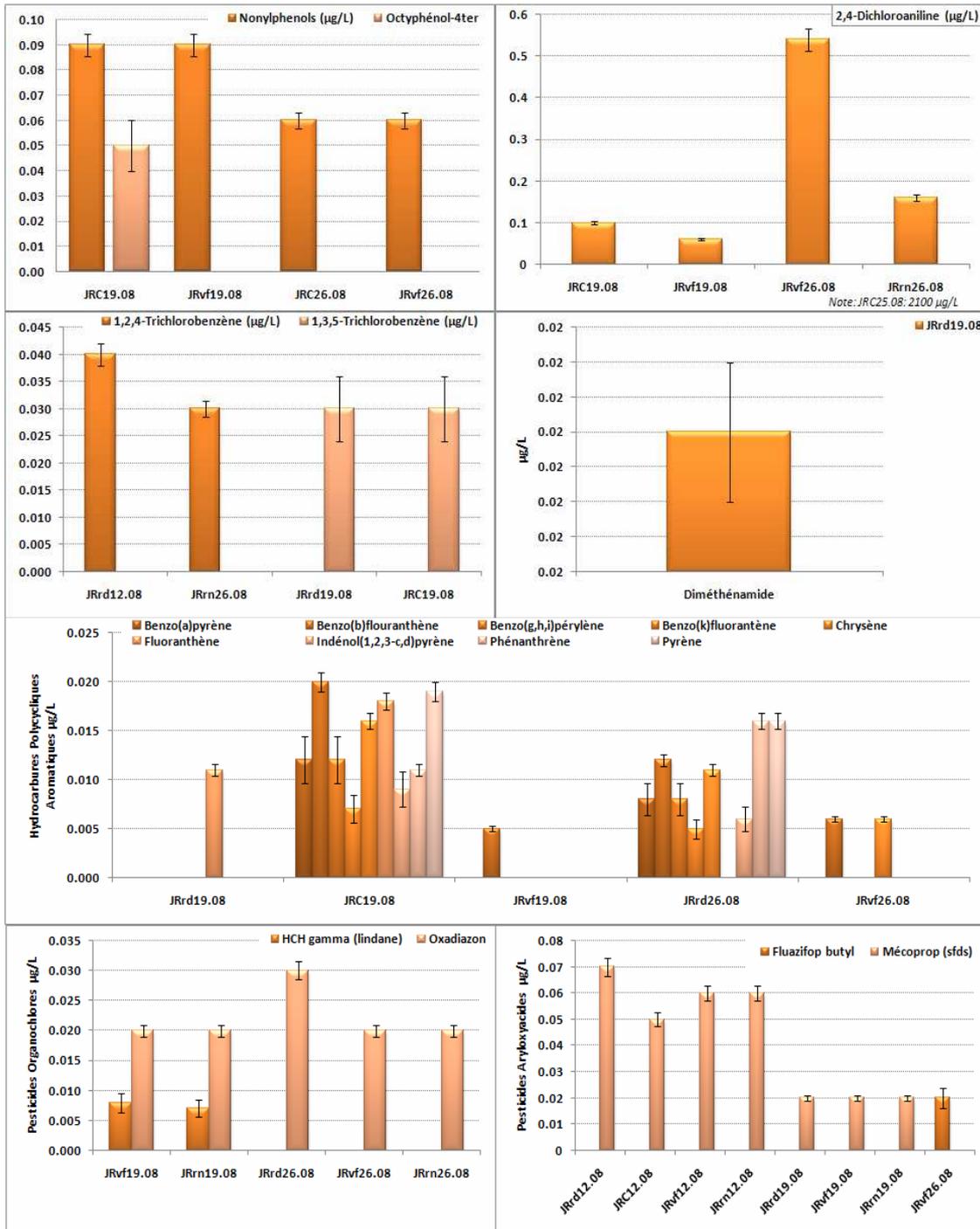


Figure III.23. Organic compounds (in total fraction) detected in the Jalle River



Figure III.24. Organic compounds (in total fraction) detected in the Bordeaux Lac

## 3.2.2. POCIS

As mentioned, pharmaceuticals were measured using POCIS. The Table III.3 shows the list of pharmaceuticals and the common purpose it serves:

**Table III.3. The pharmaceuticals measured using the POCIS samplers and the medical uses**

<b>Pharmaceutical</b>	<b>Use</b>
<b>Ofloxacin</b>	Chemotherapeutic antibiotic
<b>Sulfamethoxazole</b>	used to treat urinary tract infections and a parasitic disease called Toxoplasmosis
<b>Bezafibrate</b>	Use in a diet program and lowers cholesterol
<b>Ketoprofene</b>	For pain reliever, inflammation and fever
<b>Diclofenac</b>	anti inflammatory and pain reliever
<b>Atenolol</b>	Use to control high blood pressure and chest pain caused by angina
<b>Caffeine</b>	a central nervous system (CNS) stimulant; stimulant drug
<b>Trimethoprim</b>	Anti-biotic that treats bacterial infections
<b>Erythromycin</b>	Antibiotic; use to treat infection and inflammation
<b>Propranolol</b>	A beta-blocker that helps heart and blood circulation
<b>Bromazepam</b>	relieve anxiety, nervousness and tension; muscle relaxant
<b>Carbamazepine</b>	Anticonvulsant and mood stabilizer; treat seizures and nerve pain
<b>Clarythromycine</b>	Use to treat bacterial infections in skin and respiratory system
<b>Oxazepam</b>	Helps in the problem of withdrawal of alcohol and insomnia
<b>Lorazepam</b>	Helps in short-term management of severe anxiety

### A] Jalle River

The upstream (JRrd) significantly contributed to the measured pharmaceuticals except for Trimethoprime. Ofloxacin, Sulfamethoxazole, Bezafibrate, Atenolo, Trimethoprime, Epoxycarbamazepine, Erythromycine, Propranolol, Bromazepam, Clarythromycine, Oxazepam, and Lorazepam were not found at the collector (JRC). At JRvf, Bromazepam was not detected but Ofloxacin was detected only for POCIS immersed for 14 days.

At JRrn, Bezafibrate, Sulfamethoxazole, Diclofenac, Atenolol, Caffeine, Epoxycarbamazepine, Propranolol, and Oxazepam were detected for both POCIS D7 and D14 (Day 7 and Day 14, respectively). Ofloxacin, Ketoprofene, and Trimethoprime, were detected at D7 POCIS while Erythromycine, and Clarythromycine were detected only at D14 POCIS (Figure III.25 and Figure III.26).

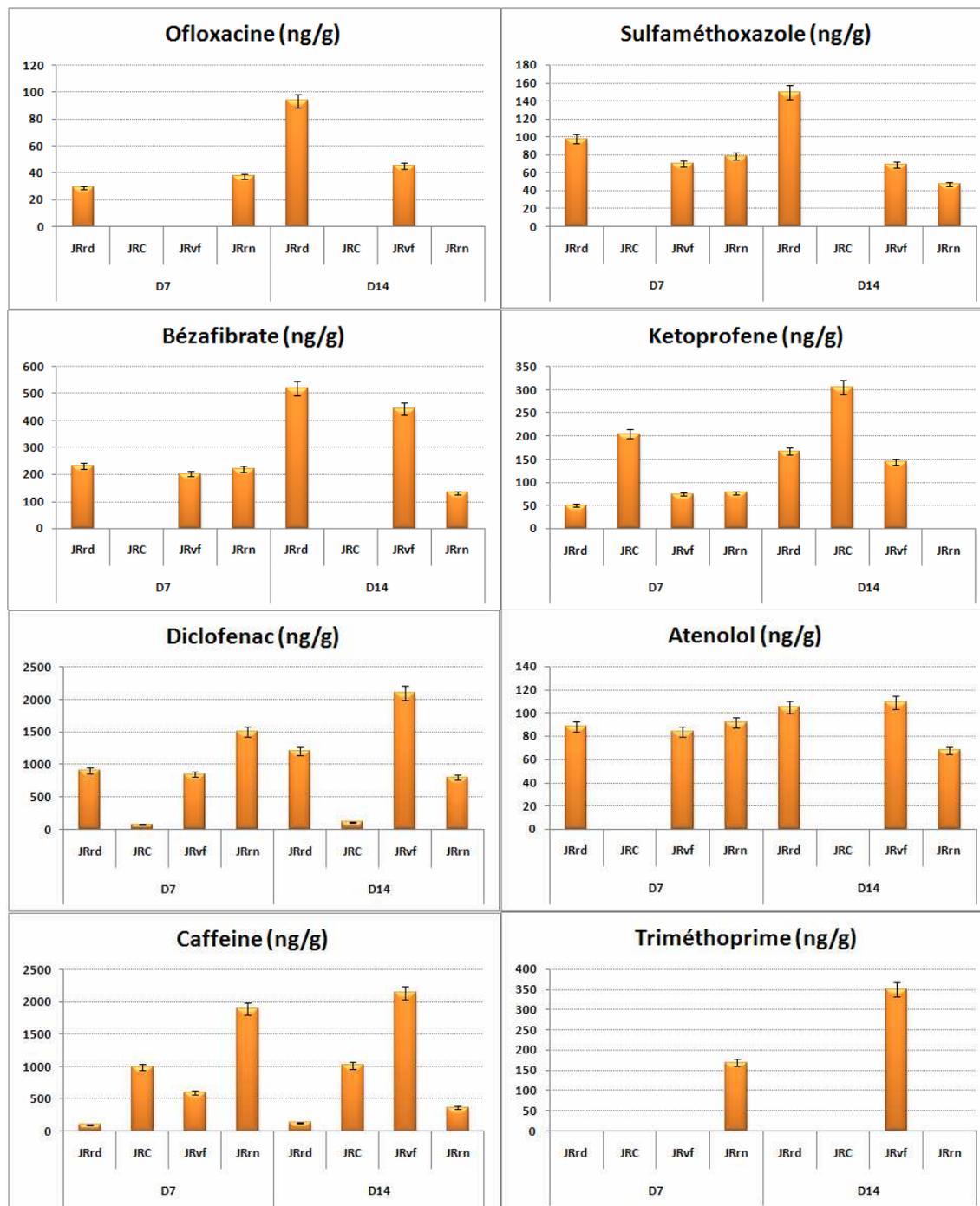


Figure III.25. Pharmaceuticals detected using the POCIS sampler in the Jalle River (Ofloxacin, Sulfamethoxazole, Bezafibrate, Ketoprofene, Diclofenac, Atenolol, Caffeine, Trimethoprime)

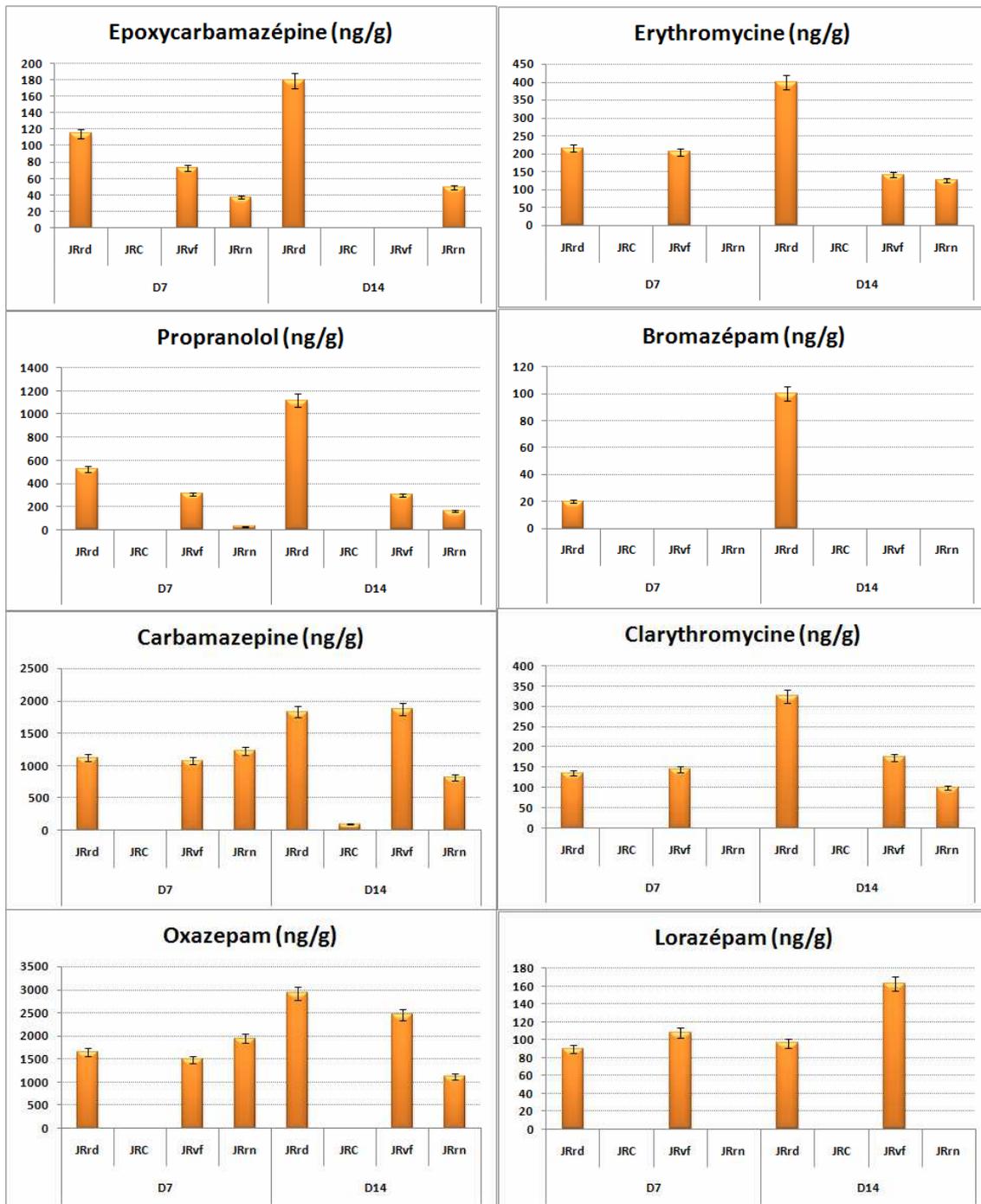
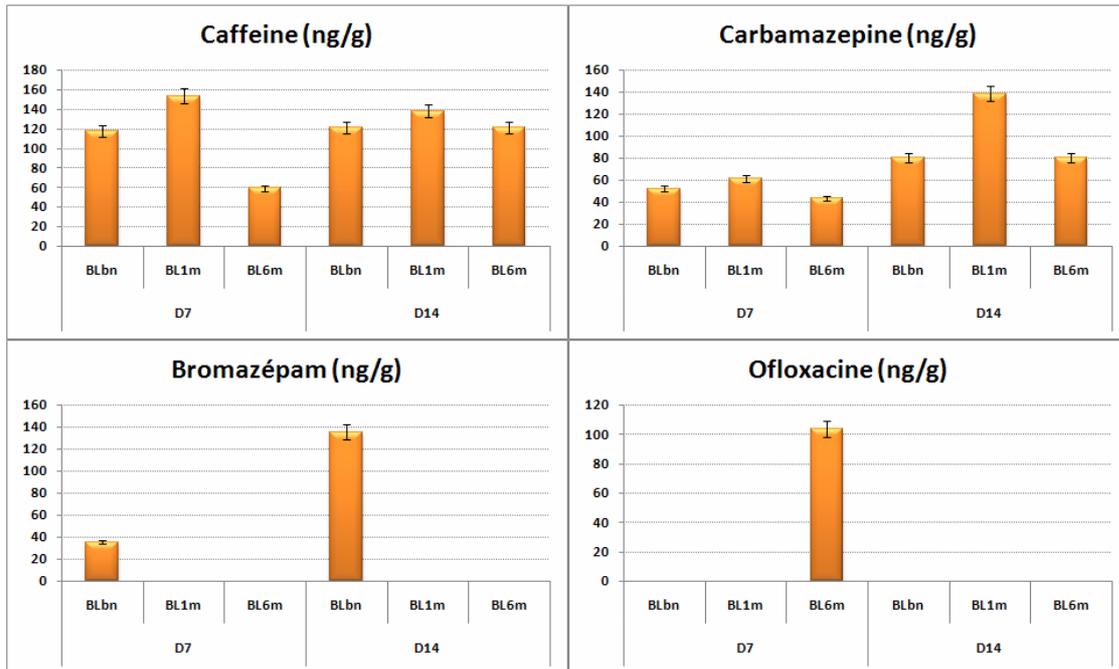


Figure III.26. Pharmaceuticals detected using the POCIS sampler in the Jalle River (Epoxy carbamazepine, Erythromycine, Propranolol, Bromazepam, Carbamazepine, Clarithromycine, Oxazepam, and Lorazepam)

**B] Bordeaux Lac**

At this site, only Caffeine and Carbamazepine showed complete detection among sites and among days of immersion. Bromazepam was detected at the ponton (ponton: BLbn). Ofloxacin was detected only at D7 (day 7) at the center of 6 meter deep (BL6m) (Figure III.27).



**Figure III.27. Pharmaceuticals detected using the POCIS sampler in the Bordeaux Lac (Caffeine, Carbamazepine, Bromazepam, and Ofloxacin)**

### 3.3. Assessment on water quality and pollution

#### 3.3.1. Trace metals

Most of the values are lesser than recommended concentration given by the EU Environmental Quality Standards (EQS), USEPA, and the INERIS for the dissolved fraction of trace elements. Cu in Periods 1 and 2, Day 1 of Bordeaux Lac and Period 1 Day 1 in Jalle River are more than the value given by the INERIS for the no effect concentration (NOEC) which is 2.54µg/L.

Hard to say if this is in a point of risk because the decision should depend on the physiological response of the organism and how fast the reaction is. The values declined after long days of immersion (i.e. 7th Day or more). This is the same case for Cd in the Jalle River (JRC) at Period 1, Day 1. The value is higher than the maximum allowable concentration (NQE-CMA). The rest of the days, however, gave lower values.

#### 3.3.2. On organics

From the total fractions, Polyaromatic Hydrocarbons (PAH) such as Benzo(g,h,i)perylene and Indenol(1,2,3-c,d)pyrene on the 7<sup>th</sup> (at the JRC) and 14<sup>th</sup> (at the JRrd) Day (Period 2) are above the required limit of the EQS. A herbicide that inhibits photosynthesis called Diuron was found above the EQS-limit also during the 7<sup>th</sup> day (Period 2) in all sites. In Bordeaux Lac, the insecticide called Imidacloprid is over the limit of EQS at BLC on Period 2 Day 7. Diuron is above the limit on the 7<sup>th</sup> day (Period) at BLC and BL6m. POCIS concentration gave a qualitative data as the sampling uptake rate is still needed in order to arrive to the quantitative analysis.

Other compounds are hard to assess due to unavailability of data. Limits are not yet indicated. If the EQS will be the basis, the results of the POCIS samples cannot be evaluated. The WFD-EQS expressed the quantitative limits in total fractions. Thus, it is a challenge on how to base the POCIS results in terms of water quality assessments.

#### 4. Conclusion and Recommendation

- Passive sampling was applied in this study to measure different types of trace metals, pharmaceuticals.
- Site reconnaissance and screening of the environmental parameters are. To have a better interpretation of the passive samples result, the background environmental parameters and site reconnaissance are recommended and needed before conducting passive sampling
- Passive sampling is not equal to bio-monitoring. The passive sampling can provide details of the free ions/analytes and its potential damage or toxicity.
- Spatio-temporal output showed the response and behavior of the two (2) different systems in terms of the location and climatic conditions.
- For a better water quality judgment, the water regulations should be resolved. Such as what fractions should be consider and how the water quality guidelines must be met.
- It is evident that the collector discharge significant amount of molecules to the water system. Although, concentrations within the water system itself might be in trace levels but the mass fluxes should be considered most especially when precipitation and run-off are high. Thus, Bordeaux Lac and Jalle River need continues water quality monitoring system.
- The results showed that passive sampling in parallel to the conventional grab methods is highly recommendable in conducting the water quality assessments.

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## **CHAPTER IV Trace metal contribution of a semi-urban catchment to the Jalle River in France**

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## Abstract

**Background, aim and scope** The objective of this paper is to assess and quantify the trace metals (total and labile fractions) contributed by the rainwater/stormwater and run-off collector situated in an active semi-urban watershed. The collected water is directly discharge to the Jalle River.

**Materials and methods** The collector was examined during two (2) sampling campaigns with differing rainfall rate (Period 1(dry) received lesser rainfall rate than Period 2 (wet)) to get the water volume it received. Simultaneously, in each period, trace metals were measured using the conventional method to collect water samples (total fraction) and passive sampling technique using Diffusive Gradient in Thin Films (DGT) for the labile fractions. Intermittent water sampling collection was done for the conventional technique, while, continuous monitoring was employed using the DGT for 7 and 14 days. Pollution mass transport was then calculated.

**Results** This study showed that the run-off and rainwater/stormwater collector hold substantial trace metals that directly receive by the Jalle River. There is evidence that the pollution concern is higher during wet period. Wet period associated with higher rainfall rate brought in more pollution fluxes at the collector to up to 5 times higher for total fraction and up to ten-fold for the DGT-labile trace metals than dry period. During wet period, the trace metal fluxes showed a minimum increase of 1.5 times for the total fraction and ten-fold for the DGT-labile phase compared to the dry period. This study is innovative as the: (1) emerging method using passive sampling is not a typical way to measure the surface run-off collectors and (2) labile fractions are not usually measured.

**Conclusion and Perspectives** DGT technique showed its potential in quantifying the trace metals at the collector. Calculated mass fluxes showed high temporal variation. Furthermore, this study showed evidence that the mass of pollution at the collector is directly proportional to the rainfall rate which is represented by the water volume.

**Keywords** catchment, rainwater/stormwater and run-off collector, trace metals, DGT technique, labile trace metals

## 1. Introduction

The process of urbanization contributes to the diffuse of different substances to the water catchments (Fletcher *et al.* 2012). Urban run-off is a major point of concern in terms of pollution loads and the impact on the receiving water (Moilleron *et al.* 2002). Stormwater and runoff are one of the sources of water degradation (Magaud *et al.* 1997; Kim *et al.* 2007; Lewitus *et al.* 2008; Miguntanna, *et al.* 2010), mainly, caused by urbanization (Goonetilleke *et al.* 2005).

For instance, discharges from the rainwater (Huston *et al.* 2012) and the load it transports during its contact to the soil introduced pollutants to the surface waters (Zgeib *et al.* 2012). These, more often, are directly discharge to the receiving water bodies (Todeschini *et al.* 2012) and affect the urban rivers (Hurley and Forman 2011). Trace metals are recognized as pollutants to the urban water catchments carried by the rainwater and urban runoff (Yuan *et al.* 2001; Boisson and Perrodin 2006; Lye 2009; Kelly *et al.* 2011).

There is a growing concern on the indirect effects of trace metal contamination affecting the aquatic system due to urban stormwater and run-off discharges (Sandor *et al.* 2001; Wong *et al.* 2006). Hence, there is a need to continuously determine and measure the pollutants in the storm water collectors (Somes *et al.* 2000). Comprehensive water quality assessments are essential to identify the critical risks that the urban water catchments might have. However, the surface run-off and rainwater quality is insufficiently tackled.

Under the European water regulations, transport of pollution and the quality of urban water run-off is a major concern for the municipalities (Moilleron *et al.* 2002). To be able to meet the “good ecological status” including the discharges of stormwater (Gregoire *et al.* 2008), EU WFD (Directive 2008/105/EC) required measuring the pollutants that affects surface waters (Gasperi *et al.* 2012).

The aim of this paper is to quantify the trace metal concentration and pollution fluxes of the water at the rainwater/stormwater collector. The trace metals were measured using the conventional grab sampling and the Diffusive Gradient in Thin Films (DGT) technique for assessing the trace metals (Cd, Co, Cu, Cr, Ni, Pb, and Zn). The first is used for describing the total fraction, while, the latter, captured the labile fraction. Labile species are of more

importance in terms of metal speciation and metal complexes (Cleven *et al.* 2005) than the total phase consisting of particulate and dissolved (Sokolowski *et al.* 2001). This is as it consist free metal ion and metal that can dissociate from complexes and colloidal particles (Schintu *et al.* 1999). Furthermore, it is considered as a key parameter for trace metal availability (Chau and Lum-Shue-Chan 1974), toxicity determination and speciation (Parat *et al.* 2006). This fraction is capable to interact and complexes with the combination of chemical, biological and environmental parameter (Peijnenburg and Jager 2003). Hence, this can help in better understanding the characteristics of the trace elements in small and labile fraction to assess its possible effects or consequences to the natural system (Karlik and Szpakowka 2001; Okonkwo and Mothiba 2005; Baeyens *et al.* 2011). For these reasons, DGT technique was employed. It is tested as being pertinent in measuring labile trace metals. Its application and advantages is already widely documented (Li *et al.* 2005; Søndergaard *et al.* 2008; Wu *et al.* 2011).

## 2. Materials and Methods

### 2.1. Site description

The study site (Figure IV.1) is located at the Northern part of Bordeaux, France in an semi-urbanized zone. The watershed is composed of 933 ha with an active catchment area covering 219 ha (private communication). This active catchment covered 23.5% of the total watershed in which 59% belongs to residential, parking and industrial are and 41% un-used land (Table IV.1). The catchment basin receives surface run-off and rainwater/stormwater from the networks (Figure IV.1 in red line) that reach to about 81 km far including connecting roads (roughly 10 km long). A rainwater/stormwater collector is designated for channeling the water directly to the Jalle River. It receives water from 28 sub-basins.

Table IV.1. Site Characteristics

Watershed area	933 ha
Active catchment basin	219 ha
Un-used land	41%
Residential area	12%
Parking	19%
Industrial zone	28%
Type of water channel	Separate

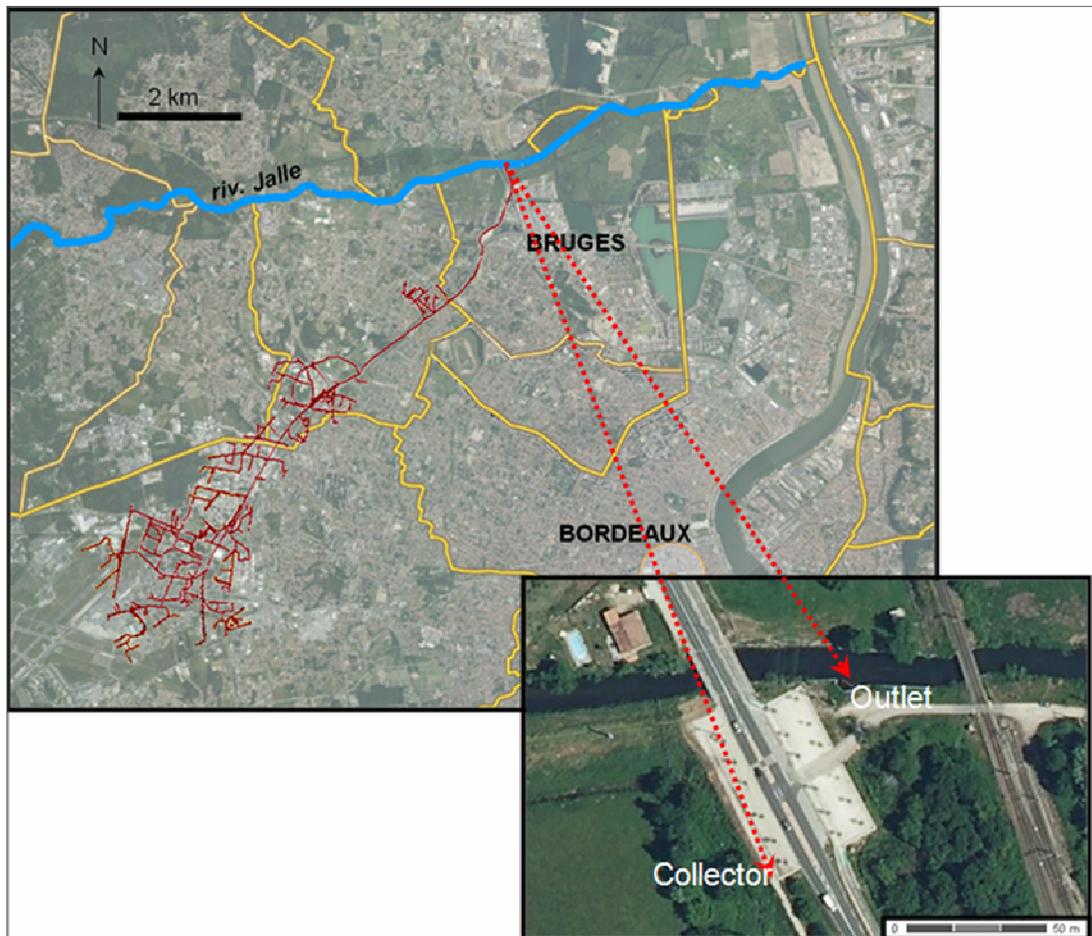


Figure IV.1. The study site: the collector discharges water to the Jalle River (superimposed on geoportail map: [geoportail.gouv.fr](http://geoportail.gouv.fr))

## 2.2. Sampling approach

Two (2) periods were chosen for the sampling campaign to compare the temporal variation. These periods represent contrasted rainfall rate as Period 1 (dry) received lesser rainfall than Period 2 (wet). The accumulated rainfall within the sampling regime is as follows: Period 1- 3.4 mm and Period 2- 35.4 mm. The sampling campaign for Period 1 was done on the 7<sup>th</sup> to the 21<sup>st</sup> of May and 12<sup>th</sup> to the 26<sup>th</sup> of August for Period 2. In the rainwater/stormwater collector, using a conventional technique, water samples were intermittently collected for the measurement of the total trace metal. Polytetrafluoroethylene (PTFE) bottles of (250 mL) were used for collection. In each period, the sample collection was done thrice (with an interval of 7 days). Figure IV.2 describes the sampling approach.

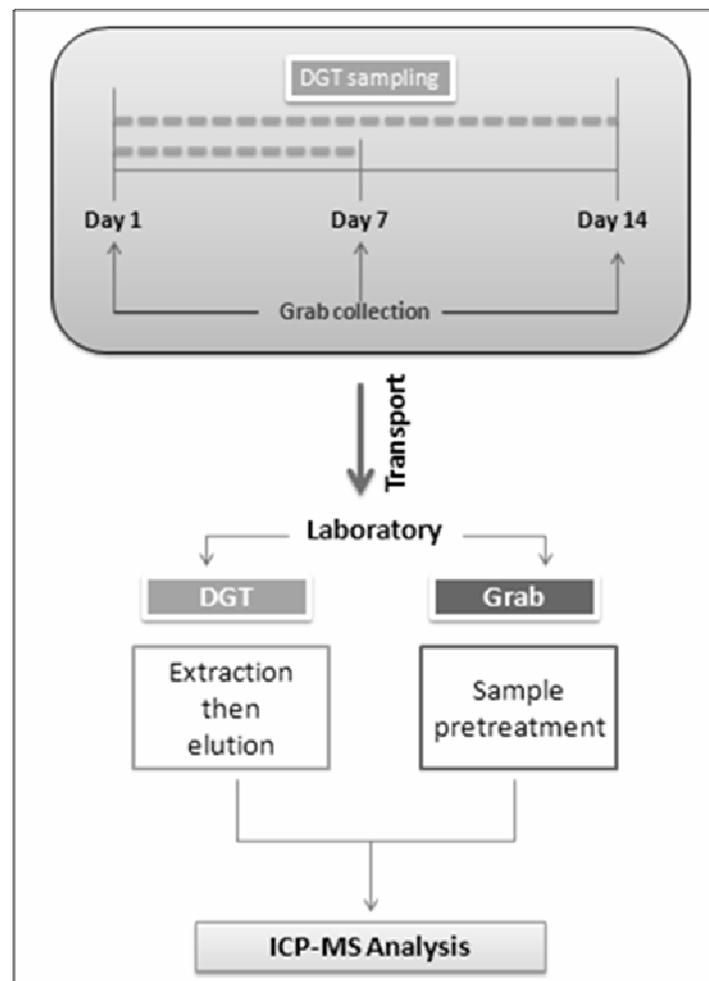


Figure IV.2. Research and sampling approach

Employing the DGT technique, samplers were placed inside the collector. In each period 4 DGT samplers were deployed. The first set of DGT samplers (n=2) was retrieved after 7 days (Day7) then the rest (n=2) was retrieved after 14 days (Day 14). Strict protocols on before and during deployments; retrieving; until transporting to the laboratory were followed. The DGT samplers were stored in the refrigerator at 4°C before doing the extraction.

### 2.3. Quality Assurance and Quality Control

DGTs were purchased at DGT Research Ltd., Lancaster, UK. The Nitric acid used is Analar grade and the Fortification Standard is of ICP-MS grade. In each of the water quality parameters considered, field and laboratory blanks were provided and detection limit of DGT samples were determined by getting the standard deviation of the blank solution multiplied by three (Li *et al.* 2005) per analyte (Cr-  $1.48 \cdot 10^{-5}$  µg/L; Co-  $1.23 \cdot 10^{-7}$  µg/L; Ni-  $2.19 \cdot 10^{-7}$  µg/L; Cu-  $1.71 \cdot 10^{-5}$  µg/L; Zn –  $3.15 \cdot 10^{-5}$  µg/L; Cd –  $1.72 \cdot 10^{-7}$  µg/L; and Pb-  $6.2 \cdot 10^{-6}$  µg/L). The relative standard deviation (RSD) is summarized in Table IV.2.

Table IV.2. Relative Standard Deviation (DGT-labile trace metal)

Average RSD (µg/L)	Dry period	Wet Period
Cd	+0.0090	+0.0025
Co	+0.0080	+0.0088
Cr	+0.0055	+0.0019
Cu	+0.0065	+0.0043
Ni	+0.0061	+0.0086
Pb	+0.0061	+0.0038
Zn	+0.0900	+0.0410

## 2.4. Chemical analysis of the trace metals

### 2.4.1. 2.4.1 Total trace metals

The water samples are analyzed LDAR 24, an accredited laboratory for chemical analyses. For trace metals most of the elements followed the NF EN ISO 17294-2 protocol of Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Elements such as Cu and Zn followed NF EN ISO 11885. Limits of detection are as follows: Cd- 0.5 µg/L; Co- 0.5 µg/L; Cr- 5 µg/L; Cu- 10 µg/L; Ni- 2 µg/L; Pb- 1 µg/L; and Zn- 10 µg/L.

### 2.4.2. DGT-labile fractions

For DGT, the resin layers were carefully removed using Teflon tweezers. Each resin was placed in a Teflon centrifuge tube with 1mL of 1M of HNO<sub>3</sub>. To allow elution, the solutions were kept for 24h. Then dilution of the eluent using de-ionized water was applied. The metal ions absorbed by the resin were analyzed using ICP-MS (ICP-MS equipment Agilent Technologies HP 4500 Series 100). The captured mass (*M*) and the time-weighted average concentration was determined following the work Davison and Zhang (1994). The process is already widely documented elsewhere (Dočekalová and Diviš 2005; Conesa *et al.* 2010)

## 2.5. Trace metal mass and fluxes

The water volume received in the collector was monitored during the sampling campaigns (e.g. water height and water flow). The diameter of the collector is 2 meters. In the absence of rainfall and run-off the water height 0.69 meter. Measured trace metal concentrations were then multiplied to the volume received to obtain the mass, shown in the formula below:

$$m = c \times V \quad \text{where,} \quad V = \sum Q$$

with:

<i>m</i>	mass (mg)
<i>c</i>	concentration (µg/L)
<i>V</i>	Volume (m <sup>3</sup> )
<i>Q</i>	Flux (m <sup>3</sup> s)

The contribution of the water catchment per hectare to the collector was then estimated ( $\text{mg ha}^{-1}$ ).

### 3. Results and Discussion

#### 3.1. Rainfall regime

The amount of rainfall accumulated on Period 1 is 3.2 mm during the span on 7 days and 3.4 mm for 14 days. Within twenty (20) days before the sampling activity, the rainfall accumulated was 6.6 mm. This actually shows scarcity in rainfall within the month. May, in this area, has only 20.6 mm lesser than the normal monthly rainfall (which is 75.3, based from year 1980 to 2012 data); only 27% of the normal. And even before this month (April) the least rainfall amount was received. It received 15.7 mm which is very far from the monthly average rainfall which is 77.2 mm. This is only 20% from the monthly average. On the other hand, the 2nd period received higher amount of rainfall (98.3 mm) compared to the normal month average (55.6). It received 43% higher than the normal. Within twenty (20) days before conducting the sampling, 71.8 mm of rainfall was accumulated. During sampling, 10 mm was accumulated within 7 days and 35.4 mm within 14 days.

#### 3.2. Trace metal temporal variation

##### 3.2.1. Total trace metal

The concentration of the measured total trace metals Figure IV.3 (a and b) were measured at three different times (days: 1, 7 and 14). Cd is below the detection limit ( $<0.5 \mu\text{g/L}$ ) in both periods. Co, Ni and Pb are higher during wet period. Cr total is above the detection limit in wet period except of Day 14. Cu is above the detection limit on wet period except on Day 7. Zn is below the detection limit on dry period Day 1 then gave high values on the following sampling campaigns. During wet period higher concentrations, in general, were observed compared to dry period.

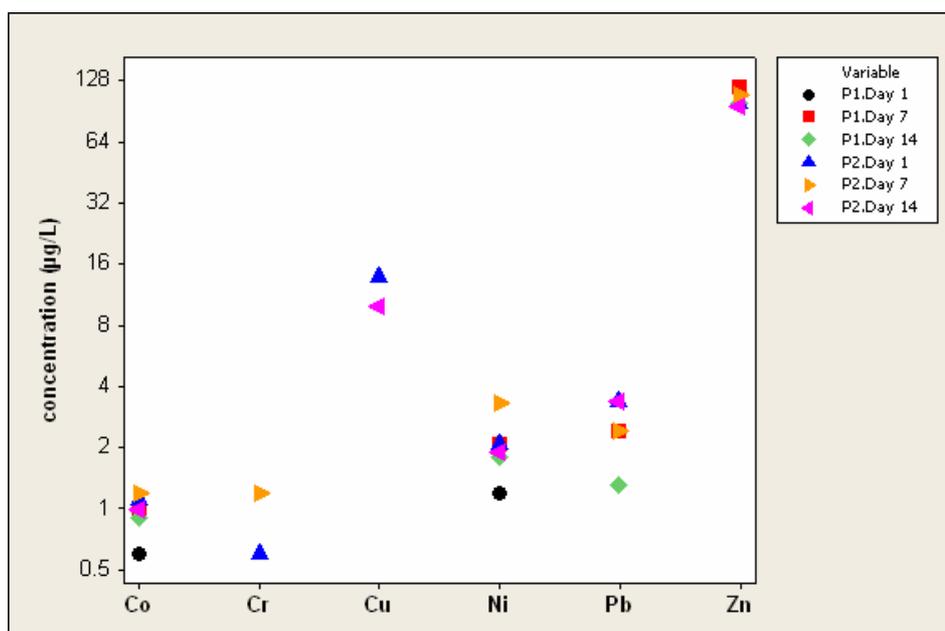


Figure IV.3. Trace metal concentrations in total fractions using the conventional sampling

### 3.2.2. DGT-labile trace metal

In researches published, the DGTs were immersed and retrieved according to a given target days or weeks; whereas, in this research continuous measurement was done. As explained in the method, DGT samplers were immersed for 7 and 14 days to see the trend of the DGT-labile trace metals. No evidence of bio-fouling was observed each time DGT samplers were retrieved. The concentrations given by all the trace elements are valuable and cannot be disregarded. The labile fractions are usually in trace level and DGT-labile trace metals are normally expressed in ng/L at time-weighted average (TWA). The results showed that the concentration values can be expressed in µg/L.

The DGT-labile trace metal measured within the collector shows variation through time (Figure IV.4). Increasing trend is observed for Zn. The increase is 9% during dry period and 25% during the wet period. Trace metals Cr, Co, Pb decrease at the 14th day. For Cd and Cu, there was a decrease after D14 during dry period, whereas, during the wet period an increase was observed. The trend of Ni is contrary to Cu and Cd.

The difference in the rainfall condition can be observed with respect to the sampling duration. During the 7 day sampling most of the DGT-labile trace metals are higher during dry period (except for Ni and Zn). The 14 day sampling, on the other hand, gave higher concentrations during the wet period except for Co. Rainfall consequence could either

introduce further trace metals or bring in a washing effect due to dilution. The rainfall rate accumulated during the dry period within 7-day sampling is 32% of the wet period; for the 14-day sampling it was only 9.60%.

The Environmental Quality Standards (EQS for surface water, dissolved fraction) requires the following limit in the concentration for each element: Cd- 0.08  $\mu\text{g/L}$ ; Co- 0.089  $\mu\text{g/L}$ ; Cr- 3.4  $\mu\text{g/L}$ ; Ni- 20  $\mu\text{g/L}$ ; Pb- 7.2  $\mu\text{g/L}$ ; and Zn - 7.8  $\mu\text{g/L}$ . The Provisional Environmental Quality limit for aquatic system for Cu is 1.4  $\mu\text{g/L}$  (INERIS 2010). From the EQS, Zn exceeded the limit in both periods and Co on the dry period.

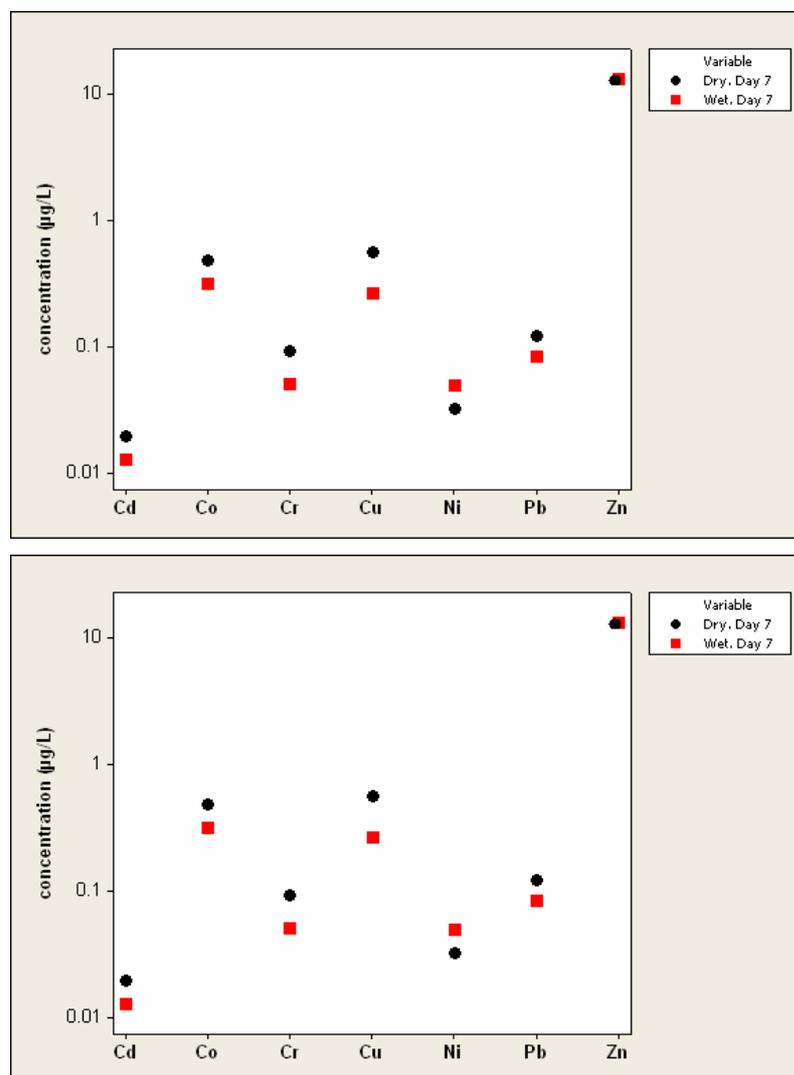


Figure IV.4. DGT-labile concentration measured within 7 (up) and 14 (down) days sampling campaigns during dry and wet periods

Table IV.3 shows the concentration of the trace metals measured from the literature. Ni and Cd in our research study site gave the lowest concentrations. Co, Cu, Cr, Pb, and Zn concentrations are close to the measured concentration at the Orge River. However, it is difficult to give an actual comparison; the result of this research focused on the labile fraction using the DGT technique, while, the others normally used the conventional sampling approach taking the dissolved fraction. Although both considered 0.45 $\mu$ m filtration, target analyte can be different. DGT made use of the chelex resin as an advantage. The chelex resin (as a chelator) can effectively discriminate the labile metal complexes in the aquatic environment (Burba *et al.* 1994; Kiptoo *et al.* 2009).

The difficulties in comparing this study to the existing literature mainly came from the methods employed. The samples from the past researches are taken directly from rainfall water or the river. Furthermore, manner of sample collection is also different as passive sampling is not employed in the past studies.

**Table IV.3. Summary of measured trace elements from the literature and this study (comparison table)**

	Dissolve fraction					DGT-labile
	Orge River catchment (Le Pape <i>et al.</i> 2012)	Noisy-le-Grand, Paris (Bressy <i>et al.</i> 2012)	Nancy (Houhou <i>et al.</i> 2009)	Lyon (Becouze 2010)	Paris district (Garnaud <i>et al.</i> 1999)	This study (2011)
<b>unit</b>	$\mu\text{g/L}$	$\mu\text{g/L}$	$\mu\text{g/L}$	$\mu\text{g/L}$	$\mu\text{g/L}$	$\mu\text{g/L}$
<b>Cd</b>				C: 0.1-2.3 E: 0.04-0.4	0.09	0.009-0.02
<b>Co</b>	0.059-0.44		3-13			0.03-0.09
<b>Cu</b>	0.460-2.23	* 3.9-11.0 ** 16.0-21.0	2-110	C : 17-74 E : 20-58	3.00	0.26-0.57
<b>Cr</b>	0.065-1.200		3-15	C : 2-21 E : 0.5-17		0.13-0.48
<b>Ni</b>	0.510-2.200			C : 4-21 E : 0.5-4		0.03-0.05
<b>Pb</b>	0.029- 0.410	*1.1-7.9 ** 7.1-15	0.1-6	C: 2-37 E: 2-39	13.50	0.03-0.12
<b>Zn</b>	0.530-16.0	*68-280 ** 460-850	8-152	C: 171-678	34.10	13.23- 16.87

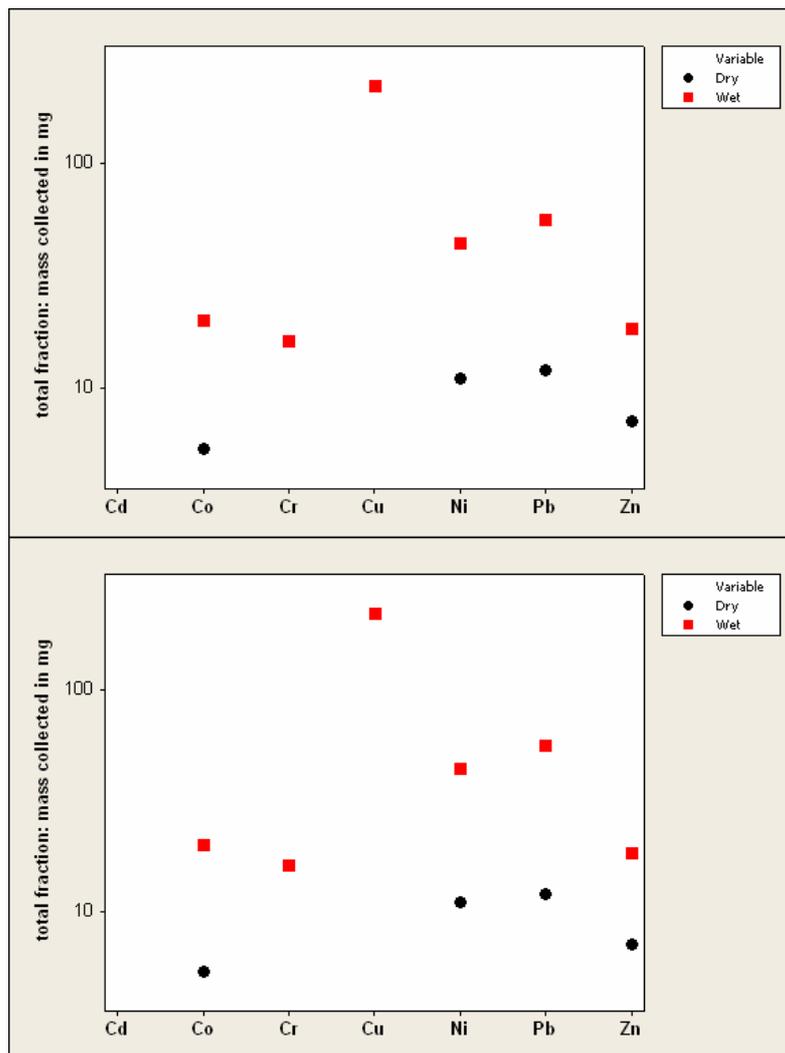
\* *bulk atmospheric deposition*

\*\* *urban run-off*

C- Chassieu; E- Ecully

### 3.3 Water volume and mass transport: Pollution Fluxes

Compared to dry period, the volume collected in wet period within 7 and 14 days are higher of 3 and 11 times, respectively. The measured mass fluxes are shown in Figure IV.5 for the trace metals in total fractions. During the wet period, the masses are higher than dry period (Co and Ni- 4 times, Pb- 5 times, Zn- 3 times) Cr and Cu were under detection limit during the dry period.



**Figure IV.5. Trace metal total fraction: accumulated trace metal masses (up) and the trace metals fluxes contributed per hectare of the active catchment basin (down) during 14 days at the collector**

Figure IV.6 shows the accumulated mass within the sampling campaigns for the DGT-labile trace metals. The percent increase from dry to wet period is as follows: Co- 265%, Cr ~63%, Cu ~118%, Ni- 296%, Pb- 354%, and Zn- 157%. For both sampling regime (7 and 14 day), there is an evidence that the mass transport is higher during wet period. This case is highly pronounced within the 14 day sampling. Within 7 days, the mass difference between the dry and wet period was calculated. Wet period is higher by at least 100 mg (Cd- 144 mg; Co- 451 mg; Cr- 3 590 mg; Cu- 1 818 mg; Ni – 873 mg; Pb- 958 mg; and Zn- 197 641 mg). Within the 14 day sampling, the mass difference is at least 1 g. The accumulated mass difference is as follows: Cd- 1 492 mg; Co- 2 331 mg; Cr- 13 490 mg; Cu- 29 904 mg; Ni – 2 639 mg; Pb- 3 205 mg; and Zn- 11 918 mg. Figure IV.7 displays the calculated mass per

hectare. This gave daily averages fluxes shown in Figure IV.8. During the wet period, the fluxes (in daily average) are higher by: Cd- 44%; Co- 0.13%; Cr- 61%; Cu- 90%; Ni- 83%; Pb- 62%; and Zn- 79%. The results indicate that the collector held masses of pollution.

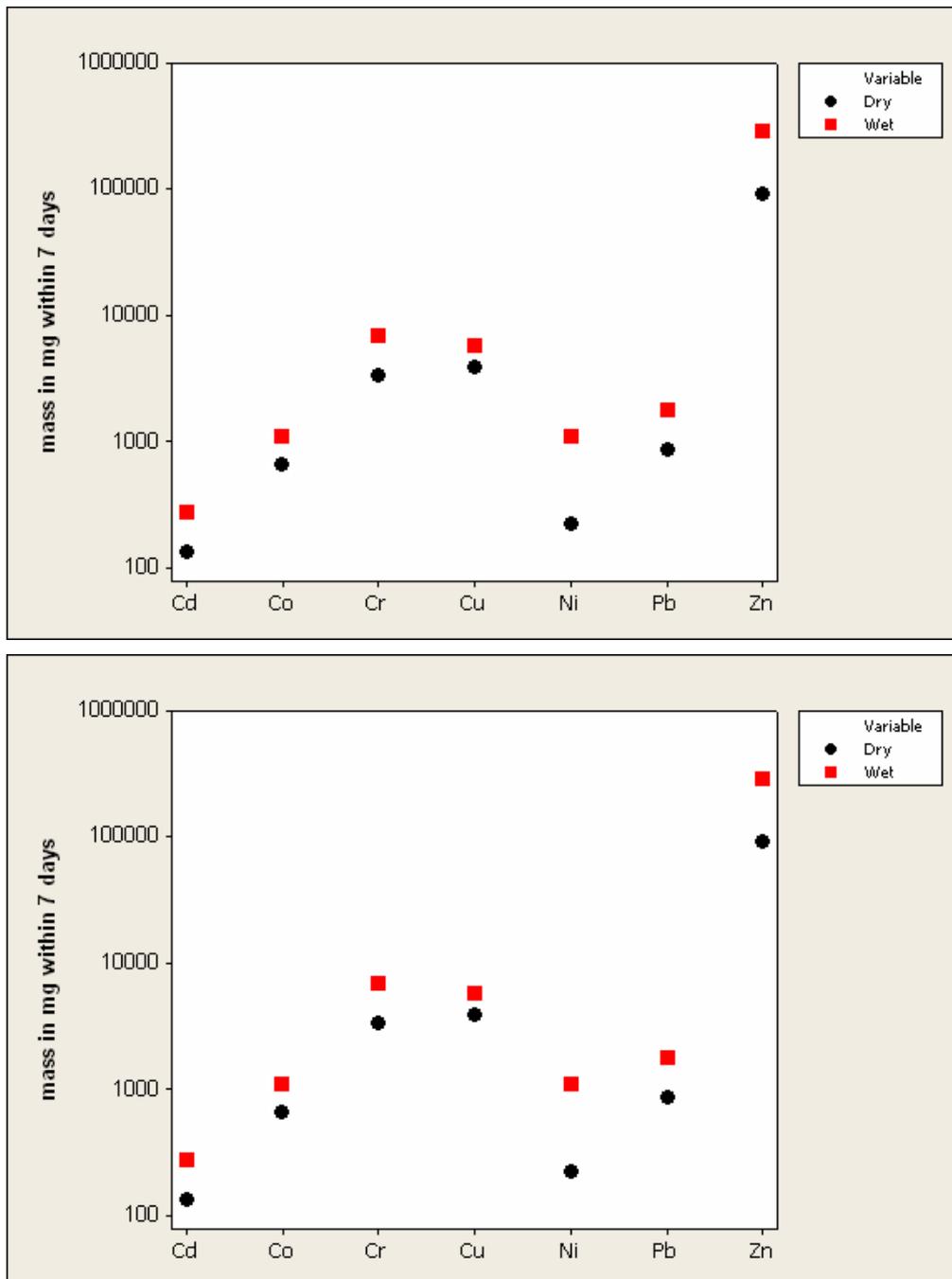


Figure IV.6. (Mass) Loads of DGT-labile trace metal at the active catchment basins in different segments under the sampling regimes (dry and wet) during 7 day (up) and 14 day (down) sampling regime

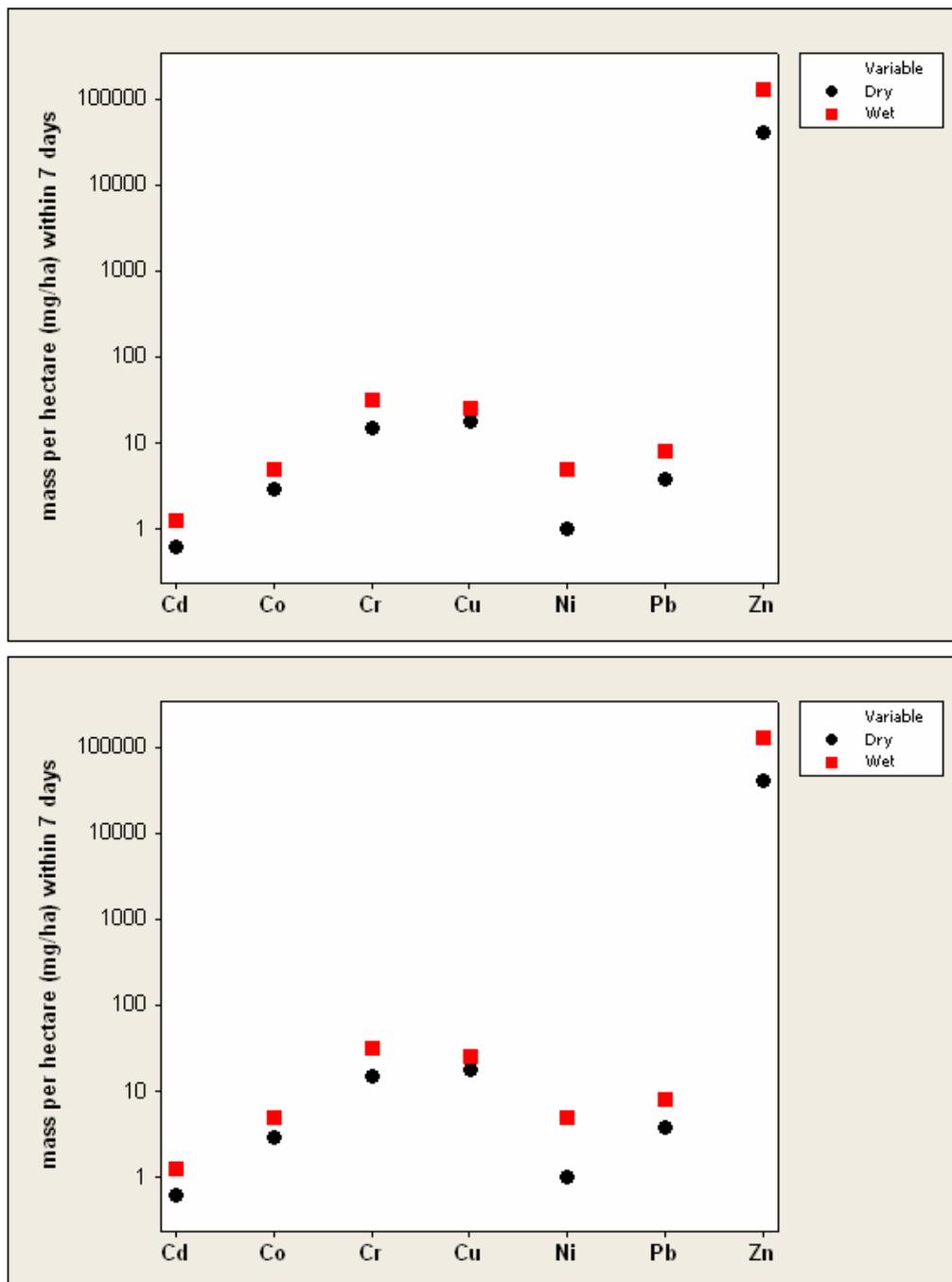


Figure IV.7. Mass per hectare of the active catchment basin accumulated within 7 days (up) and 14 days (down)

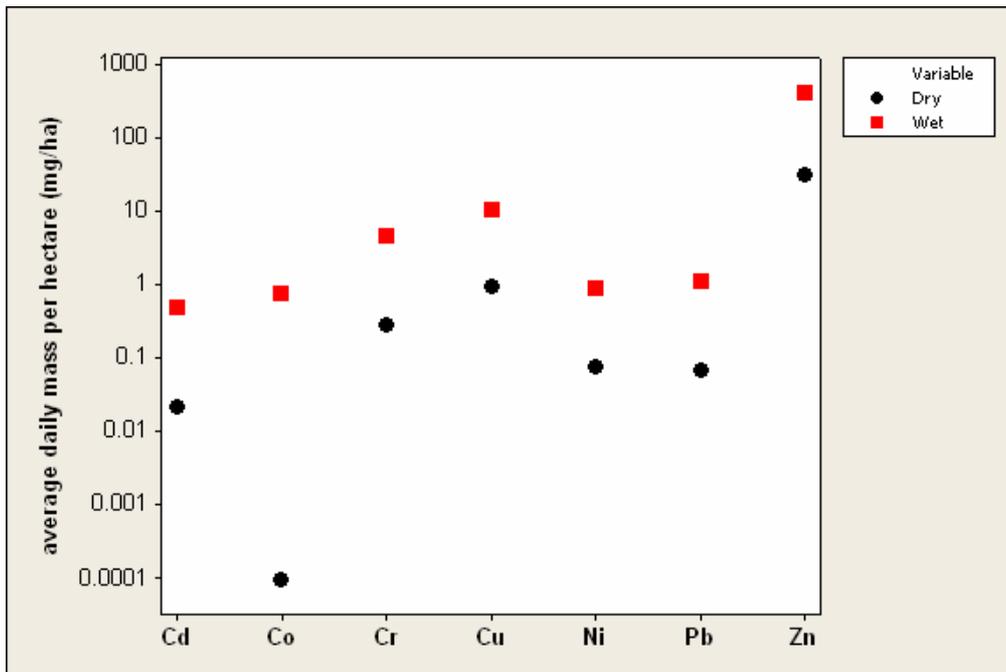


Figure IV.8. Average daily fluxes of trace metals at the collector for dry and wet periods

#### **4. Conclusion**

Measuring the trace metals at the rainwater/stormwater collector located at the watershed catchment is imperative. This allows assessing the quality of the water that the collector discharges. The importance and advantages in using the DGT technique is established in application to measuring the trace metals and appraising pollution. This technique allowed following the trace metal trend during Period 1 (dry) and Period 2 (wet). Considerable difference in the concentrations of the total and DGT-labile fractions was observed. Thus, variation in terms of the temporal trend is significant.

There are trace elements that are found higher in concentration during dry period. Concentration could be higher but the pollution fluxes brought about by the collected rainwater and surface runoff can be more dangerous as a whole. The accumulated mass fluxes of the DGT-labile trace metals at the collector are higher even up to more than a ten-fold during the wet period.

The temporal variation in terms of concentration gave substantial information that the rainwater/stormwater collector hold fluxes of pollution. This could eventually pose problem to the Jalle River as a direct receiving body. Thus, continues water quality and pollution transport assessments are necessary.

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## **CHAPTER V Assessment of trace metals during episodic events using DGT passive sampler: A proposal for water management enhancement**

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### **Abstract**

The potential of the Diffusive Gradient Thin-Films (DGT) as a supplemental method for water quality monitoring was employed has been tested through 3 sampling campaigns to measure the trace metals (Cd, Co, Cr, Cu, Pb, Ni and Zn) present in the surface water of a highly urbanized river. Specifically, the study done in the Pasig River (Philippines) seeks to: assess the applicability of DGT passive sampler in an urban context exhibiting highly contrasted hydrological conditions (greatly influenced by episodic events) and sediment disturbance (dredging) and provide proposal for a better water management. The results indicate that: (1) DGT is highly recommended as part of a routine analysis for water quality monitoring; (2) DGTs are able to capture the fluxes even in very contrasted flow regimes; (3) DGT are suitable to trace the labile fluxes of metals from the lake to the estuary; and (4) at the confluence of the Marikina River water management should be intensified. Moreover, recommendations were made for developing pertinent water monitoring protocol and management scheme.

**Keywords** Trace metals, DGT, in-situ passive sampling, surface water, water quality monitoring, Pasig River, Philippines

## 1. Introduction

Pollution of surface water is a worldwide issue of environmental concern (Ouyang 2005). Among the water bodies, estuary is challenging. The manner of using (Hartnett *et al.* 2011), the interfaces among the saline gradient and the continuous tidal actions make the system diverse and complex (Winn *et al.* 2003). Trace metals are among the few persistent contaminants introduced into this type of water resource (Severini *et al.* 2009). Their distribution (Zwolsman *et al.* 1997) and bioavailability in the estuaries are now of major environmental concern in terms of water management (Masson *et al.* 2011).

The development of monitoring approaches requires essential elements of the water system under study such as: (1) being adapted; (2) giving representative information; and (3) entailing consistent and specific approach or methodology (Strobl and Robillard 2008). Sampling approaches, normally, involves conventional spot and grab sampling for water quality monitoring. However, this can disturb the natural chemical reaction in the samples

Aside from the fact that these trace metals are very sensitive so that accuracy of data can be a problem. Accordingly, in-situ measurements are being advised. It can give more reliable information on the distribution of the chemical species in natural water (Zhang and Davison 1995; Lu *et al.* 2002; Allan *et al.* 2008; Vrana *et al.* 2005). Another difficulty is the lack of reliable and low-cost water quality sensors for continuous monitoring (Aisopou *et al.* 2012). Normally, the budget constraint should also be considered but the analytical procedure must not be at stake because of this reason.

The emerging in-situ passive sampling appears to give good responses to the above mentioned problems. Additionally, advantages include (Graveline *et al.* 2010): (1) allowing accumulated weighted average or high-time resolution of concentration (making it possible to assess the total load carried by a stream over a given period of time); and (2) capable of measuring the presence of the contaminants that the conventional sampling could not be able to detect (passive samplers can detect even trace to ultra trace level). From the actual experience, this: (3) in terms of prioritization, can be able to locate the most challenging (deteriorating water quality) area at a shorter period of time; and (4) does not need huge quantity of water to transport and store in the laboratory before analysis. Inferences can be made since it has an operationally defined measure of DGT- labile trace metals that contains the “bioavailable” fraction (INAP 2002). Success on the use of the DGT in tracing and

monitoring labile trace metal species had been documented (Alexa *et al.* 2009; Docekalova and Divis 2005; Pérez and Anderson 2009; Vystavna *et al.* 2012a; Sherwood *et al.* 2009; Munksgaard and Lottermoser 2010).

In this paper, the trace metals such as Cadmium (Cd), Cobalt (Co), Chromium (Cr), Copper (Cu), Nickel (Ni), Lead (Pb) and Zinc (Zn): (a) in total, using the conventional method, normally, employed by the local water authorities and (b) DGT-labile metal fractions, using the DGT technique were evaluated to help in determining the water quality state of an estuary in the Philippines. The use of the DGT is a pilot study in this country, which can provide a more holistic situation for water resource managers on the trace metal distribution and bioavailability. The aim of this paper is not to compare the total to DGT-labile trace metals but to give an overview of their behavior in response to the captured episodic events and to provide a supplemental water quality measurement strategy for a better water resource assessment.

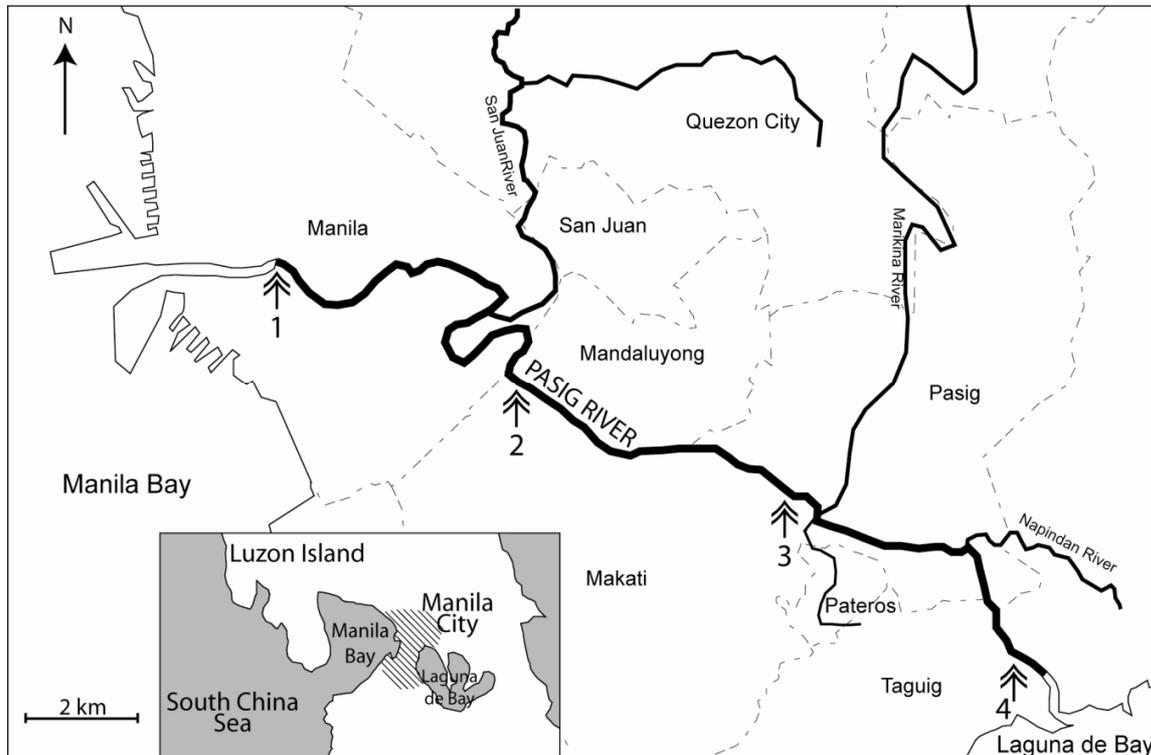
## 2. Materials and Methods

### 2.1. Study site

The surface area of the Pasig River is 1,710 km<sup>2</sup>. This stretches to about 27 km with water volume of 6.5 million m<sup>3</sup>. The width is from 62 m to 120 m with an average of about 90 m. The shallow part is around 1 m, while, the deepest is 5 m. The shoreline length is almost 5 km. Average low flow is 12 m<sup>3</sup>/s, with a maximum flow of 275 m<sup>3</sup>/s during dry and wet seasons respectively (PRRC 2009). Four major and important tributaries drain to this river. These are the San Juan River, Marikina River, Napindan River and Pateros-Taguig River. The minor tributaries, around 43, have the surface area ranging from 2 km<sup>2</sup> to 400 km<sup>2</sup>.

As the main river in the National Capital Region (NCR), commonly called Manila (c.a.~11,500,000), joining the Manila Bay (downstream), to the west, and the Laguna Lake (upstream), to the east (Figure V.1). It is influenced by fluxes from industries, residential houses, informal settlers, and other commercial areas. The river also receives wastewaters from surrounding cities where about 50 percent of the pollution load comes from the industry with an equal percentage coming from domestic liquid wastes (Cruz 1997). Industries include: mill factories, ceramic and tile industries, steel industry, oil depots,

chemical industry, sugar refinery, power plant, food and beverage and gas stations. Despite the alarming water quality, the river is still in function such as for swimming, fishing, navigation (boats, ferries, ships, etc.), growing of lilies and the riparian area serve as recreational area such as parks.



**Figure V.1. Map of the Pasig River with the identified sampling points (Point 1: downstream; Points 2 and 3: midstream; and Point 4: upstream)**

The Pasig River was selected for this pilot activity since: (1) it is one of the major and important river basins in the Philippines; (2) the highly urban situation and lack of water treatment plants (although, industries are mandated to have such facilities) pose water quality problems such as contamination; (3) the condition such as low and high flow permits the hydrological representativeness; and (4) the chosen sampling sites are under the water surveillance of the local authorities mainly headed by the Pasig River Rehabilitation Commission (PRRC).

## 2.2. Sampling

Four sampling points were considered (Figure V.1) taking into account the river sections (upstream, midstream and downstream), the salinity gradient and impacts of

anthropogenic activities. The approximate distance of each sampling point from each other is 7 kilometers. Point 1 was at the mouth of the river, towards the Manila bay, Points 2 (near San Juan River) and Point 3 (close to the Marikina River) were located in the midstream of the river and Point 4 is near the outlet of Laguna Lake at the eastern part of the Pasig River.

Seasonal variations (dry and wet) were taken into account so sampling was done three times as seen in Table V.1. Pasig River is classified under the Climate Type I under the Philippine Corona System which has a two (2) distinct seasons: wet (May to October) and dry (November to April). The seasonal variation influences the hydrological condition of the river so the sampling campaigns were done in the months of April-May 2010, January 2011 and May-June 2011. These are representatives of the intermediate (between the dry and wet) period (Sampling Period 1); dry season (Sampling Period 2) and start of the wet season (Sampling Period 3). To fully capture the hydrological condition (especially the intermediate period) and estuarine ecotone of this river, more than 2 weeks (n=18 days) was selected. In addition the length of the deployment period chosen corresponds to the recommended average immersion in water (about minimum of a week to a month).

**Table V.1. Sampling regimes (Expected vs. actual experienced seasons)**

Sampling Date	Period 1 April to May	Period 2 January	Period 3 May to June
<i>Expected</i> season	intermediate period	dry season	wet season
*Mean normal precipitation rate 1971-2000 (mm)	21.4(Apr )-165.2(May)	19.0(Jan)	165.2 (May)-265.0(Jun)
<i>Actual</i> season	dry season	wet season	wet
**Actual precipitation rate (mm)	30.6(Apr )-48.6(May)	93.4(Jan)	196.4 (May)- 462.2 (Jun)
**Precipitation rate within the sampling period(mm)	6	79	79.8

\*CDS/CAB/PAGASA,DOST (Port Area, Manila station) : (unpublished data, 2012)

\*\*provided by Manila Observatory (unpublished data, 2012)

However, unexpected events which can potentially have some bearings on hydrological conditions were encountered: Sampling Period 1 experienced dry season; Sampling Periods 2 and Period 3 covered wet period (Table V.1). Compared to the normal precipitation rate, for the year 2010, April is a little bit higher (0.43 %) than the normal while May is only 3.43 % of the normal; for the year 2011, January, May and June were higher (4.92 times, 0.19 % and twice, respectively) than the normal precipitation rate.

The country during these periods experienced climatic variation called the El Niño Southern Oscillation (ENSO) phenomenon. This phenomenon is characterized by "warm events or drought" due to the movement of the warm sea water from the western Pacific

followed by the "wet events" coming from the easterly trade-wind-induced flows of colder water from the eastern Pacific (Harger 1995). The seasonal surface circulation in the Philippine archipelago affects the surface water movement with strong variation on currents and tides (Han *et al.* 2009). In addition to this situation, during the 1<sup>st</sup> sampling period, simultaneous to the sampling activity, a dredging activity was on-going. Improving the canal system specially in diverting the water during floods to the Napindan Hydraulic area was one of the objectives.

Accessibility and security of the DGT probes were also considered as the probes have to be immersed in the river for a long period. Environmental parameters such as pH, salinity and conductivity, water temperature and dissolved oxygen (DO) were determined *in-situ* using an automatic sampler, YSI 6600 V2 data sonde. The total organic compound (TOC) of the Pasig River ranges from 3.4 to 4.5 mg/L during May 2010 and 3.5 to 7.4 mg/L for January 2011 (Materum 2010). In parallel, conventional water sampling following the normal procedure of the local water authorities using bottles was performed. The unfiltered water samples were collected using acid-rinsed (1:10 HNO<sub>3</sub>) 150 mL Nalgene bottle (n=2 per site) during each sampling period. These then were stored in a refrigerator.

The DGT probes (n=2) were left fully-immersed for a period of 18 days in each sampling station placed in a specially manufactured container made in bamboo (Figure V.2). Field blank (n=1) per sampling campaign was provided. Cooling compartments and pre-cleaned re-sealable plastic storage bags properly marked were prepared before the retrieval. Upon retrieval, each DGT was rinsed with deionized water (Milli-Q at 18 mega ohms cm) and immediately placed in the pre-cleaned resealable plastic bags then put in the cooling compartment. Subsequently, DGTs were kept in the refrigerator until the extraction was performed.

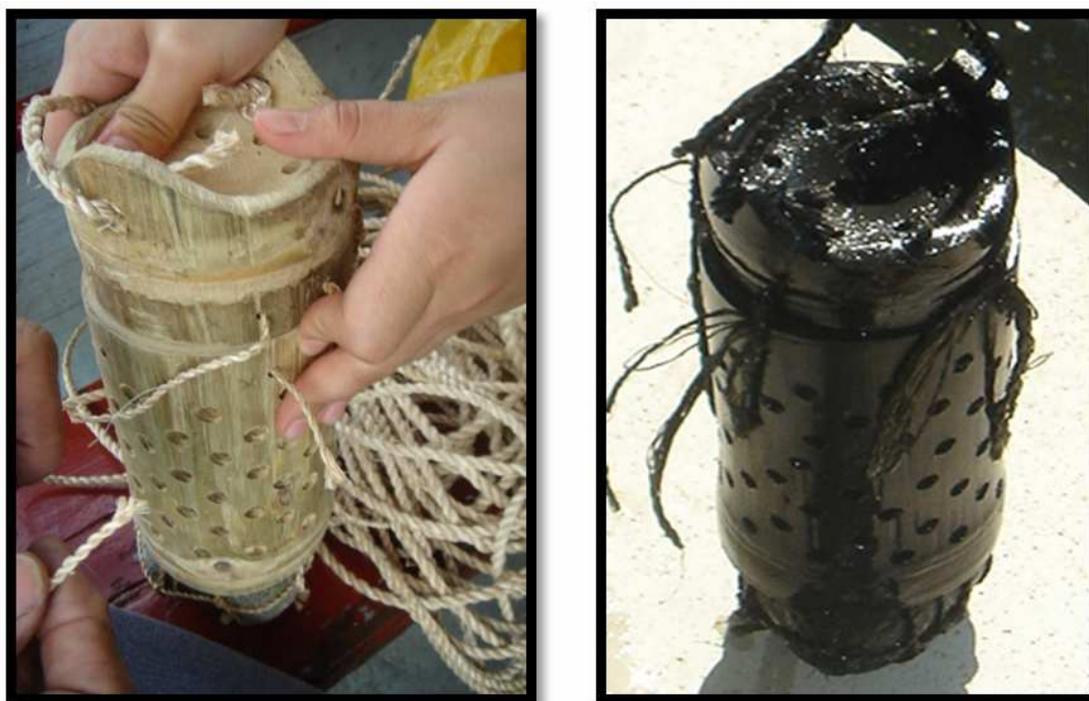


Figure V.2. Bamboo container before and after deployment (Period 1)

### 3. Materials and Quality Control

The nitric acid used is Fisher Scientific Analar grade. DGTs were purchased at the DGT Research Ltd, Lancaster, UK. DGT field blanks (n=3) were extracted and analyzed using the same procedure done for the DGTs deployed in the river. In each of the water quality parameters considered, laboratory procedural blanks were done and detection limit were determined by getting the standard deviation of the blank solution multiplied by three (Zheng *et al.* 2012; Pattke *et al.* 2012). The blank values were then subtracted to the values obtained from the field-deployed DGTs. Precision of the replicates of all the total trace metals collected conventionally is 10 %. While, the Relative Standard Deviation (RSD) obtained from DGT is shown in Table V.2. RSD from the DGT samplers seemed to be higher than the values obtained from the total trace metals.

Table V.2. Mean %RSD of measured DGT-labile trace metal concentration

%RSD/ Sampling regime	Cd	Co	Cr	Cu	Pb	Ni	Zn
Period 1	3.40	36.79	5.37	48.98	10.97	41.63	8.05
Period 2	33.10	2.65	8.17	4.54	4.48	3.90	2.52
Period 3	1.65	3.69	5.66	1.33	7.56	0.07	3.91

### 3.1. Determination of trace metals

#### 3.1.1. Total trace metals (on conventional approach: water samples from bottles)

At the laboratory, since samples are from an estuary, dilution using deionized water (Milli-Q) was applied and prepared in a Teflon centrifuge tube. The protocols for clean room; laboratory sample handling including pretreatment for total trace metal; and the use of inductively coupled plasma-mass spectrometry (ICP-MS) and instrument analysis followed the analysis of surface water for trace metal elements by ICP-MS guidelines (Shafer and Overdier 1995). Measurement of selected trace metals was performed using ICP-MS equipment Agilent Technologies HP 4500 Series 100. 10 mL each of previously acidified samples (using 65 % HNO<sub>3</sub> (Merck Suprapur®)) were filtered with 0.45 µm syringe filter cartridges (Millipore Millex®-LCR hydrophilic PTFE, 25 mm). Calibration curves of the trace metals of interest were made beforehand using Merck CertiPUR® ICP multi-element standard solution VI for ICP-MS. TMDA-70 (lot 1007), a water sample from Lake Ontario fortified with trace metals purchased from Environment Canada, served as the certified reference material for verifying the quality of the analytical results.

#### 3.1.2. DGT-labile trace metals (in-situ passive sampling)

In the laboratory, resin layers were carefully removed using Teflon tweezers. Each resin was placed in a Teflon centrifuge tube with 1mL of 1M of HNO<sub>3</sub> (Aung *et al.* 2008). To allow elution, the solutions were kept for 24h. Dilution of the eluent using deionized (Milli-Q) was applied, subsequently. The solutions were then analyzed using ICP-MS. Details on the process are extensively discussed in many journal articles already (Zhang and Davison 1999 and Li *et al.* 2005). The environmental concentration of trace elements was calculated using the following formula (DGT Research 2002):

$$C_{DGT} = \frac{M\Delta g}{D At}$$

Where,  $C_{DGT}$  is the measured DGT labile trace metal concentration;  $A$  is the exposed area of the DGT probe;  $\Delta g$  is the thickness (PAA hydrogel);  $D$  is the diffusion coefficient which is water temperature dependent (obtained from the study of DGT Research 2002);  $t$  is the total time of deployment; and  $M$  is the mass of the labile metal captured at the binding phase. The latter is calculated as follows:

$$M = \frac{C_{el} (V_{gel} + V_{HNO_3})}{f_e}$$

Where,  $C_{el}$  is the concentration of the metals in the elution solution;  $V_{gel}$  is volume of the resin gel;  $V_{HNO_3}$  is the volume of  $HNO_3$  added to the resin and  $f_e$  is the elution factor.

## 4. Results and discussions

### 4.1. Variation of routine environmental parameters

Environmental factors such as physical, chemical and biological constituents of the water quality affect the physical and chemical condition of a water body (Wei *et al.* 2009; Vystavna *et al.* 2012b). As shown in Table V.3 the results on the routine environmental parameters indicate spatial and temporal variation of dissolved oxygen (DO), salinity and conductivity. The environmental factors were evidently influenced by the episodic events during the sampling periods mostly expressed in DO. The DO exhibited different oxidic conditions through periods.

The Department of Environment and Natural Resources (DENR), in Philippines is the main authority which manages and implements the water regulations. One of the regulations is the Department Administrative Order 34 (DAO) which is for the Water Usage and Classification or Water Quality Criteria. It requires a minimum of 5 mg/L for DO. Periods 1 and 3 failed to comply in this regard. However, compared to the set limit of the Canadian Council of Ministers of the Environment (CCME 1996) for marine and estuaries, this is lower, DO should be above 8mg/L. In this case, only the upstream met the limit.

Table V.3. Environmental water quality parameters measured in the sampling periods in the identified sampling points (*mean values*)

Sampling Period/Point	Water Temperature (°C)	pH	Salinity	Dissolved oxygen (mg/L)	Conductivity (ms/cm)
<b>PERIOD 1</b>					
Point 1	31	7.89	3.60	0.45	22
Point 2	31	8.35	2.00	0.55	15
Point 3	31	8.15	0.78	0.85	8
Point 4	33	8.32	0.55	1.05	6
<b>PERIOD 2</b>					
Point 1	26	7.73	0.39	5.90	0.81
Point 2	26	7.32	0.39	6.32	0.83
Point 3	26	7.31	0.39	6.52	0.83
Point 4	27	7.52	0.40	8.20	0.84
<b>PERIOD 3</b>					
Point 1	31	6.80	8.44	1.89	16
Point 2	31	7.03	4.19	1.55	8
Point 3	31	7.00	1.98	1.66	4
Point 4	32	7.01	0.39	2.26	1

## 4.2. Distribution of trace metals

### 4.2.1. Total trace metals

The range of concentration of total trace metals is presented in Table V.4. Period 1 gave the highest total trace metal concentration among all the periods with values of an order of magnitude to two more than the 2 other periods. This is the case for Cr, Cu and Cd. Others (Pb, Ni and Zn) have close range of concentrations for the 3 periods with some having problem of under the limit of detection. The only metal which increased its concentration during the last period is Co.

**Table V.4. Range of concentration of the measured trace metals: (total using conventional sampling method and the labile trace metal using DGT passive samplers) (RSD for the total trace metals is  $\pm 10\%$  while for  $C_{DGT}$  is indicated in Table 2)**

Period 1	<i>Total (ng/L)</i>			<i>C<sub>DGT</sub> (ng/L)</i>		
	<i>Range</i>	<i>Mean</i>	<i>Sum</i>	<i>Range</i>	<i>Mean</i>	<i>Sum</i>
Cd	9100-27300	17200	68790	86-94	89	360
Co	70-740	340	1350	28-81	52	210
Cu	8160-27100	17230	68900	87-310	170	690
Cr	2700-6330	4810	19260	200-240	210	880
Pb	1080-5440	2530	1010	94-120	110	440
Ni	** -2270	---	2270	150-430	260	1020
Zn	2800-5170	3820	15290	830-1030	910	3640

Period 2	<i>Total (ng/L)</i>			<i>C<sub>DGT</sub> (ng/L)</i>		
	<i>Range</i>	<i>Mean</i>	<i>Sum</i>	<i>Range</i>	<i>Mean</i>	<i>Sum</i>
Cd	** -60	30	100	140-150	140	570
Co	**	**	**	120-280	180	720
Cu	1490-1700	1590	6350	510-870	620	2480
Cr	2350-3810	2860	1140	6840-7620	7070	28290
Pb	1080-2340	1670	6690	50-640	350	1410
Ni	**	**	**	210-250	230	920
Zn	7740-1850	1170	4660	790-1240	980	3910

Period 3	<i>Total (ng/L)</i>			<i>C<sub>DGT</sub> (ng/L)</i>		
	<i>Range</i>	<i>Mean</i>	<i>Sum</i>	<i>Range</i>	<i>Mean</i>	<i>Sum</i>
Cd	**	**	**	1-18	1	5
Co	700-1500	1160	4650	62-100	88	360
Cu	**	**	**	150-250	180	730
Cr	900-1500	1250	5000	12-20	18	75
Pb	1100-2500	17500	7000	6-20	9	37
Ni	1600-2000	1860	7450	20-30	24	100
Zn	2000-9000	3960	15850	430-1470	1000	3990

\*\*below the limit of detection

DAO 34 has recommended water quality limit for Cr, Cd and Pb but Cu is in dissolved form. If this will be followed, then Cr in Period 1 sampling points 1 and 3 and Cd concentrations in all sampling points during Period 1 were above the limit (Figure V.3). But Pb is within the limit. Figure V.4 shows the total trace metal concentration percent

contribution along periods. Notably, with reference to the lake, all trace elements increased as they reach Point 3.

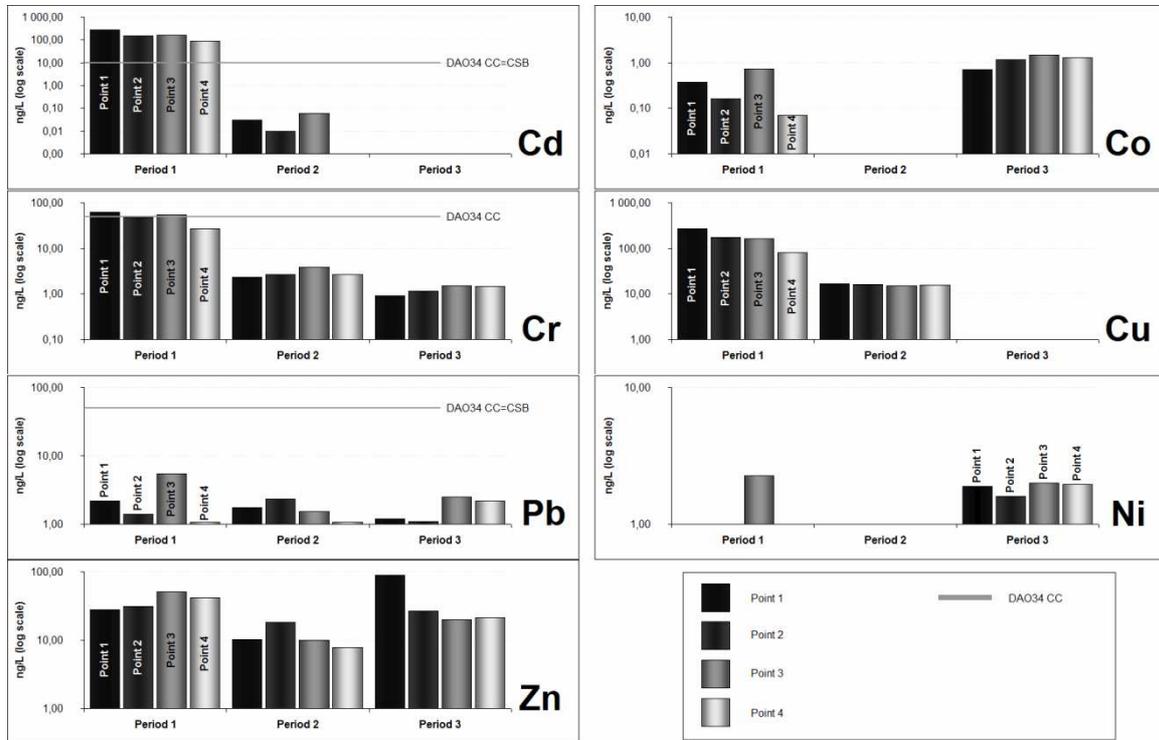
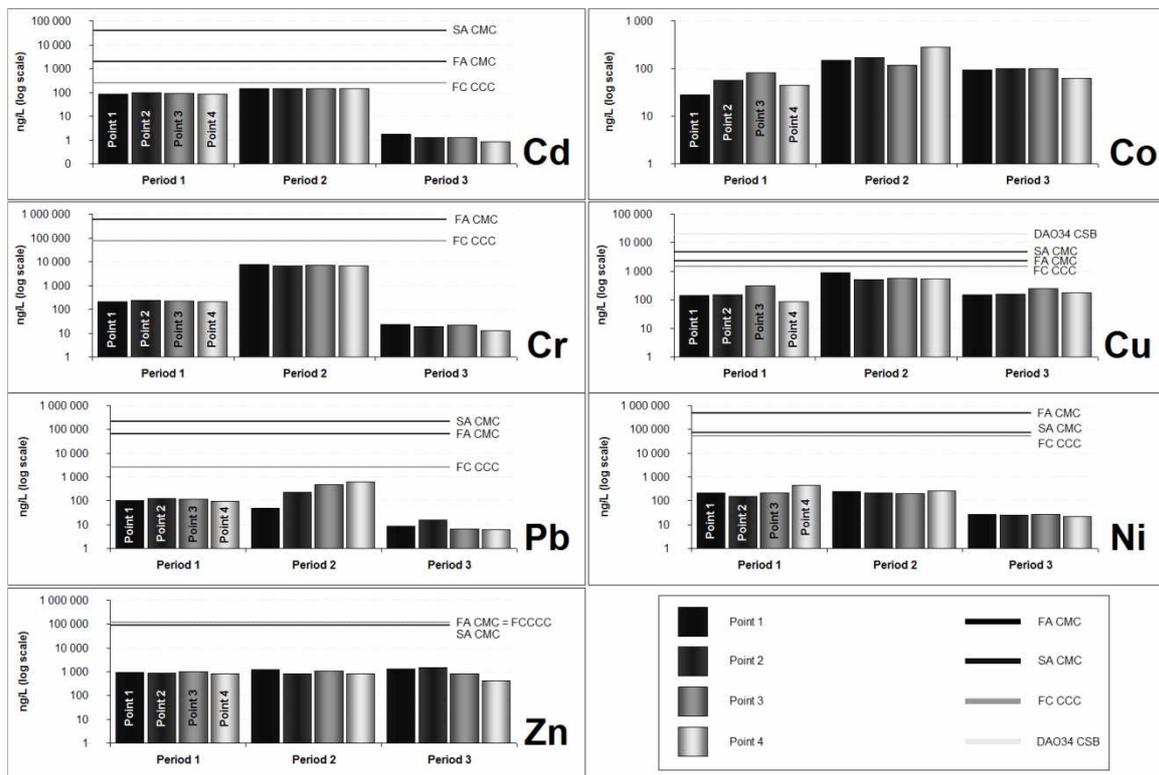


Figure V.3. Total trace metal concentration (DAO 34: Water Usage and Classification/Water Quality Criteria; DAO 34 CC: Class C for fresh surface water corresponding to fishery water, recreational water class II and industrial water supply class I ; DAO 34 CSB: Class for coastal and marine waters corresponding to the recreational water Class I and fishery water class I DAO 35: Revised Effluent Regulations of 1990)



**Figure V.4. Calculated DGT ( $C_{DGT}$ )-labile metal concentrations (from US EPA Water quality guidelines: FA CMC: Freshwater in Acute Criteria Maximum Concentration; FC CCC: Freshwater Chronic Criterion Continuous Concentration; and SA CMC: Saltwater Acute Criteria Maximum Concentration)**

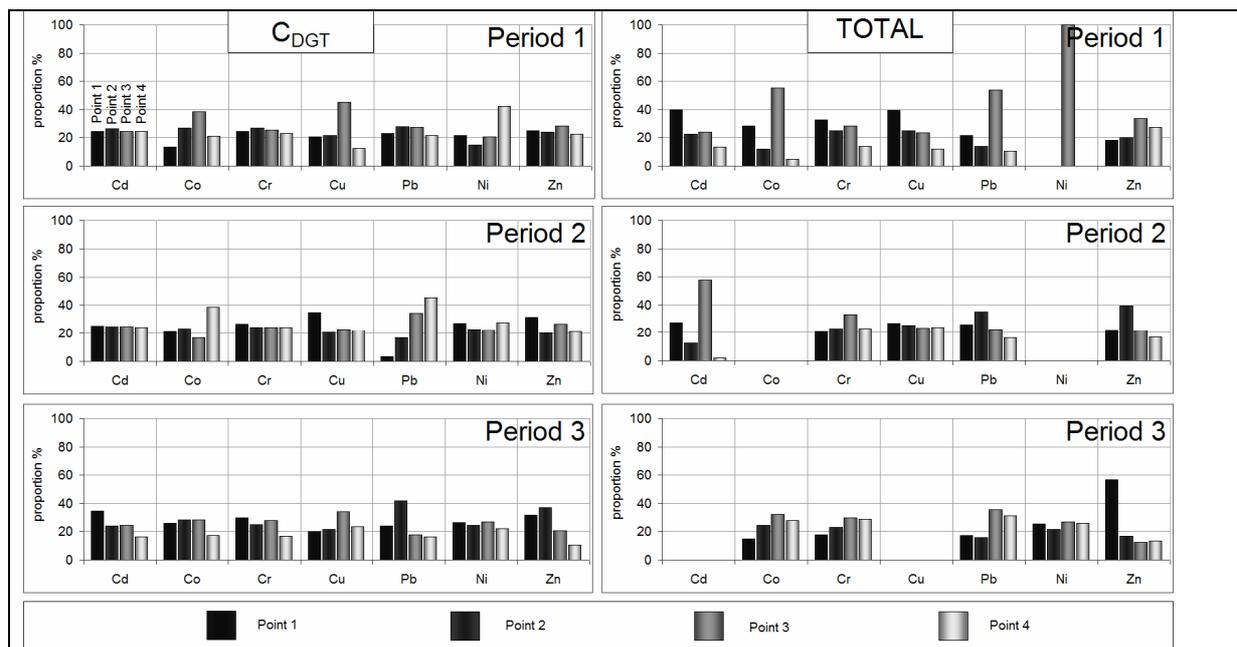
The results obtained revealed that some trace metals were not measured as depicted by the values of under the limit of detection (Table V.4) such as in Period 1, with the noticeable exception of Ni at point 3. It was then observed during the Period 2: Co, Ni and Cd at point 4; and Period 3: Cu and Cd. Evidently, some reasons can be pointed out: (i) some trace metals are in very low concentration, (ii) sampling volumes were not sufficient, and (iii) problems occurred during the analysis. This is even if the sampling and analytical procedures had been in the best possible conditions and norms following also the recommendations of the scientific community and local authorities. Thus, it shows the limitations of the sampling procedure made in the case the trace metals (Co, Ni and Cu, for example, during Periods 2 and 3).

#### 4.2.2. DGT-labile trace metals

The concentrations varied through periods. At Period 1, the concentrations decreased except for Ni and Zn. Increase then followed at Period 2 except for Co and Pb. At the last period,

only Cr, Ni and Cd continuously increased. Similar to the total trace metals, most of the concentrations increased at the confluence of Marikina River (sampling point 3), with reference to the lake. Figure V.5 illustrates the calculated DGT concentration ( $C_{DGT}$ ) in each period and each site. Periods 1 and 2 exhibited higher value than Period 3, except for Zn which was quite constant during all the sampling periods. Period 2 gave the highest values compared to the others with the concentration of an order of magnitude to two, particularly for Cr. For all the periods, it seemed that the DGT-labile trace metals did not exceed the recommended water quality criteria on dissolved fraction (Figure V.5) basing on the U.S. Environmental Protection Agency (USEPA 2012) and DAO 34 for Cu, Co, on the other hand, is not included in the criteria due to a lack of toxicological data (Diamond et al 1992).

Contrary to the results obtained in measuring the total trace metals there is no missing data. The DGT probes were able to record the DGT-labile trace metals in terms of detection; managing the problems of trace level quantities and sampling and analytical procedures. All the probes deployed served their function and was able to deliver the necessary information (in terms of concentrations and fluxes). The values obtained are in the range of the ng/L. For most of trace metals, the DGT-labile forms are lower than the observed total fractions, which is a normal/logical trend. However, there are some exceptions Table V.4 observed during the 2<sup>nd</sup> period, where DGT-labile concentrations of Cd and Cr exceeded the total fractions. This is not common but can be attributed to: (1) different sampling procedures obtained; (2) manner of sampling in terms of time (as DGT uses the concept of weighted average time while the conventional procedure is instantaneous); (3) trace metal behavior, itself, depending on how it responds to the natural system or episodic event (e.g. surface-run-off, atmospheric contribution, etc.) which can induce higher level of labile trace metals.



**Figure V.5. Percent contribution per site of each trace elements in total and DGT-labile fractions for each sampling Period**

#### 4.2.3. Trend of trace metals

Concentrations of the trace elements during Period 1 can be attributed to the dredging activity in the Pasig River as the silts and sediments are resuspended to the water column. Sediment disturbance can cause mobilization of contaminants (Eggleton and Thomas 2004) and affects the affinity of the trace elements. Dispersion of the trace metal in the water column is predominantly of the particulate phase and increase in dissolved concentration is mostly related to the environmental condition (Van den Berg *et al.* 2001).

During Period 2, precipitation rate increased the water flow and turbidity explaining the trace metal trend. Most of the measured DGT-labile trace metals are of highest concentration. Also high rainfall rate caused substantial elevated urban surface run-off which came from different sources (agricultural, industrial, residential, etc.) accompanied by the trace elements captured from the atmosphere. This condition then allowed a rapid horizontal mobility of the trace elements going to the bay. The concentration of the trace metals could even be higher if not for the flushing and dilution effect.

Both Periods (2 and 3) experienced rainfall events. In which, sediment resuspension can also be expected. The strong tidal currents releases significant amount of trace metals in the water column (Wu *et al.* 2005). Table V.1 shows that the amount of rainfall accumulated

for Periods 2 and 3 (within the sampling dates) are almost the same. However, the trace metal concentrations in Period 3 are dissimilar to Period 2. The difference in concentrations in these 2 periods seems notable. The rainfall pattern can give an explanation. Both periods (2 and 3) experienced run-off and atmospheric contributions but the dilution effect was higher in the last period. In actual fact, 18 days before the sampling campaign was conducted for Period 2, 13 mm amount of rainfall was accumulated. Whereas, the same number of days prior to the sampling campaign for Period 3, the generated rainfall was 123.6 mm. Thus, added to the creation of a washing effect prior to the sampling Period 3.

It is observed that the river seemed to display progress through periods. Even so, the lack of water treatment plants for domestic sources and uncontrollable dumping can still bring the river to its old problematic state. Also although, DAO 35 which is the Revised Effluent Regulations of 1990 required industries to have treatment plants, the non-compliance is a problem. The continuous release of chemical substances will adversely affect the surface water (Hartman *et al.* 2006).

## 5. Water management implication and recommendation

Urbanization and rapid developments affected the water quality of the Pasig River dramatically. The consistent increase of most of the trace elements through periods from the lake to sampling point 3 is interesting. This can imply that in between sampling points 3 and 4 or within sampling point 3, itself, there are regular contributors. Although, it is obvious that each sampling points contribute as well, the area can be identified as a priority by the water management authorities. In addition, among the trace metals, the contribution of Zn and its trend seemed different both in total and labile-DGT measurements. Zn is a typical urban related pollution (Thévenot *et al.* 2007; Mazzei *et al.* 2008).

The research conduct affirms that monitoring helps in understanding various hydrological processes and is a useful tool for the water managers (Khalil *et al.* 2010). The results obtained can provide sound and useful information that is needed in the assessment, restoration, and protection of the aquatic ecosystem (Ouyang 2005). Furthermore, it aids in ensuring the water quality compliance to the water regulations or guidelines (Aisopou *et al.* 2012). Since the monitoring system is usually limited, a more practical, reliable and economical sampling approach is necessary. Consequently, it should commence with these essentials:

1. Defined objectives (until how far can it reach);
2. Kind of results expected;
3. Specific target elements and analytical partitions that are of main interest; and
4. The appropriate methodologies and protocol.

To better interpret the data acquired, the determination of the effect on the trace elements on the aquatic ecosystem is important to understand (Gay and Maher 2003; Morilli and Usero 2008). For instance, the trace metals in flowing water can be into (Wetzel 2001 c.f. Gibbs 1973): (1) ionic forms; (2) complexed with organic materials; (3) adsorbed to and precipitated onto solids; and (4) incorporated in crystalline structures. Hence, total trace metals can be measured if the particulate fractions are one of the concerns. This is useful to describe the current state of the river. However, the total concentrations may not reflect the real bioavailability (portion that can enter into the systemic circulation) if health risks are of major concern (Moreda-Piñeiro *et al.* 2012). Even the dissolved fractions cannot serve as good predictors in bioavailability. Rather, the free metal ion complexes should be the one to consider (Janssen *et al.* 2003; Meyer 2002; Alfaro-De la Torre *et al.* 2000). This is because the bioavailability depends on chemical form and the free metal ion activity exhibits its relationship with the biological effects (Campbell 1995).

For these reasons and from the advantages given in the studies (Zhang and Davisson 1995; Sondergaard *et al.* 2008; Yapici *et al.* 2008) involving this technique, DGT was employed. The emphasis is on its capability to do quantitative measurements of labile species (ionic forms and easily dissociable complexes can be taken up) that more likely represent the bioavailable fractions of the trace metals (Schintu *et al.* 2008). Although, this paper is not a promotion of DGT, instead it is taking advantage on the use of the emerging technology in order to achieve an enhanced water management system. In this research, there is a strong indication that using DGT sampler as an additional, if not alternative, sampling technique is highly recommended. This is in the bearing of its usefulness and being effective, mostly as if it concerns bioavailability and drinking water issues, for routine water quality monitoring.

From the sampling experiences and output, a sampling strategy (Figure V.6) is proposed. The conventional approach can be applied both for the total and dissolved trace metals while the passive sampling approach in this case refers to the use of DGT. The graphs could represent each of the scenarios encountered during the sampling campaigns. So, three

(3) scenarios were depicted: (1) Scenario 1 describes the dry event but with the sediment disturbance (introduced episodic event) caused by dredging; (2) Scenario 2 is from wet season to rainfall events; and (3) Scenario 3 is a wet event to continues rainfall. Of course, the concentration can vary but the figures can give ideas on how the concentrations can be somehow expected. The curves in dotted and broken lines represent the predicted uncertainty in each of the scenario. Assuming that the hydrological condition is greatly affected by the climatological condition, RSD (relative standard deviation) was computed using the precipitation data (Table V.1) obtained in each period (Period 1:  $\pm 3.45$ ; Period 2:  $\pm 2.34$ ; Period 3:  $\pm 1.59$ ). However, another source of uncertainty is the contribution of dredging. Therefore, we can assume that RSD could be higher.

There could be different stages that can be drawn. In scenario 1 there are: Stage 1- dredging starts; Stage 2 - dredging continues and the trace metals increase; and Stage 3 - there could be a point wherein the concentrations could stabilize (could be quick or long time) before it further increase or decrease. For scenario 2: Stage 1-start of the rainfall; Stage 2- rainfall continues accompanied with run-offs; Stage 3- peak of the concentration; Stage 4- dilution starts; and Stage 5 - washing effect. Scenario 3 is the last part of scenario 2, wherein, Stage 1 is the same with Stage 4 and Stage 2- washing effect continues.

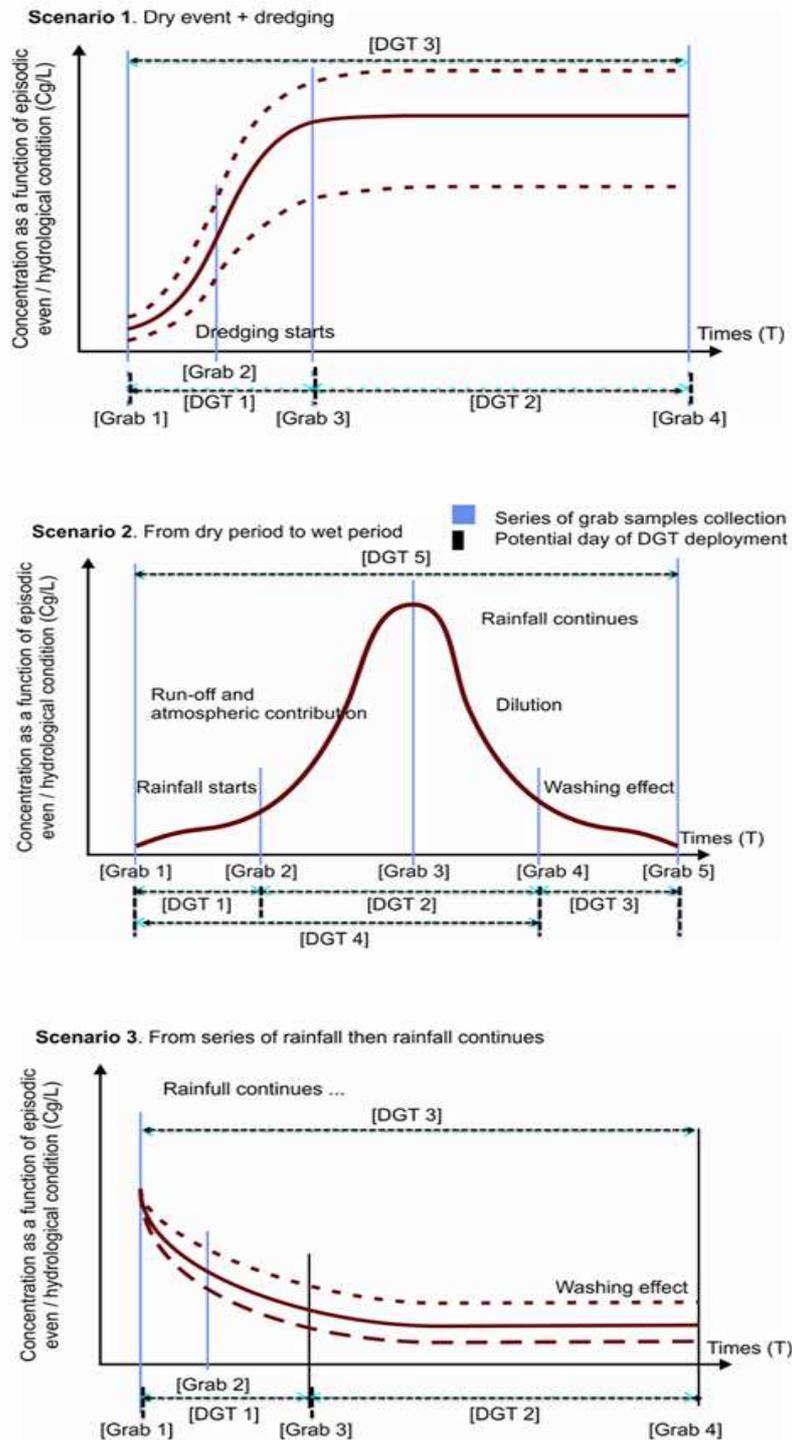


Figure V.6. Illustration of sampling approaches employing the frequencies of sample collection or using conventional (grab) and passive sampling (DGT) in different conditions (Scenario 1: dry event with dredging activity; Scenario 2: from dry event to wet period ; Scenario 3: pronounced rainfall)

Figure V.6 would like to imply that series of grab collection in each of the scenario are needed (and should be frequented) in order to satisfy the quality of data needed using the conventional approach. Scenarios 1 and 3 need at least 4 times of water sample collections. Scenario 2 requires more water sample collection than the 2 other scenarios.

The idea of DGT follows the time-weighted average (at the specific time of immersion), with this sampling design, at least 2 ways for Periods 1 and 3: Approach 1.  $DGT1 + DGT2 = C_{DGT}$  (This allows temporal variation.) and Approach 2.  $DGT3 = C_{DGT}$  (This covers the whole duration of the event at a given time.).

For Period 2, at least 3 ways can be suggested which are:

Approach 1:  $DGT1 + DGT2 + DGT3 = C_{DGT}$ ;

Approach 2:  $DGT4 + DGT3 = C_{DGT}$ ;

Approach 3:  $DGT5 = C_{DGT}$ .

Approaches 1 and 2 allow temporal variation. The difference is the stages that the technical experts would like to capture. DGT4 includes the minimum and maximum values of concentration while the DGT3 integrated the washing effect. DGT2 describes the increase of concentration as the rainfall and the surface-run-offs have added their contribution. DGT5 covers the dry period to the wet period.

Based from the above mentioned combinations or decisions, reliable results can be generated. If episodic events are the primary concern, for example, it is good to have combinations like in scenario 1: DGT1 vs. DGT 2. Wherein, the concentrations at the start of the dredging campaign can be compared to the time wherein the dredging was on-going. It is also advisable to conduct sampling before the dredging activity. It is up to the technical expert to define the time of water sampler immersion. While, if the objective is just to see the water quality of the water DGT 5 for scenario 2 and DGT 3 for scenarios 1 and 2 could be a good recommendation. This manner considers the maximum and minimum values to be integrated in the time-weighted average concentration that DGT can provide. The ability to make comparisons and assessments is one of the advantages of series of sampling campaigns.

From the experience of the research conduct, with substantiation, the hydrological condition (season-driven) is an important factor for consideration. The baseline information obtained from this research provides better understanding of the Pasig River. Figure V.7 illustrates the proposed and recommended better water management scheme. Depending on the goals of the water managers, they can utilize the results for planning. The data and

assessments can be conveyed to the stakeholders, environmental educators and water policy-makers.

## 6. Conclusion

Water quality assessment is a vital element. This provides basis in doing water management plans and actions. In order to provide good and solid information reliable and practical monitoring techniques should be employed. This research considered three periods (i.e. Period 1: dry and dredging; Period 2: wet to dry; and Period 3: series of rainfalls) for the conduct of the water sampling.

Classic method was employed to measure the trace metals in total fraction. Total trace metals using grab sampling provided a picture of the water quality but not enough to make a strong generalization as sampling frequency should be increased. However, this fraction can only describe the general status of the water quality. If the real concern is the risk on the aquatic system, real dissolved fraction should be considered. This fraction is found to have relation when biological and chemical reactions within the aquatic system are involved. For this reason, the use of the DGT technique was employed.

Pasig River is a dynamic system as it is an estuary in nature. The environmental parameters facilitated in describing and differentiating the environmental chemistry in the water column for each period. Following this, the reliability and the sensitivity of the DGT probes were tested as they were able to capture and follow the environmental signals from different seasonal changes and episodic event.

This study was able to arrive in giving qualitative and quantitative results. For instance, it was observed that among the trace metals Zn do not follow the seasonal trend. This signifies that permanent contributors are present as indicated by the increase in concentration. The outcome showed the representativeness (spatially and temporally) of the trace metals (both in total and dissolved factions) in describing the status of the water. Moreover, the most problematic site was able to indentify. The results pointed out that this is the confluence near the Marikina River. The study provided a sampling design for employing conventional and passive approaches drawn in different scenarios. The result demonstrated that if freely dissolved fraction is of concern, the DGT technique in monitoring the water quality of the Pasig River is applicable and recommended to other different water conditions.

Hence, this paper deduces that passive sampling, using DGT in this case, can be part of the routine water quality monitoring.

Water quality assessments need reliable and empirical results from practical and pertinent sampling method like the DGT technique. This paper recommends continues water quality monitoring and assessments as proposed in (Figure V.7). This is as the river is found to be dynamic and receptive to seasonal changes. In doing so, defined objective in conducting water quality measures such as on the concern on the potential ecological risks in the water.

Each of the sampling procedures should correspond to the objectives of the monitoring activity. From this, local authorities should be able to provide reliable water quality information and locate the highly polluted area. For instance, in terms of the concern of the trace metal flux contribution, as previously stated, the confluence of the Marikina River was identified as the area that needs to be prioritized.

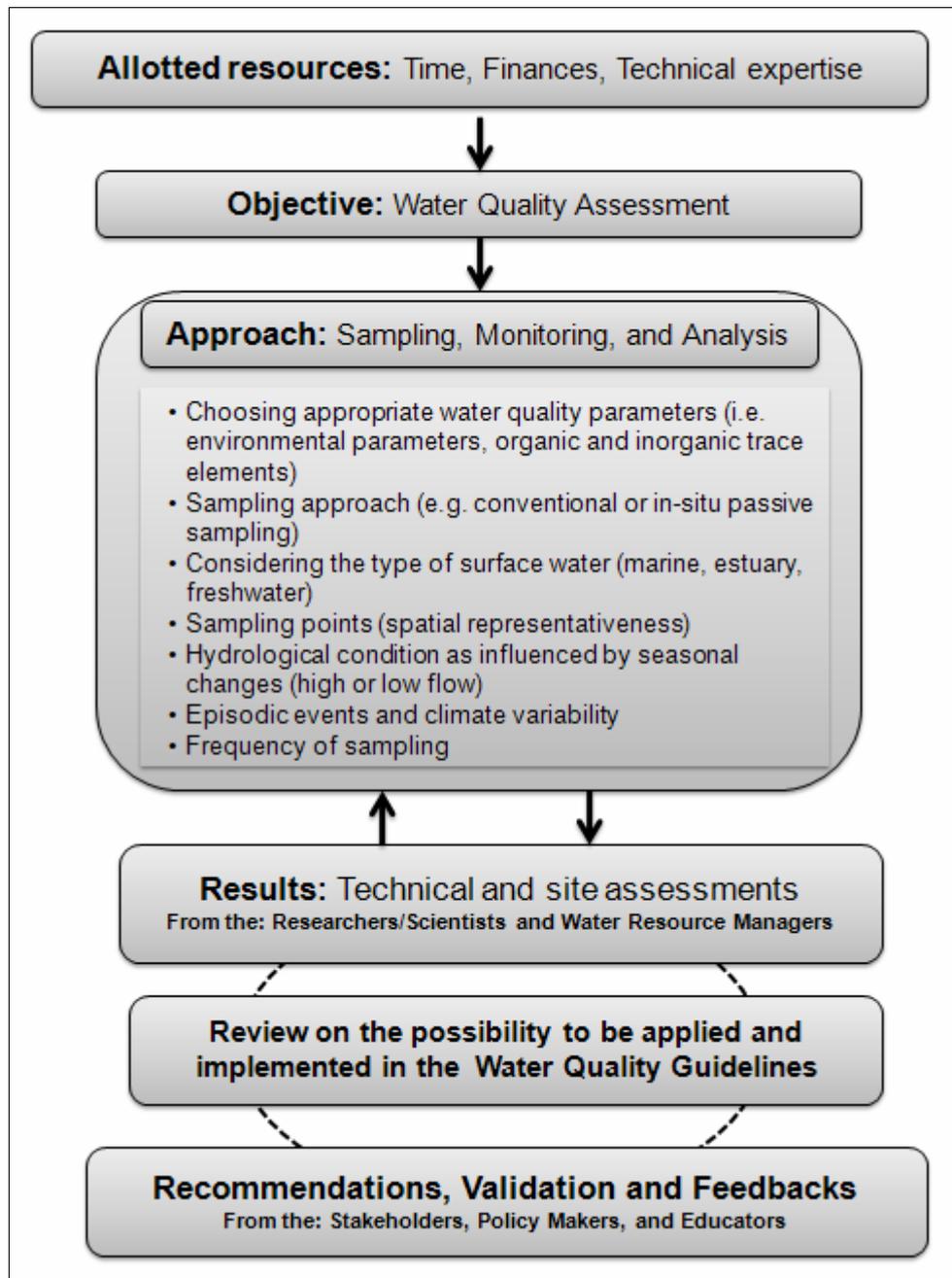


Figure V.7. Recommended water management scheme for a water system like the Pasig River

### **Acknowledgement**

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## **CHAPTER VI The response of the trace metals to highly contrasted weather conditions in an urban estuary**

*Submitted to: Earth and Environmental Science Journal*

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### **Abstract**

The trend of trace metals was followed in an urban estuary (Pasig River in Manila) together with their response to 3 different climatic periods (Period 1 dry and dredging event; Period 2: intermediate from dry to wet event; and Period 3: continuous rainfall) and hydro-chemical parameters of the surface water. The measured concentrations show that DGT-labile trace metals substantially responded well to the seasonal changes.

The statistical analyses revealed that only Period 2 is significantly different among periods. Principal Component Analysis (PCA) conducted was able to give the principal components and correlations among trace metals and the physico-chemical parameters. Distances (or differences) of the periods were able to define and illustrate the spatio-temporal trends. From this study, it appears that climatic variations (influenced by precipitation) induce strong variation on the trace metal trends in a complex urban water catchment. At the same time, the sensitivity of the in-situ Diffusion Gradient in Thin films (DGT) probes were tested and validated in this study.

**Keywords:** trace metal, urban water, tropical climate, run-off, Principal Component Analysis, DGT

### **Highlights**

- Labile trace metals trend in an urban estuary river during contrasted climatic events
- PCA discriminates 3 different periods characterized by climatic conditions and punctual events
- In-situ sensor like DGT is reliable for mid and long term water study
- Zn in the Pasig river differs from the other trace metal measured during 3 events and periods revealing a potential continuous feeding through urban run-off
- Labile trace metals spatio-temporal trend has been precise regarding the precipitation, punctual events and hydro chemical parameters
- First study about trace metals in the Pasig River, Manila, Philippines

## 1. Introduction

The behavior of the trace metal in estuaries varies greatly due to the environmental factors like hydrodynamic residence time, mixing patterns of transport processes (Hatje *et al.* 2003 and Masson *et al.* 2011) and reservoir management (Masson *et al.* 2006). Furthermore, trace metals trend differs according to seasonal changes and suspended sediments concentrations (Park *et al.* 2011). Precipitation events can serve as an atmospheric wash out that delivers trace metals to the aquatic ecosystem through deposition mechanism (Özsoy and Örnektekin 2009). Presence of metals in solution in urban run-off (Herngren *et al.* 2005) and in wet weather pollutant discharge is an environmental interest particularly in the aspect of surface water quality (Ki *et al.* 2011) due to possible effects on the aquatic system and the biota.

Assessing the quality of water bodies is one of the important tasks in answering environmental issues. The focus mostly is on trace metals in labile forms due to their toxicity in nature, stable complexes and associated risks (Pinheiro and Domingos 2004). However, in measuring these specific forms, collecting voluminous water is tedious and analyses can be costly. In this case, the use of the Diffusive Gradient in Thin-Films (DGT) is indispensable. It has the ability to perform speciation of trace metals (Davison and Zhang 1999) at a lower cost. Furthermore, DGT is an in-situ method that it can perform good measurements in sequestering labile trace metals (Zhang and Davison 1995; Naylor *et al.* 2004; Li *et al.* 2005; Søndergaard *et al.* 2008; Vystavna *et al.* 2012a) and can detect very low concentrations (Zhang *et al.* 1995). In fact, this technique for measuring trace metal and monitoring water bodies is already widely-used and delivers valuable results with lesser sampling activities needed (Alfaro-De la Torre *et al.* 2000; Clarisse *et al.* 2009; Gao *et al.* 2010; Wu *et al.* 2011).

The purpose of this research is mainly to know the trace metals response to differing climatic scenarios and physico-chemical conditions in a dynamic system. The DGT probes were used as in-situ samplers because of the advantages mentioned above. The Pasig River in Manila, Philippines, naturally, an estuary was studied. In this research, three different physico-chemical and hydrological conditions were considered. These differences can lead to a premise that the trace metals behavior and trend will also be significantly distinct from each period. Statistics coupled with multivariate analysis were performed to better explain the DGT-labile trace metal trends and assess the response of a highly urbanized estuary to

differing episodic events influenced by precipitation and a sediment disturbance (dredging activity). The specific objectives were: (1) to describe the trend of the DGT-labile trace metal (Cd, Co, Cr, Cu, Ni, Pb and Zn); (2) to identify the relationship of the trace elements in the changing water environment of the estuary system; and (3) to evaluate spatio-temporal pattern with respect to seasonal effects.

## 2. Materials and Methods

### 2.1. Site description

The Pasig River is an estuary that is about 27 km long and approximately 80 m wide. The catchment is composed of 4 main tributaries (San Juan River, Marikina River, Napindan River and Pateros-Taguig River) and 43 minor tributaries. It is located at the heart of Manila, Philippines (Figure VI.1) and connects Laguna Lake (east), the biggest freshwater lake in the Philippines and the Manila Bay (west). Manila Bay serves mostly as a shipyard while the Laguna Lake is a multiple use resource that include aquaculture and fishery (open fishing), irrigation, power generation and navigational lane. This site is situated in a highly industrialized and urbanized area with a rough estimated population of 11,500,000 plus fluxes of informal settlers which are about 30% of the total Metro Manila region (Aiga and Umenai 2002). This water body normally receives fluxes of wastes of different forms due to the deficiency of the water treatment plants (Villanueva *et al.* 2013). Solid wastes are, without restraints, directly thrown to the Pasig River.

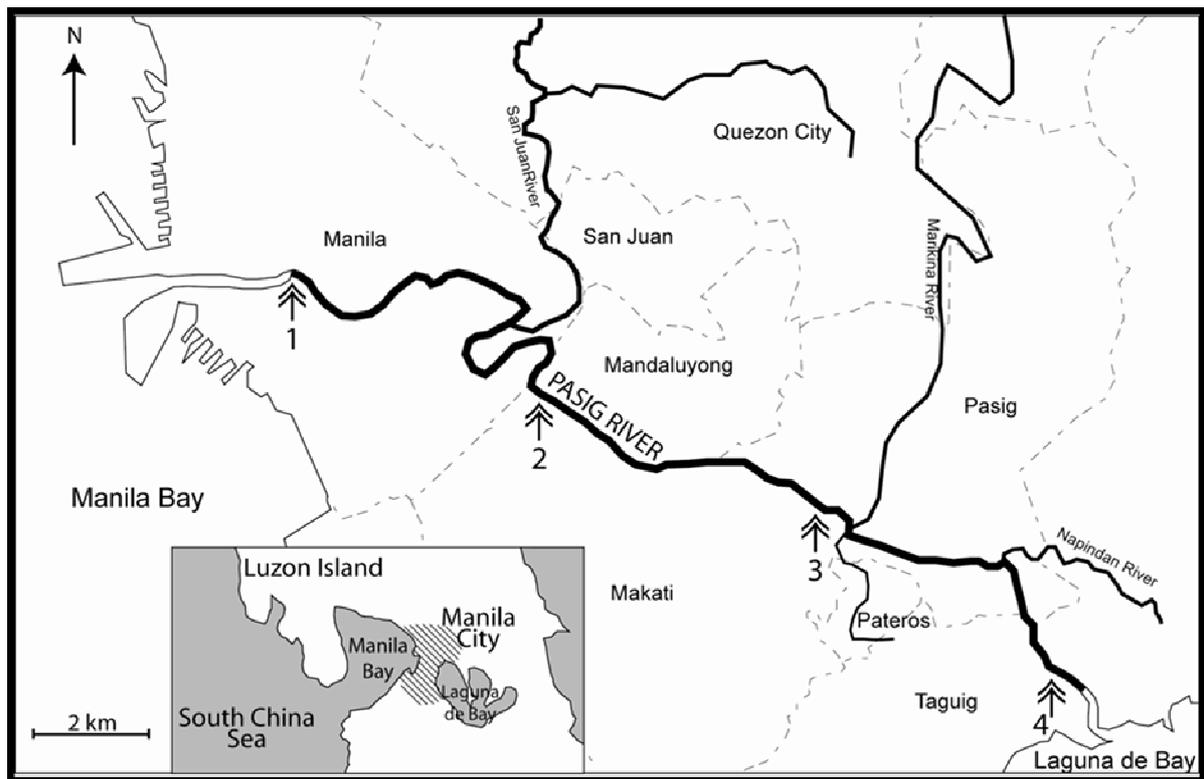


Figure VI.1 The Pasig River map and sampling sites (Point 1: mouth of the Manila Bay; Point 2: near the convergence of the San Juan River; Point 3: near the confluence of the Marikina River; and Point 4: near the Laguna Lake)

## 2.2. Sampling Design

The sampling design was considered seasonal patterns in the study area. Three (3) sampling campaigns were conducted which corresponded to: Period 1, drought with an ongoing dredging activity (April to May 2010), Period 2, interim: from drought to wet season (January 2011), and Period 3, wet season (May to June 2011). Table VI.1 explains the rainfall behavior during the sampling campaigns.

**Table VI.1 Rainfall rate during the sampling campaigns (This defines the difference among periods.)**

Rainfall (mm)	Period 1	Period 2	Period 3
Days before sampling			
10	0.8	5.4	19.6
20	0.8	14.4	125.2
Accumulated within the sampling period			
	6	79	79.8

Provided by Manila Observatory (unpublished data 2012)

Four sites (Figure VI.1) were chosen representing the upstream (point 1: mouth of the Manila Bay), midstream (points 2 and 3 which are near the San Juan and Marikina River, respectively); and downstream (point 4: mouth of the Laguna Lake). In each site, DGT in duplicates were fully immersed for 18 days. A DGT field blank was used per sampling campaign. Strict protocols of DGT deployment (Villanueva 2013) were followed for all sampling campaigns. Immediately, after the retrieval, the DGT probes were rinsed with de-ionized (DI) water and placed in pre-cleaned properly marked resealable plastic containers. A cooling compartment was prepared to transport the probes directly to the laboratory. Afterward, the DGTs were put in the refrigerator before the extraction and analysis (using IC-PMS) of the trace metals.

During each sampling campaign, physical parameters such as dissolved oxygen (DO), water temperature, salinity, conductivity and pH were measured in-situ using a YSI 6600 V2 data probe at a depth of approximately 1m.

### 2.3. Determination of the trace metal

Standard solution Chelex-100 DGT probes were purchased at the DGT Research Ltd, Lancaster, UK. DI water has resistivity of ( $18\text{M}\Omega\text{ cm}^{-1}$ );  $\text{HNO}_3$  is Fisher Scientific Analar grade. DGT field blanks were extracted and analyzed using the same procedure employed for the DGTs immersed in the water. Laboratory procedural blanks were prepared. The detection limits were determined following the procedure of Pattke *et al.* 2012. The relative standard

deviation (RSD) is provided in Table VI.2. The dredging activity could have affected Period 1.

Table VI.2 Mean %RSD of measured DGT-labile trace metal concentration

DGT-labile trace metal	Period 1	Period 2	Period 3
Cd	3.4	33.1	1.65
Co	36.79	2.65	3.69
Cr	5.37	8.17	5.66
Cu	48.98	4.54	1.33
Pb	10.97	4.48	7.56
Ni	41.63	3.9	0.07
Zn	8.05	2.52	3.91

In the laboratory, the membrane filter and the diffusive gel were carefully removed from the piston using the Teflon tweezers. The gel was separated and placed into a clean polypropylene microcentrifuge tube. 1 ml of 1M of HNO<sub>3</sub> was added. After 24 hours, dilution was performed. The trace metals were determined using inductively coupled plasma-mass spectrometry (Thermo Scientific \*ELEMENT 2\* ICP-MS). From the elution solution, the mass of the trace metals (M) accumulated was calculated using the following equation:

$$M = \frac{C_{el} (V_{gel} + V_{HNO_3})}{f_e}$$

where:

$C_{el}$  is the concentration of the metals in the elution solution

$V_{gel}$  is volume of the resin gel

$V_{HNO_3}$  is the volume of HNO<sub>3</sub> added to the resin

$f_e$  is the elution factor

Then, using the following equation the environmental concentration of trace elements was calculated:

$$C_{DGT} = \frac{M \Delta g}{D \Delta t}$$

Where:

$C_{DGT}$  is the measured DGT labile trace metal concentration

$A$  is the exposed area of the DGT probe

$D$  is the diffusion coefficient, water temperature dependent (DGT Research 2002)

$t$  is the total time of deployment

$M$  is the mass of the labile metal captured at the binding phase

The detailed laboratory procedure (Dunn *et al.* 2007; Aung *et al.* 2007) and calculations (DGT Research 2002) are already established and can be found elsewhere (INAP 2002; Vystavna *et al.* 2012b).

#### 2.4. Statistical test and multivariate analysis

In order to determine the significance among periods using the concentrations of the trace metals, series of non parametric statistical tests were employed. The Completely Randomized Design (CRD) with sub-sampling (considering the periods) was performed using one-way ANOVA test. Hypothesis is at  $H_0$ : there is no difference among period means and  $H_a$ : at least two period means are different. The result rejected  $H_0$ . Thus, it confirms that there is at least 2 periods that are significantly different (at  $p \leq 0.05$ :  $0.964 < 2.8477$ ).

To determine which among the trace metal mean concentration are different, multiple comparison of mean using the Duncan Multiple Range Test (DMRT) was performed. Hypothesis is at  $H_0$ : there is no difference among trace metal mean concentration and  $H_a$ : at least two trace metal mean concentrations are different. This is since the ANOVA is not significant and there are equal replications (Table VI.3).

Table VI.3 ANOVA test result

Source of Variation	df	Sum of Square	Mean Square	Fc	F-tab 0.05
Among Trace Metal	6	53 726 555	8 954 425	0.96	2.85
Period within Trace Metal	14	130 013 234	9 286 659	366	1.85
Samples within Period	63	1 594 648	25 311		
Total	83	185 334 438			

To determine which among the period means are different, multiple comparison of mean was done. Given that the ANOVA is significant and there are equal replications, Least Significant Difference (LSD) was carried out. To validate the previous results, cluster analysis was performed.

Next, the Principal Component Analysis (PCA) was done in order to pin down the subset/s of a particular variable that can explain the relationship among the physico-chemical parameters and the trace metals. Furthermore, this aided in illustrating and explaining the spatio-temporal variation. The concentrations recorded from the physico-chemical parameters (DO, water temperature, salinity, pH, and conductivity) and the trace metals were used as variables to obtain the PCA results.

PCA is being used in surface water assessments in order to analyze the generated data (Kalscheur *et al.* 2012; Nnane *et al.* 2011; Tortajada *et al.* 2011) by examining data variability (Reid and Spencer 2009). The correlations among the parameters were obtained. The means and variances were then computed. Values of the variables were normalized. After that Varimax rotation was generated. Factorial axes were extracted after obtaining the Eigenvalues and the cumulative percentage. From the general rule, only the components having Eigenvalues values of  $\geq 1$  should be included (Mazlum *et. al.* 1999 c.f. Chatfield and Collin 1980). For the component loadings, the variables in the axes having coefficients  $\geq 0.60$  should be considered (Mazlum *et. al.* 1999 c.f. Mahloch 1974). In selection, the decision criterion categorized the variables as follows (regardless of the sign):

- $\geq 0.70$ : important contributor
- 0.75-0.60: reasonably important
- $< 0.60$ : of less importance and could be disregarded

### **3. Results**

#### **3.1. Environmental parameters**

The physical condition recorded during each sampling period is described in Figure VI.2. Period 2 gave the least recordings for salinity, dissolve oxygen (DO) and conductivity. The periods are best described by the DO as the oxygen levels greatly varied through periods. DO ranges 0.45 to 1.05 mg/L on Period 1; 5.9 to 8.2 mg/L on Period 2; and 1.55 to 2.26 mg/L on Period 3. Only Period 2 passed the department administrative order (DAO 34) of DO requirement which is  $>5$  mg/L. Total organic carbon (TOC) was measured in Pasig River and ranged from 3.4 to 4.5 mg/L during May 2010 and 3.5 to 7.4 mg/L for January 2011 (Materum 2010). The salinity and water is pronounced on Period 3 (0.39 to 8.44 psu) which also indicates water mixing.

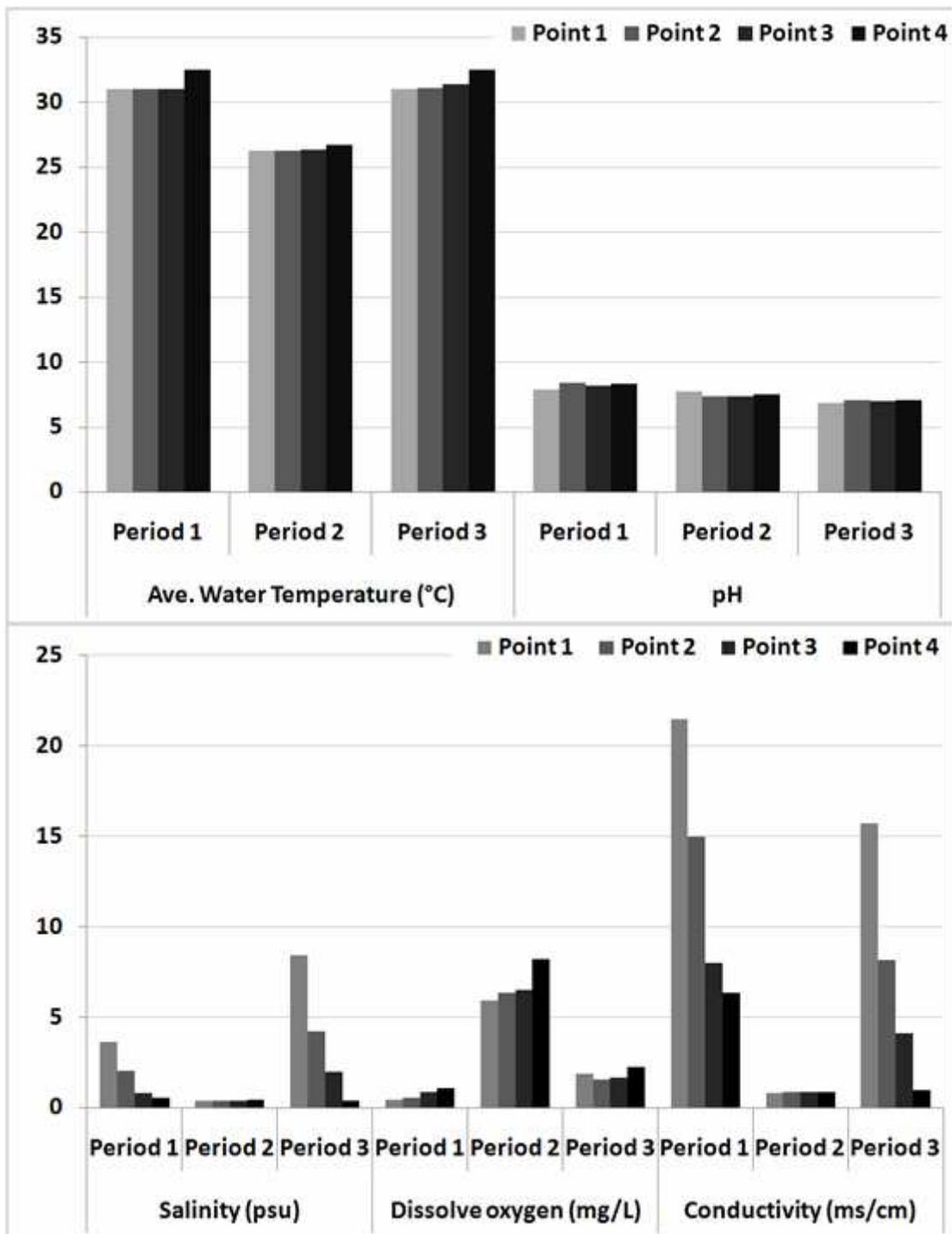


Figure VI.2 Physico-environmental parameters: water temperature, pH, salinity, DO, conductivity in each sampling point organized in per period

### 3.2. The DGT-labile trace metal trend

The general trend observed is that most of the trace metal concentrations greatly increased during Period 2 then drastically decreased during Period 3 (Figure VI.3). But throughout the period, Zn gently increased through time. With respect to the calculated mean concentrations, changes from Period 1 to Period 2 are as follows: (1) only Ni decreased (9.4%); (2) Zn and Cd increased as 7.3% and 60.3%, respectively; and (3) an increase in concentration of around 3 folds was observed for Co, Cu and Pb. Cr increased greatly to about 32 times (from Period 1 to Period 2). While from Period 2 to Period 3 only Zn increased (2%). The rest of the trace metal concentrations decreased extensively.

During Period 1, the only DGT-trace metal (at maximum) found at the river end is Ni located near the mouth of the bay (Point 1). Minimum Ni was detected at the confluence of San Juan River (Point 2) while Co has the least at the mouth of the bay (Point 1). Maximum concentrations were mostly near the confluence of San Juan River (Point 2: Cr, Cd and Pb) and convergence of Marikina River (Point 3: Co, Cu and Zn). The minimum concentrations of Cr, Cu, Zn, Cd and Pb were found near the mouth of the lake area (Point 4). In this period, at the river ends (Points 1 and 4), lesser values of Cr, Co, Cu, Cd and Pb were found. In contrast, Ni has the lesser values in the midstream (Points 2 and 3). While, Zn concentration spatially varies.

In Period 2, minimum value of Pb is found near the mouth of the bay (Point 1); Cr, Cu and Zn were at the confluence of San Juan River (Point 2); Co and Ni near Marikina River area (Point 3); and Cd near the mouth of the lake (Point 4). Maximum values of Cr, Cu, Zn and Cd were found near the mouth of the bay (Point 1) while Co, Ni and Pb at the mouth of the lake (Point 4). At this period, the maximum values are all found at the river ends (Point 1 and 4).

For Period 3, Cu has the least concentration at the mouth of the bay (Point 1). Maximum values were traced in the sampling points except near the lake: Cr and Cd were found near the bay area; at the confluence of San Juan River (Point 2: Co, Zn and Pb); and near at the Marikina River (Point 3: Ni and Cu). Most of the minimum values were at the mouth of the lake (Point 4: Cr, Co, Ni, Zn, Cd and Pb).

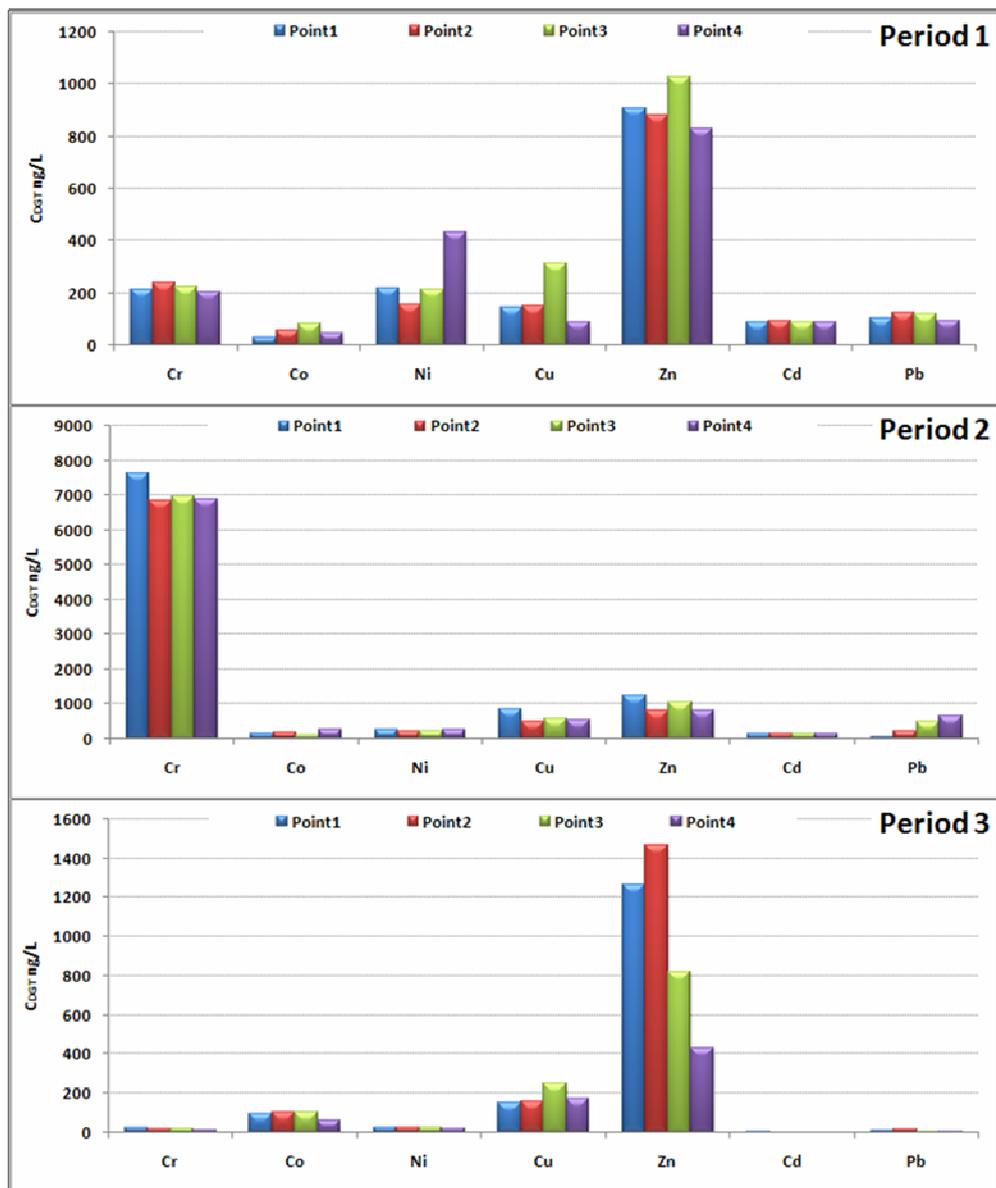


Figure VI.3 DGT-labile trace metal concentrations for Periods 1, 2, and 3 across the sampling points

### 3.3. Significant difference (among periods and among trace metal concentrations)

From the ANOVA test performed, it confirms that there is at least 2 periods that are significantly different ( $p \leq 0.05$ ). The DMRT result (Table VI.4) shows that all the trace metal mean concentrations are not significantly different ( $p > 0.05$ ). On the other hand, the Least Significant Difference (LSD) result showed in Table VI.5 identified that Periods 1 and 3 are insignificantly different ( $p > 0.05$ ). This sufficiently means that Period 2 is significantly different among other periods.

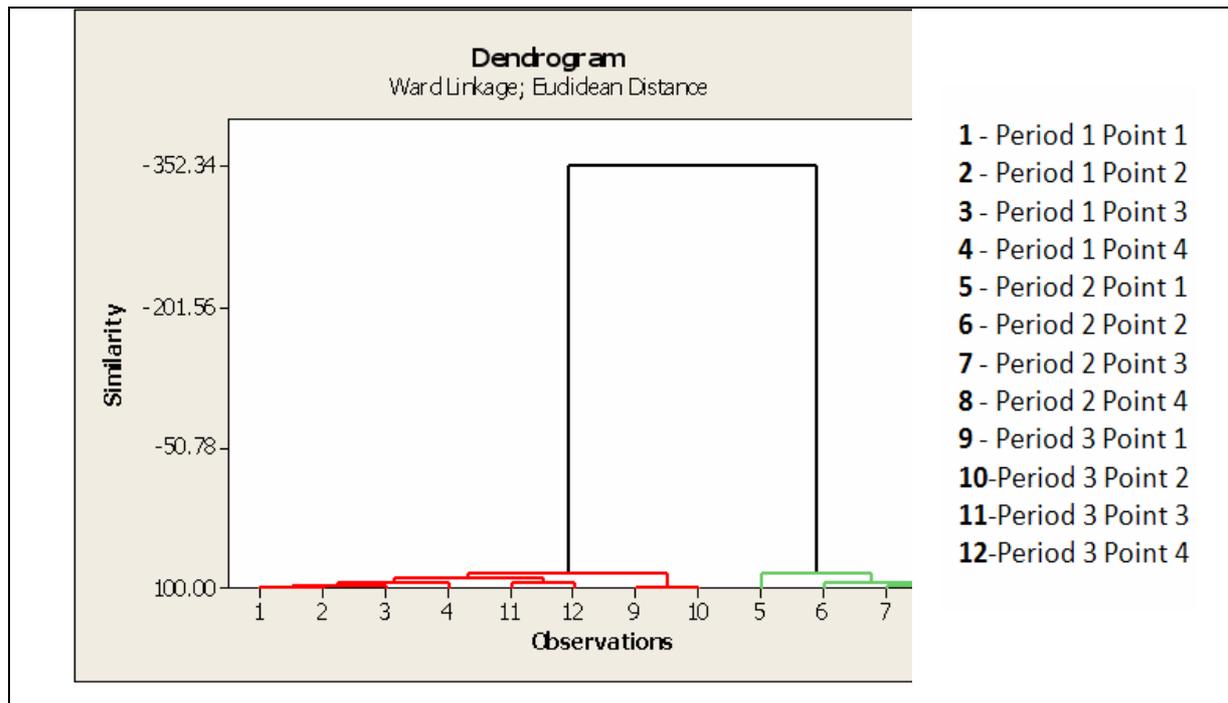
**Table VI.4 Duncan Multiple Range Test Result (Means having the same letters are not significantly different at 5% level of significance.)**

DGT- labile Trace Metal	$R_p$	Treatment (Subset $\alpha=0.05$ )
Cr	2437	a
Co	106	a
Ni	170	a
Cu	325	a
Zn	961	a
Cd	77	a
Pb	157	a

**Table VI.5 Least Significant Difference Test Result (Means having the same letters are not significantly different at 5% level of significance.)**

Period	LSD result	treatment
1	7242.02	B
2	38305.53	A
3	5289.18	B

The cluster analysis performed generated a dendrogram (Figure VI.4). The dissimilarity between the periods agreed to the statistical analysis performed. Automatically, Period 2 was isolated (left). Within this cluster, point 1 (Bay area; number 5) was distinctly segregated. This site at this period has the highest Cr, Cu, Zn, and Cd concentration, while, Pb concentration was the lowest. Periods 1 and 3 are clustered together.



**Figure VI.4** Generated dendrogram. Numbers indicate sampling regime (Periods) and sampling points. (Legend is provided at the left)

The probable sources of insignificance between Period 1 and 3 were traced. Observations on the the spatial patterns of Periods 1 and 3 showed that for both periods, most of the maximum concentrations of each trace element are found at the midstream (Points 2 or 3). Most of the minimum concentrations of each trace element are at the endstream (Points 1 or 4). Percent contribution of each trace metal mean concentration was then obtained. Figure VI.5 shows the result. Zn is found to contribute more than the other trace metals in Periods 1 and 3. For Period 2, however, Cr showed to have contributed the most.

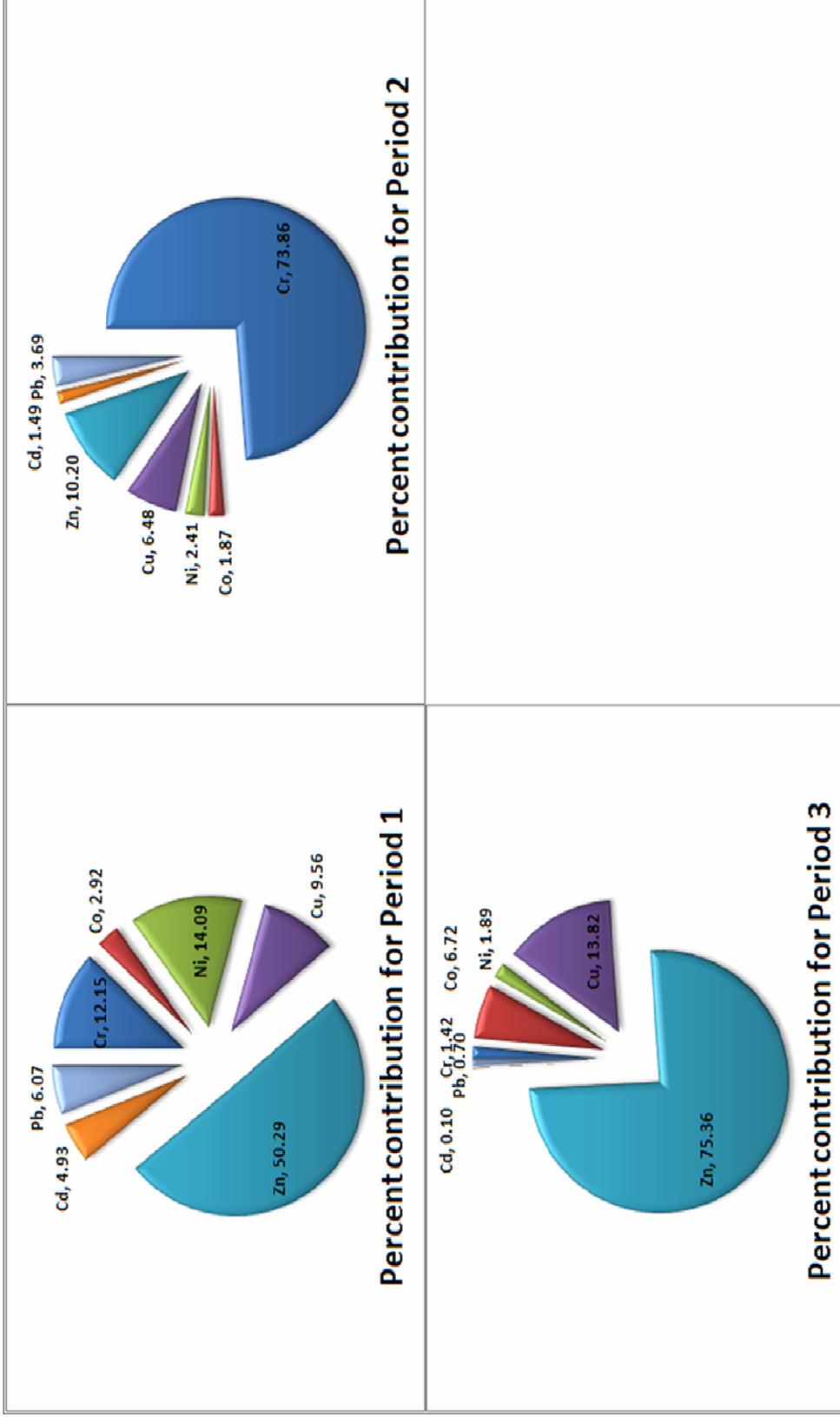


Figure VI.5 Trace metal mean contribution (in percent) for each period.

### 3.4. Principal Component Analysis (PCA) application as an auxiliary method

Employing the PCA, varimax rotation is generated 177 times, obtained automatically. Table VI.6 present the Eigenvalues and Variance. About eighty-seven percent (86.77%) of the total variance explained all the Factors 1, 2, and 3 (F1: 54.34%; F2: 19.98%; and F3: 12.45%).

From the given decision criterion category, the important contributors (Figure VI.6) for F1 axis (horizontal) are DO, water temperature, Cd, Co, Cr, Cu, and Pb and pH and Ni for F2 axis. Reasonably important contributors are seen in F1 (salinity and conductivity) and F2 (salinity) axes.

Focusing on the physico-chemical parameters in, primary factors that can explain the concentration tendency of the labile trace metals measured were determined. Correlation result is provided in Table VI.7. As a main observation, DO give inverse relationship to other physico-chemical parameters. This inverse relationship is more pronounced with the with respect to the water temperature. The second factor is the confirmation of the proportional relationship in between conductivity and salinity.

The first indentified factor follows the trend of most of the trace metals (except for Zn). This is as direct relationships were found in between DO and the trace metals. Conversely, water temperature is indirectly proportional to the trace metals. Ni follows this tendency but on a weak correlation. Zn, however, behaves differently.

Table VI.6 Eigenvalues and Variance

	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8	PC9	PC10	PC11	PC12
<i>Eigenvalues</i>	6.5	2.4	1.5	0.7	0.4	0.2	0.2	0.04	0.02	0.01	0.001	0.000
	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	F11	F12
Variance (%)	54.34	19.98	12.45	6.15	3.05	1.83	1.52	0.37	0.22	0.09	0.01	0.00
Total												
Variance (%)	54.34	74.32	86.77	92.92	95.96	97.79	99.31	99.68	99.90	99.99	100.00	100.00

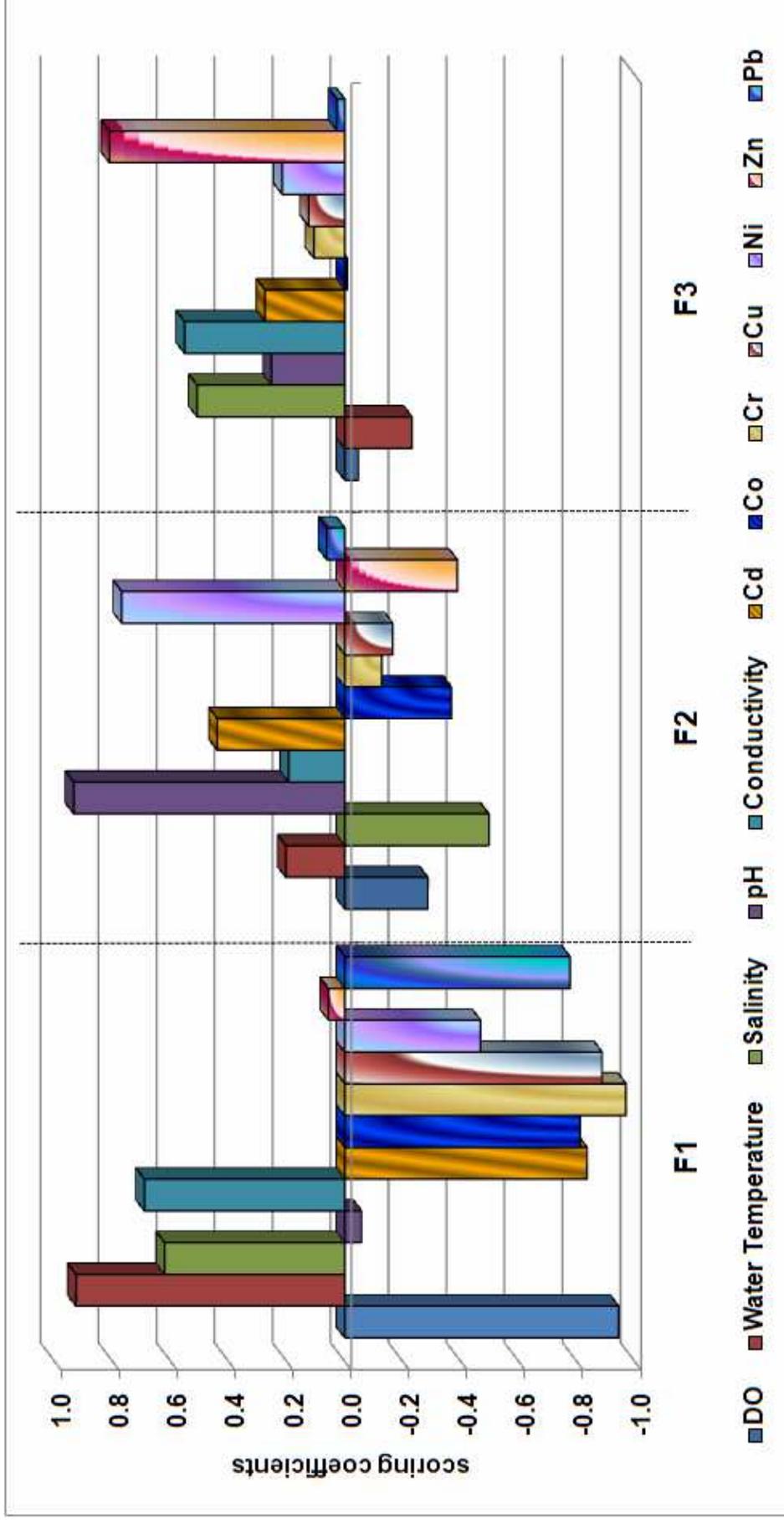


Figure VI.6 PCA Factorial Loading Scoring Coefficients

Table VI.7 Correlation table

	DO	Water Temperature	Salinity	pH	Conductivity	Cd	Co	Cr	Cu	Ni	Zn	Pb
<b>DO</b>	1.00											
<b>Water Temperature</b>	-0.92	1.00										
<b>Salinity</b>	-0.42	0.36	1.00									
<b>pH</b>	-0.25	0.09	-0.40	1.00								
<b>Conductivity</b>	-0.70	0.52	0.69	0.26	1.00							
<b>Cd</b>	0.65	-0.78	-0.59	0.52	-0.29	1.00						
<b>Co</b>	0.88	-0.77	-0.28	-0.25	-0.60	0.48	1.00					
<b>Cr</b>	0.95	-0.98	-0.48	-0.06	-0.63	0.80	0.77	1.00				
<b>Cu</b>	0.84	-0.91	-0.48	-0.04	-0.63	0.71	0.69	0.92	1.00			
<b>Ni</b>	0.24	-0.28	-0.52	0.75	-0.12	0.75	0.12	0.38	0.28	1.00		
<b>Zn</b>	-0.02	-0.18	0.53	-0.13	0.25	-0.04	0.06	0.06	0.16	-0.12	1.00	
<b>Pb</b>	0.76	-0.67	-0.41	0.08	-0.38	0.68	0.71	0.69	0.47	0.40	-0.14	1.00

The factorial axes (Figure VI.7) illustrate the spatio-temporal distribution of the concentrations among periods (Pd.) per sampling point (Pt.). The scores plot shows that the sampling points (Pt1, Pt2, Pt3, and Pt4) assembles or are grouped closely per period. This gives clearer picture in terms of illustrating the differences among periods than the earlier performed statistical analyses. The differences account to the spatio-temporal changes or the seasonal variation in each point.

The results agreed to the statistical analyses performed as Periods 1 and 3 shows close proximity. The difference is that Period 1 clusters together, while, Period 3 is dispersed. In the illustration, it also confirms that Period 2 is different as it is completely isolated in axes F1F2 and F1F3.

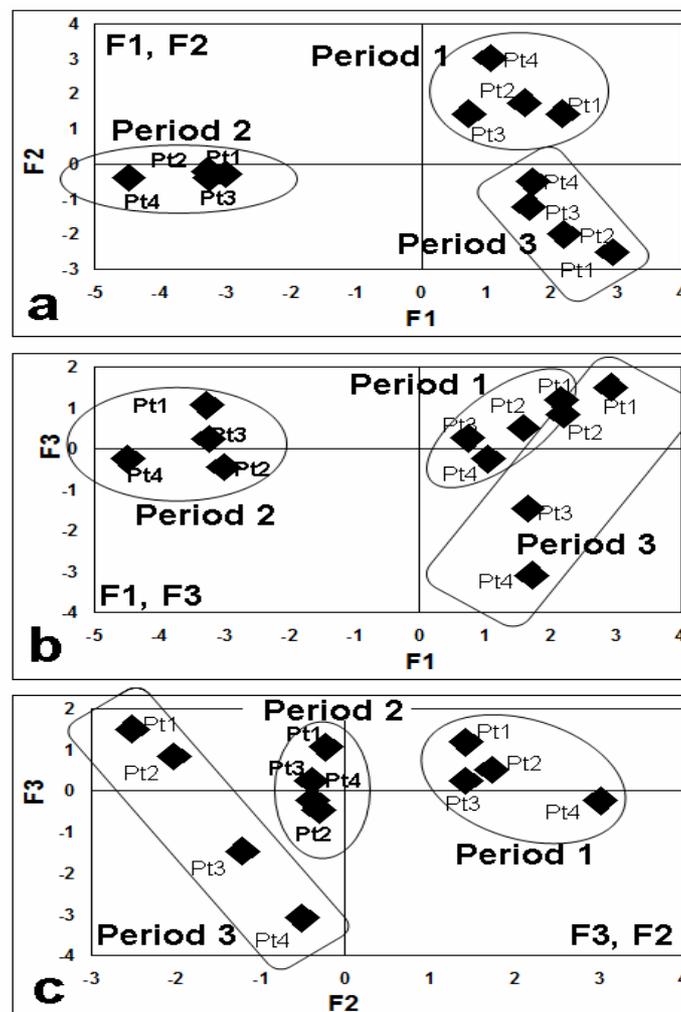


Figure VI.7 Factorial axes and the spatio-temporal trend (a.F1F2 axis; b. F1F3 axis; c. F3F2 axis)

#### 4. Discussion

Using the concentration of the trace metals, the statistical analyses are applied to further interpret and present the data to assess the trend of the trace metals in differing episodic events. The statistical analyses done presented that among periods; only Period 2 is statistically significant.

In integrating the physico-chemical parameters using the recorded measurements, the spatial similarities (Periods 1 and 3) and differences (Periods 1 and 3 vs. Period 2) were identified by PCA. The result was able to provide better illustrations of the spatio-temporal trend. It permitted the highlighting of the differences of the periods with regards to the generated PC loadings set in the F1 F2, and F3 axes. The identified important to moderately important factors, additionally, explained how the changes in the trend can be visualized. Notably, the difference on the Zn trend indicates that there is consistent and continuous loading of Zn in the area. The concentration was neither affected by the seasonal changes nor the sediment disturbance.

The changes in the concentration through periods depicted the response and sensitivity of the DGT-labile trace metals on the episodic events represented by the periods. Period 1 can be explained by the combination of two (2) episodic events which are drought and dredging. Essentially, the area experienced shortage on rainfall. Prior to the sampling campaign, there was only 0.8mm of rainfall event for a period of 20 days. Then a 33 mm of rainfall was accumulated within this sampling period. This implied river low flow. Also, simultaneous to the sampling campaign, a dredging activity is in the process. Dredging is considered as an ecological disturbance that can affect the sediment structure (Mackie *et al.* 2007). Sediment resuspension can induce metal release in the water column due to hydro-chemical influences (Je *et al.* 2007). Both particulate forms (Nayar *et al.* 2004) and bioavailability (Lewis *et al.* 2001) of trace metals can be expected to increase.

Periods 2 and 3, on the other hand, both experienced pronounced rainfall with accumulated amount of ~79 mm. During these periods, measured trace metals were influenced by atmospheric contribution (Witt *et al.* 2010) and surface run-off. The atmosphere is a source of variety of trace metals (Witt *et al.* 2010). Anthropogenic (Gandois *et al.* 2010; Song and Gao 2009) and urban influences such as industrial activities, local emissions, pollutant transport, and vehicular emission contributes to the

metallic elements of atmospheric precipitation (Migliavacca *et al.* 2005 and Vuai and Tokuyama 2011).

Even if these 2 periods experienced the same amount of rainfall the concentrations showed immense difference (except for Zn which experienced increase on the last period). Considering the characteristics of this period (corresponding to a long dry period then to short but intense precipitations), the scavenging of trace metals in the atmosphere and in the surrounding through surface run-off explained the high concentrations observed. Dust and rains scavenged dissolved substances (Cheng and You 2010). Atmosphere receives aerosols containing metals and dispersed metals (Gandois *et al.* 2010). Then atmospheric precipitation occurs (Migliavacca *et al.* 2012). As the rainfall dropped, trace metals are delivered to the receiving body (Dunn *et al.* 2007) such as rivers (Aung *et al.* 2007) resulting to metal contribution.

Physico-chemical environmental parameters are very important in explaining the chemical spatial distribution of the trace metals (Figure VI.8) as portrayed by the PCA results. The dissolved oxygen (DO) plays an important role which is highly influenced by seasonal changes (Sokolowski *et al.* 2001). Temperature, salinity and organic matters are important factors of adsorption, aggregation and flocculation. These parameters have an action-reaction relationship with DO. High salinity and high temperature can cause decrease in DO in the water. Moreover, the high temperature can bring in increases of organic matter. DO and the organic matter are indirectly proportional; the relationship is interdependent. This means that high supply of the organic matter can cause DO depletion or anoxia (Joachimski *et al.* 2001). Then this can lead to denitrification and reducing agents and substances. The level of water oxicity influences the trace metals. In oxic water, trace metals are mostly driven by sorption reaction; while, trace metals are controlled by sulfide precipitation in anoxic water (Buffle and van Leuwen 1992). The trace metal distribution is affected by the pH through acid-base reaction (vanLoon and Duffy 2000).

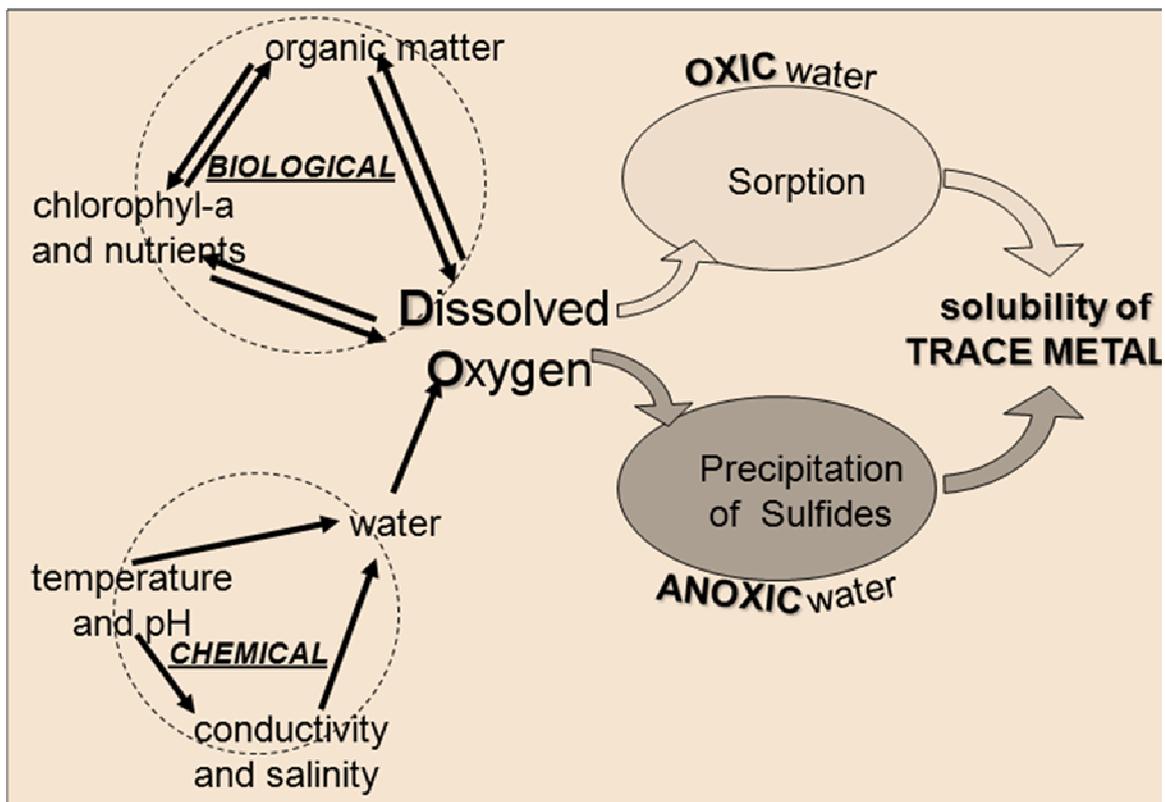


Figure VI.8 The schematic diagram of the interaction of the environmental factors to the trace metals for the Pasig River (as an estuary)

From the abovementioned descriptions, the Pasig River in Period 1 can be described as very close to anoxic waters ( $DO < 1 \text{ mg/L}$ ). In this case, the dominance of metal sulfides can be expected. This can give a reason why despite the dredging activity, the DGT-labile trace elements are lesser compared to Period 2. Sulfides are strong reducing agents. And with the water pH ( $> 6$ ), it accordingly, promoted insolubility of the trace metals. Furthermore, this sulfide precipitation are non receptive to trace metals sequestering agents (i.e. the resin in the DGT). Even though, the pH does not vary much along periods, in this research, it still explains the importance of the hydrogen ion activity and allows trace metal speciation.

This is highly opposite to Period 2. During this period, it obtained the highest trace metals concentrations in relation with the water temperature (highest in this period) and the oxic waters. The trace metal sorption became highly active.

The 3<sup>rd</sup> Period, experienced hypoxic water as DO level is also low. During this period also, the salinity among the Pasig River stretched showed evident water mixing.

Although, the salinity values are lower in Period 1, water mixing was also observed. In this line, flocculation of trace metals can be experienced in the area where the lowest salinity was found (Gerringa *et al.* 2010 and Biati *et al.* 2010). This explains why Point 4 during this period has the least trace metal concentrations (except for Cu and Pb). Figure VI.9 gives the full explanation on the DGT-labile trace metal trend.

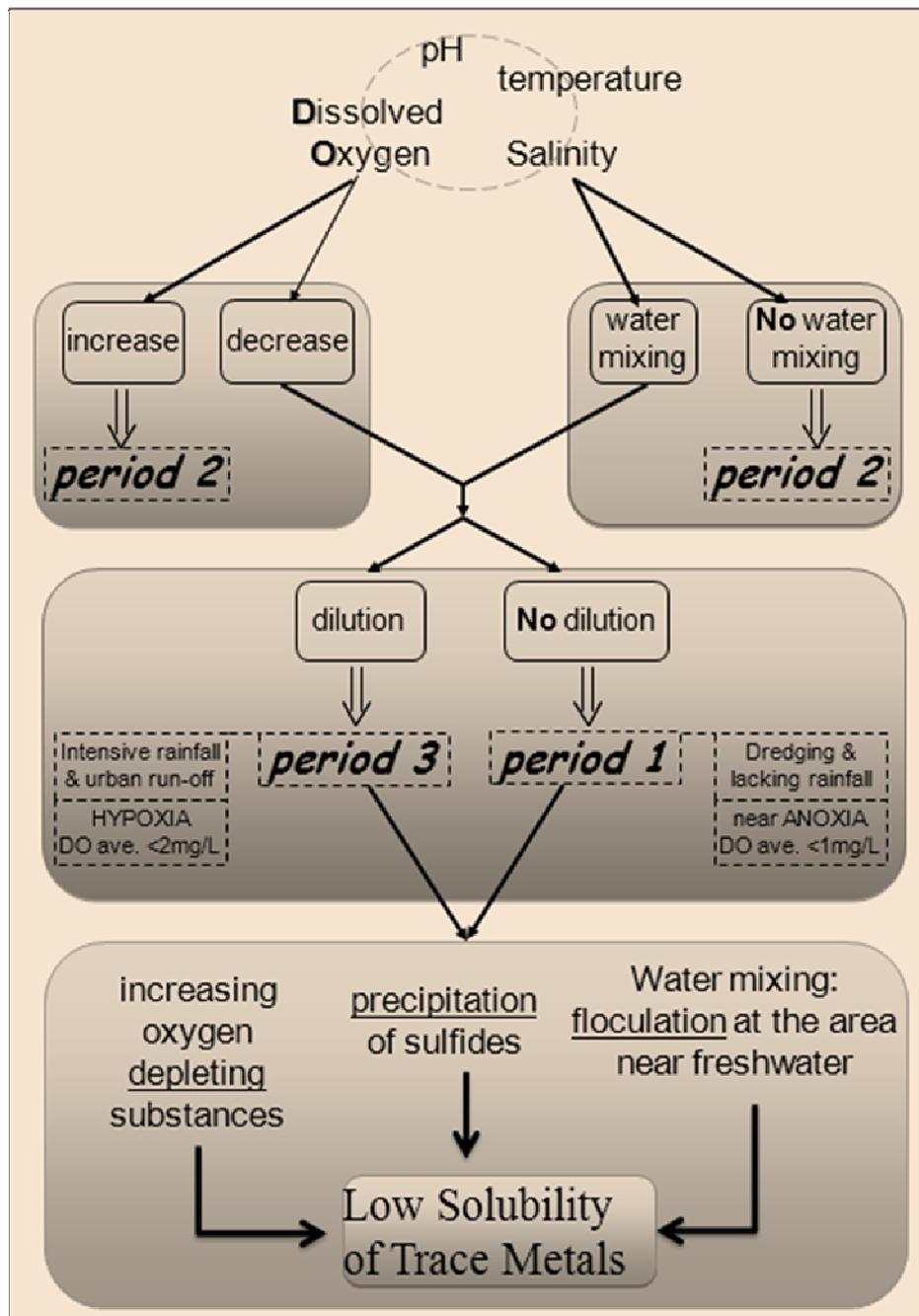


Figure VI.9 Trace metal spatio-temporal trend. Scheme for identifying the influential factors and explaining the sampling regime (Period) similarities and differences

The conditions in Period 3 plus dilution effect gave the least trace metal concentration (except for Zn). Twenty days before the sampling activity, the accumulated rainfall amount was only 125.2 mm already, whereas, Period 2 received only 14.4 mm.

Zn has different trend. In this study, Zn seemed to be not affected by the dilution effect and the varying temperature and DO. During Period 1, the trend cannot be explained by the dredging activity because it is not associated with the suspended solids (Zgheib *et al.* 2011). The site water pH gives weak possibility of Zn solubility. Hence, the continuous Zn concentration increase means that there are sources that constantly supplies labile Zn in the area.

## 5. Conclusion

The trace metal trend using DGT probes showed their active responses to 3 different periods, each defined by the physico-chemical and hydrological conditions in the estuary. The significant similarities and differences of the trend of the trace metals were verified by applying statistical analyses and PCA. According to the statistical results using the concentration of the trace metals, Period 2 is significantly different. Despite of this, the PCA results managed to show the differences, in terms of distance, of these periods. Applying the PCA using the trace metals and the physico-chemical parameters, it was found out that Periods 1 and 3 are statistically insignificant because of the physico-chemical conditions that is opposite of Period 2 (e.g. water temperature and DO inverse relationship). It was found out that Periods 1 and 3 showed almost the same physico-chemical conditions which differs only on the measured concentration (e.g. DO and salinity). That can be explained by the hydrological condition as affected by dilution factor that then played part to the amount of concentration and trend of the trace metals. Zn, however, did not follow the trend of other trace metals. Also in this study assessed and confirmed the sensitivity of DGT as a passive sampling device.

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## **CHAPTER VII Assessment on the pharmaceuticals and illicit drugs in the waters of the Pasig River**

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### **Abstract**

Pharmaceuticals (Atenolol, Salbutamol, Carbamazepine, Cetirizine, Ibuprofen, and Simvastatin) and drugs and their metabolites (ecgonine methylester, methamphetamine, amphetamine, ecstasy or MDMA, cocaine, benzoylecgonine, and THC-COOH) were measured in the natural water system lacking wastewater treatment plants named the Pasig River in Manila Philippines. The occurrence of these organic compounds is influenced by the modes of disposal. The concentrations are found to be lower than the documented past studies. This can be explained by the excretion, system of transport, physico-chemical characteristics of the aqueous system and the manner of sampling. Although, concentrations may seem low, the calculated mass fluxes should not be disregarded. Furthermore, this revealed that the tributaries contribute significantly to the pollution load of the Pasig River.

**Keywords:** pharmaceuticals, illicit drugs, metabolites, excretion, disposal, Pasig River

## 1. Introduction

There is an increasing trend in the production and consumption of pharmaceuticals nowadays (Sim *et al.* 2010). Accordingly, relentless releases of the pharmaceuticals and illicit drugs to the aquatic systems are observed. Even though, they are commonly detected in the environment at low concentration levels (Hernando *et al.* 2006), it still poses a major environmental concern. This is as they are made for biological activity and meant to give biological reactions. Consequently, exposures could possibly lead to adverse effects and release of toxicological potential (Reif *et al.* 2008). Past studies measured these compounds at the inlet and/or outlet of the waste water treatment plants (Van De Steene *et al.* 2010; Madureira *et al.* 2010; Yang *et al.* 2011). These studies showed that the typical wastewater treatment plants do not completely eliminate these organic compounds. Hence, these are not enough to solve the uprising concern.

Even if this is the case, unfortunately, not all the countries are able to provide treatment plants. This is a normal case in the developing countries like the Philippines. Thus, the water bodies become direct recipients of the wastes and excretion without any control. Apparently, albeit evident water pollution is present, the surface waters carry on their utility for the populace. The Pasig River in Manila, situated in a highly urbanized and industrialized region, embodies this reality.

The need to know the state of the water quality with respect to the fate and occurrence of these organic compounds is vital. This can facilitate in assessment measures. Assessments of the water quality, however, do not rely solely to measuring the concentrations. Further work is needed such as calculating the mass fluxes (Monbet 2004; Reinstorf *et al.* 2008; Letzel *et al.* 2009; Hu *et al.* 2011). The mass transport presents source zones and the discharges in the sites (Abelson *et al.* 1999; DiFilippo and Brusseau 2008). In this case, it can provide the estimate aquatic exposure to the pharmaceuticals and drugs present.

The objectives of this research is to (I) quantify target (Atenolol, Salbutamol, Carbamazepine, Cetirizine, Ibuprofen, and Simvastatin) and drugs and their metabolites (Ecgonine Methylester, Methamphetamine, Amphetamine, Ecstasy or MDMA, Cocaine, Benzoylecgonine, and THC-COOH) in an aqueous system lacking waste water treatment

plant; (2) examine the emission and describe the distribution and spatio-temporal profile of these organic compounds along the river stretch; and (3) present the mass flow rates of the chosen pharmaceuticals and illicit drugs in the river.

## 2. Materials and Methods

### 2.1. The study site and sampling design

The study site is located in Manila named Pasig River. The normal flow direction is from east to west. There are four major tributaries (east to west: Napindan, Taguig-Pateros, Marikina, and San Juan Rivers) with more than forty minor tributaries. Two sampling campaigns (Periods 1 and 2) were chosen. There are seven sampling sites (Figure VII.1) designated for monitoring the river (Manila Bay, PUP, Punta, Hulo, Guadalupe, San Joaquin, and Napindan). The end streams are near the mouth of the Manila Bay (downstream and saline water) and Napindan which is near the Laguna Lake (upstream and freshwater). These sampling sites were chosen according to the: (1) sectioning of the river covering the end streams and the mid streams; (2) nearness to the major tributaries; and (3) accessibility and security of the site as the POCIS samplers are needed to be immersed for more the two weeks. Despite of this, loss of POCIS samplers are experienced in Manila Bay during Period 1 and in Guadalupe and San Joaquin during Period 2.

The POCIS samplers were left immersed for 18 days (Period 1: 13-31 January 2011 and Period 2: 19 May - 06 June 2011) in duplicates (n=2) per site. Field blank (n=1) was provided per sampling campaign. Strict protocol and sampling procedures were followed from site reconnaissance to laboratory transport. Physico-chemical parameters (water depth, water temperature, conductivity, total dissolved solids, salinity, dissolved oxygen, pH, turbidity, and chlorophyll *a*) were determined *in-situ* using an automatic sampler, YSI 6600 V2 data sonde. Flow rate and water discharges were monitored within the sampling periods in each of the sampling points. To consider this, the inflow, diffuse and tributaries were measured.

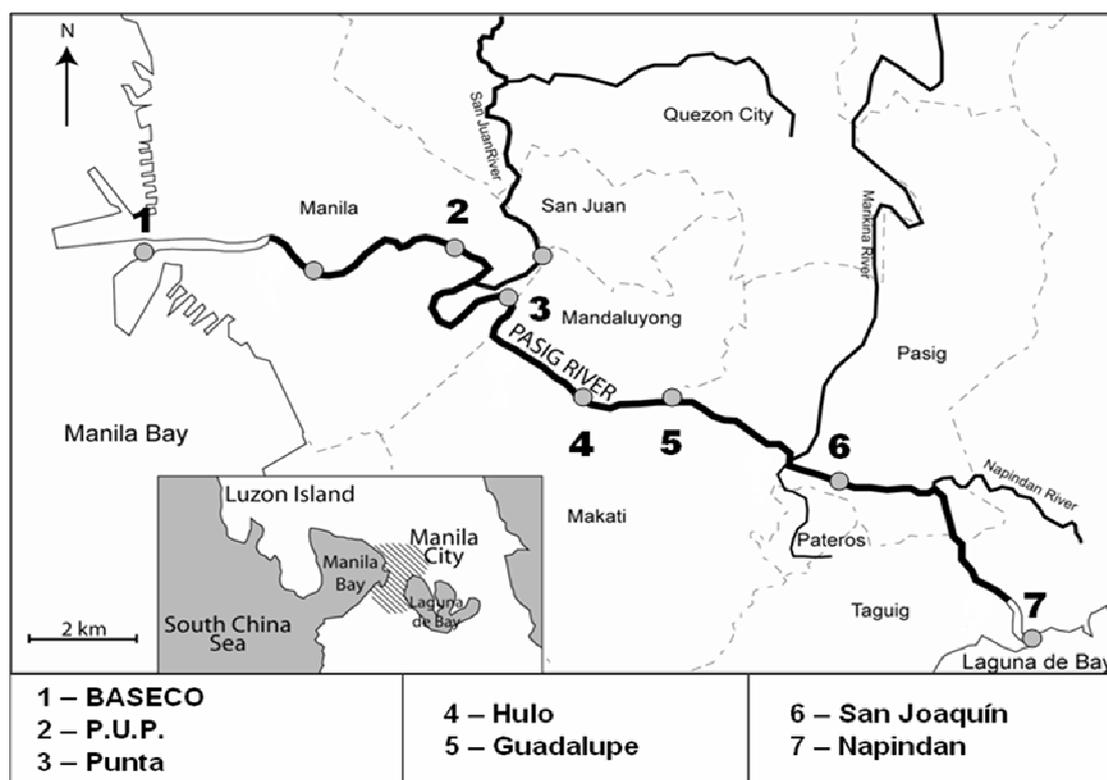


Figure VII.1. The Pasig River located in Manila and serves as a channel of Manila Bay and Laguna Lake; the sampling sites are identified

## 2.2. Assembling POCIS, extraction, and analysis

The sorbents OASIS HLB were bought at Waters SAS and the polyethersulfone (PES, 0.1  $\mu\text{m}$  pore size) were bought at VWR International S.A.S. The POCIS were assembled putting the sorbent in between the PES and then fixed firmly by steel frames. These steel frames were cleaned by methanol before using. After the deployment, the extraction procedure followed in the laboratory. The metal frames were disassembled to separate the sorbent from the PES. Ultrapure water (Option 3, Elga) was used to put the sorbent to the solid phase extraction (SPE) cartridge. Detailed descriptions and methods for extraction, materials used, eluent preparation, and analysis by LC-MS/MS are fully discussed in Harman *et al.* 2011. Tested compounds and the respective physico-chemical properties are shown in Table VII.1. Blanks were under limit of detection (Salbutamol: <1 ng/L; Atenolol: <2 ng/L; Carabamazepine: <2 ng/L; Cetirizine: <1 ng/L; Ibuprofen: <1 ng/L; Simvastatin: <10 ng/L; Ecgonine Methylester: <10 ng/L; Amphetamine:<10

ng/L; MDMA:<10 ng/L; Methamphetamine:<1 ng/L; Benzoyllecgonine:<1 ng/L; Cocaine:<1 ng/L; and THC-COOH:<25 ng/L). Strong pH shift in some samples (Methamphetamine during Period 2) was encountered. Methamphetamine chromatographic peak shape became too poor for analysis in many samples. All narcotics (and Cetirizine) were analyzed directly against deuterated internal standards. That is deuterated internal standards of each and every compound (narcotic) was spiked to the POCIS sorbent prior to elution. No deuterated internal standards available for the pharmaceuticals (except Cetirizine). Quantification of these compounds therefore by standard addition. The extraction recovery is presented in Table VII.2. Recovery is excellent in all cases.

Table VII.1. Physico-chemical properties of the tested organic compounds

Chemical	Chemical Formula	CAS No.	Molecular Weight	Therapeutic/Chemical Class	log $K_{ow}$ (c)	$pK_a$
Atenolol	C <sub>14</sub> H <sub>22</sub> N <sub>2</sub> O <sub>3</sub>	60966-51-0	266.34	Antianginal, antihypertensive	0.16 (l)	9.2 (l)
Salbutamol (Albuterol)	C <sub>13</sub> H <sub>21</sub> NO <sub>3</sub>	35763-26-9	239.31	Bronchodilator	0.64 (a)	9.3 to 10.3 (d)
Carbamazepine	C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O	298-46-4	236.27	Anticonvulsant	2.45 (a)	14 (g)
Cetirizine	C <sub>21</sub> H <sub>25</sub> ClN <sub>2</sub> O <sub>3</sub>	83881-51-0	388.89	Allergy, cold, and cough agent; antihistamine	1.62 +/- 0.63 (b)	1.6 (h)
Ibuprofen	C <sub>13</sub> H <sub>18</sub> O <sub>2</sub>	79261-49-7	206.28	Anti-inflammatory Drug and Analgesic	3.97 (a)	4.91 (d)
Simvastatin	C <sub>25</sub> H <sub>38</sub> O <sub>5</sub>	79902-63-9	418.57	Statin	4.68 (f)	4.3 (e)
Cocaine	C <sub>17</sub> H <sub>21</sub> O <sub>4</sub>	50-36-2	303.353	Cocainics	3.08 (j)	8.59 (e)
Benzoylcegonine	C <sub>16</sub> H <sub>19</sub> NO <sub>4</sub>	519-09-5	289.33	Cocainics: metabolite of cocaine	2.17 (c)	10.8 (c)
Ecgonine Methyl ester	C <sub>10</sub> H <sub>17</sub> NO <sub>3</sub>			Cocainics: metabolite of cocaine	-0.29 (k)	>8.0 (m)
Methamphetamine	C <sub>10</sub> H <sub>15</sub> N	537-46-2	149.23	Amphetamine	2.07 (c)	9.87 (c)
Amphetamine	C <sub>9</sub> H <sub>13</sub> N	300-62-9	135.21	Amphetamine	1.8 (j)	9.8 (i)
MDMA	C <sub>10</sub> H <sub>13</sub> NO <sub>2</sub>	4764-17-4	193.25	Amphetamine	1.67 (j)	9.9 (n)
THC-COOH (11-nor <sup>9</sup> -Carboxy-THC)	C <sub>21</sub> H <sub>28</sub> O <sub>4</sub>	6480-14-4	344.45	Cannabinoids: metabolite of THC	6.21 (j)	4.5 (n)

(a) Heijman et al. 2007; (b) Schaffer et al. 2012; (c) González-Mariño et al. 2010; (d) Ying et al. 2009; (e.) Babić et al. 2007; (f) guidechem.com; (g) Scheytt et al. 2006; (h) Mukherjee 1994; (i) Castiglioni et al. 2008; (j) van der Aa et al. 2010; (k) chemspider.com; (l) Jones et al. 200 ; (m) Valente et al. 200 ; (n) Dioumaeva and Hughes 2013

**Table VII.2. Extraction recovery data**

Compound	Control	Peak Area				Extraction Recovery %	RSD %
		Extract n=1	Extract n=2	Extract n=3	Extract Average		
Salbutamol	8119	7899	8010	7762	7890	97	1.3
Atenolol	4823	4883	4987	5229	5033	104	2.9
Carbamazipine	24219	22412	22014	21502	21976	91	1.7
Cetirizine	17045	15898	16383	14958	15746	92	3.8
Ibuprofen	241	172	192	197	187	78	5.8
Simvastatin	1234	958	988	978	975	79	1.3

### 2.3. Environmental concentrations (sampling rate $R_s$ ) and determination of the mass flux

The concentration in water was calculated following the equation of Huckins *et al.* 2002 as a function of the mass of the sorbent, sampling rate and deployment time. The sampling rate chosen only considered the nearest water condition that Pasig River has. Parameters such as water temperature, type of water (i.e. influence of salinity), water pH, type of water exposures, etc. Then calculated concentrations were then multiplied to the mean volumetric discharge flow rate to obtain the mass fluxes per sampling site of each period (Table VII.3).

**Table VII.3. Mean volumetric flow rate ( $Q = m^3/s$ ) along the Pasig River**

	Period 1	Period 2
Manila Bay	94.05	85.29
PUP	80.54	60.37
Punta	90.75	82.29
Hulo	57.75	52.37
Guadalupe	57.75	52.37
San Joaquin	28.88	26.18
Napindan	31.35	28.43

### 3. Results and Discussion

#### 3.1. Physico-chemical (background) trend of the Pasig River

Pasig River, as an estuary is greatly affected by the physico-chemical variations (Villanueva *et al.* 2013a). There is a high spatio-temporal variation along the stretch. Dissolved oxygen (DO), pH, turbidity, and chlorophyll *a* are higher on Period 1. While, water temperature, conductivity, total dissolved solids (TDS), and salinity are higher in Period 2. The difference in these two periods can be traced by the difference in the water temperature. This gave significant direct and indirect effects on the physico-chemical characteristics of the water. Period 1 has an average water temperature of 26°C, while, Period 2 has 31°C. If the water temperature is high, indirectly, the dissolved oxygen can decrease as the circulation is being hindered (Villanueva *et al.* 2013b).

Period 1 represents oxic water as DO ranges from 4.34 mg/L to 8.46 mg/L. pH (activity of the hydrogen ion) is in alkaline level ranging from 7.29 to 7.54. The chlorophyll *a* is high (207 µg/L to 492 µg/L), it can be the cause of high turbidity (52 NTU to 804 NUT) in this period. Salinity is weak as only the Manila Bay gave a value of 4.41 the rest ranges from 0.39 to 0.40. TDS and conductivity followed the trend of salinity; Manila Bay has TDS-5.19 g/L and conductivity- 8.21 µs/cm but the rest ranged from 0.52 to 0.54 for TDS and 0.82 µs/cm to 0.86 µs/cm for conductivity.

Period 2 illustrate that the water is suffering from hypoxia (DO ranges 1.23 mg/L to 3.15 mg/L). Also during this period, water is in the borderline of acidity and alkalinity as pH is recorded with a range of 6.60 to 7.10. The chlorophyll *a* (ranging from 9 µg/L to 17 µg/L) and turbidity (5 NTU to 371 NTU) dropped. Total dissolve solids (TDS) ranged 0.53 g/L to 9.56 g/L. The suspension of the colloid particles is more evident in this period. The salinity (0.39 to 8.97) could have affected the TDS. More pronounced water mixing was observed until the midsection of the river. Conductivity ranged 0.94 µs/cm to 16.27 µs/cm.

### **3.2. Fate and occurrence of the pharmaceuticals and drugs in the Pasig River**

The prescribed dosages taken from the generic medicines are in Table VII.4. When ingested, absorption process and the pharmacokinetics regulate the excretion rate.  $pK_a$  is the acid dissociation constant or ionization constant that works as a function of pH. It is one of the parameters that can describe the transport of drugs into cells and across membranes (Babić *et al.* 2007). The absorption depends on distinctiveness of the individuals. Prescribed dosage depends on the age (kid or adult) and weight. Other diseases and complications are being considered too so as not to have negative side effects. The manner of ingestion (such as if taken by water, food, or other food supplements or not) can affect the process as well. Other complementary medications and/or supplements affect the body reaction and sorption process. Ekins *et al.* (2005) and Zhang *et al.* (2012) briefly explain the process of organic compounds as it is ingested. Absorption and distribution happens based on membrane permeation, physical properties, protein binding and transporters. Metabolism partakes through enzymes and receptors. Absorption, distribution, metabolism and excretion are affected by the drug's ionization state (Wan *et al.* 2003). Only some percentage is being excreted through urine or feces. Absorption and metabolites lessens the occurrence of the parent compound in excretion (de García *et al.* 2013). It is interesting to quantify how the population affects the river in terms of the organic molecules. However and unfortunately, the prescription rate data are not available.

Excretion is one of the means of transport of the pharmaceuticals and drugs to the river. Excretion can be through lactation, urine, or feces as the same compound, metabolites or conjugates (Jelic *et al.* 2011; Aydin and Talinli 2013). The mode of disposal affects the distribution of these compouPasig River. It can be a direct discharge, or through sanitary sewer and run off process. Aside from excretion, there can be cases that these pharmaceuticals are disposed without even consuming it, usually when the expiration date is encountered.

Table VII.4. Prescribed dosage and excretion

	Prescribed dosage	% excreted
<b>Atenolol</b>	50-100mg daily	*40-50%
<b>Salbutamol (Albuterol)</b>	2.5-5 mg (up to 4x daily)	Urine (after 24h): 58-78%; 60% metabolites
<b>Carbamazepine</b>	Adults: 100-1200 mg daily Kids: 400-600 mg daily	Urine: 72% unconjugated metabolites, only 3% as parent compound
<b>Cetirizine</b>	Adults: 10 mg daily Kids: 5 mg daily	*Urine: 60-70%, feces: 10%
<b>Ibuprofen</b>	1.2-1.8 g daily	** 1%-8%
<b>Benzoylcegonine</b>	Not prescribed	<sup>x</sup> BE: 24.7±7.9; COC 1.1±0.8
<b>Methamphetamine</b>	Not prescribed	*Urine: 55%; 6-10% is amphetamine

\*PubChem ([http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?cid=2083&loc=ec\\_rcs](http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?cid=2083&loc=ec_rcs) accessed 12 April 2013)

\*\*Jemba (2006)

**Prescribed dosage, manufacturer and distributor-** Atenolol: Centurion Lab., Generics Pharmacy; Salbutamol: Ahlcon Parenterals Ltd.; Generics Pharmacy; Carbamazepine: Remedica Ltd.; Labmate Pharma Inc.; Cetirizine: Centurion Lab., Generics Pharmacy; and Ibuprofen: Shijiazhuang Pharma Grp. Zhongnou Pharmaceutical, Pacific Pharmaceutical Generics Inc.

The Pasig River is surrounded by 3, 646, 144 inhabitants. Only 12% are able to have a sewerage system (USAID, accessed 2013). The rest use different inland waterways to channel the untreated waste to the river. An estimate of a daily urine contribution of 612 552 L of pass to sewers and 4 492 049 L of untreated urine (per second: 7 L and 52 L, respectively) to the Pasig River.

From the measurements done, the following are under detection limit: Simvastatin (<10 ng/POCIS), Ecgonine Methylester (<10 ng/POCIS), Amphetamine (<10 ng/POCIS), Ecstasy (MDMA or 3,4-methylenedioxy-N-methylamphetamine: <10 ng/POCIS), Cocaine (<1 ng/POCIS), and Tetrahydrocannabinol or THC-COOH (<25 ng/POCIS). Carbamazepine, Cetirizine and Ibuprofen were detected mostly in all sites and sampling periods.

For the organic compounds that are above detection limit, respective sampling rate (*Rs* presented in Table VII.5) is used to calculate the concentration. However, there is no available sampling rate for Salbutamol (Albuterol) in the literature. Salbutamol is above the detection limit in PUP (1 ng/POCIS) and Hulo (1 ng/POCIS) in Period 1 and most of the sites during Period 2 except for Napindan. In Period 2, Salbutamol showed increases in value along sites having Hulo as the maximum (mean: 3.1 ng/POCIS).

**Table VII.5. Detection and concentration ranges, sampling rate (*Rs*)**

	<b>Range</b> <i>R<sub>w</sub></i> (ng/ <i>POCIS</i> )	<b>Range</b> <b>Concentration (ng/L)</b>	<b><i>Rs</i></b>
<b>Atenolol</b>	<2 to 21.5	***1.48-4.95	0.129
<b>Salbutamol (Albuterol)</b>	<1 to 3.5	***	
<b>Carbamazepine</b>	<2 to 31.7	***0.38-2.47	0.354
<b>Cetirizine</b>	<1 to 30.3	***0.82-6.85	0.088
<b>Ibuprofen</b>	<1 to 22.1	***0.44-4.06	0.100
<b>Benzoyllecgonine</b>	<1 to 3.9	***0.97-1.54	0.083
<b>Methamphetamine</b>	<1 to 15.1	***0.60-7.73	0.102

\*\*\*(*start with under detection limit; <sup>x</sup>Jabobs et al. 1990*)

The ranges of estimated aqueous concentration are as follows (Figure VII.2): Atenolol – 1.5 ng/L to 5 ng/L; Carbamazepine – 0.38 ng/L to 2.5 ng/L; Cetirizine – 0.82 ng/L to 7 ng/L; Ibuprofen – 0.4 ng/L to 4 ng/L; and illicit drugs: Methamphetamine -0.60 ng/L to 8 ng/L and the metabolite of Cocaine, Benzoyllecgonine- 0.97 ng/L to 1.54 ng/L.

Period 2 has higher concentration for Atenolol, Carbamazepine, Cetirizine, Ibuprofen, and Benzoyllecgonine. Highest concentrations of Atenolol, Carabamazepine, and Ibuprofen are found in PUP; at Punta for Cetirizine and Benzoyllecgonine; and in Hulo for Ibuprofen and Methamphetamine. Lowest concentrations are found at the Napindan area. The continuous increase of concentration of most of the organic compounds as it they reach the PUP site could mean that there are sources nearby.

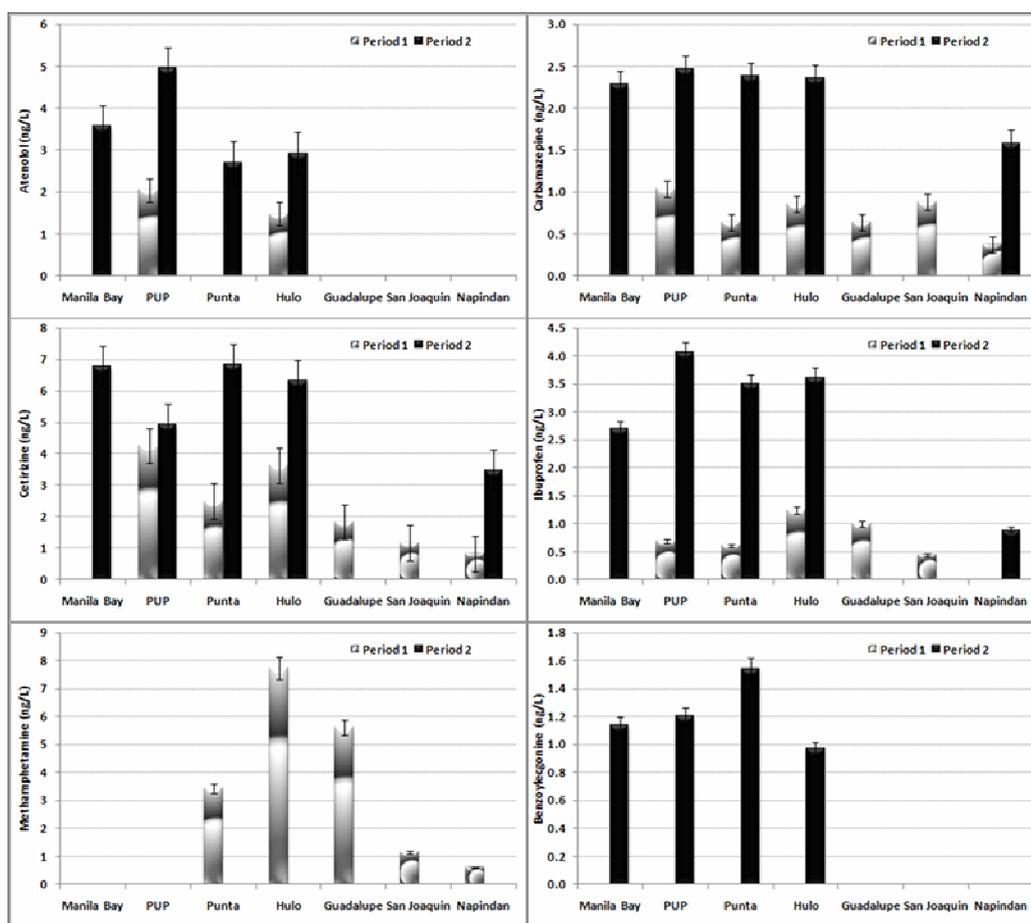


Figure VII.2. calculated concentrations of Atenolol, Carbamazepine, Ceftriaxone, Ibuprofen, Methamphetamine, and Benzoylcegonine

Despite the lacking of wastewater treatment plant in the area, these concentrations are lesser than the individual reported concentration (disregarding the recorded: under detection limit) at the influent and effluent at waste water treatment plants and surface waters. The past studies and detected concentrations of each of the pharmaceuticals and drugs are presented in Table VII.6. In these studies, there are evidences that these treatment plants cannot fully remove the organic compounds (Roberts and Thomas 2005; Maurer *et al.* 2007; Spongeberg and Witter 2008; Calisto *et al.* 2011; Hedgespeth *et al.* 2012). Also the rivers are affected by the discharges from the wastewater treatment plants can be observed (Kasprzyk-Hodern *et al.* 2009; Li *et al.* 2013). The study of Boleda *et al.* (2009) somehow showed that treatments employing granular activated carbon (GAC) filtration, Reverse Osmosis, and remineralization showed promising performances in eliminating the organic compounds.

**Table VII.6. Environmental occurrence of the pharmaceuticals and drugs**

Compounds	Concentration	Location	Reference
Atenolol	3.8-37 ng/L	San Francisco Bay water	Klosterhaus <i>et al.</i> 2013
Atenolol	Set 1 River Taff -upstream: 5-258 ng/L -downstream: 190-560 ng/L WWTP Cilfynydd -influent: 3090-33106 ng/L -effluent: 1260-7602 ng/L  Set 2 River Ely -upstream: <1-152 ng/L -downstream: 103-510 ng/L WWTP Coslech -influent: 8102-25146 ng/L -effluent: 1292-3168 ng/L	San Francisco Bay water	Kasprzyk-Hodern <i>et al.</i> 2009
Atenolol	Final effluent: 317 (130) ng/L	Switzerland	Maurer <i>et al.</i> 2007
Carbamazepine	0.37-178 ng/L	Duoro River estuary, Portugal -receives effluents from 8 WWTPs	Madureira <i>et al.</i> 2010
Carbamazepine	STP affected: 291- 675 ng/L Yangtze River: 17-46 ng/L	Yangtze River	Yang <i>et al.</i> 2011
Carbamazepine	5.2-44.2 ng/L	San Francisco Bay water	Klosterhaus <i>et al.</i> 2013
Carbamazepine	Influent: 0.0248-0.0509µg/L Effluent: 0.0337-0.1112µg/L	Northwest Ohio	Spongeberg and Witter 2008
Carbamazepine ( <i>n.a.=not available;</i> <i>n.d.=not detected</i> )	Influent: 47.5-67.3 ng/L Lagoon1: 187-198 ng/L Lagoon 2: 159-181 ng/L Effluent: 150-220 ng/L Upstream: n.d. -0.59 ng/L Dowsntream: 104-141 ng/L Mackinaw River: n.a. 13.7 ng/L	Mackinaw River, Illinois, USA.	Li <i>et al.</i> 2013
Carbamazepine	Jarama River: 363-67715 ng/L Manzanares River: 387-2997 ng/L Guadarrama River: 522-615 ng/L Henares River: 112 ng/L Tagus River: 121 ng/L	Spanish territory, the Madrid Region (MR)	Valcárcel <i>et al.</i> 2011
Carbamazepine	South WWTP after primary treatment: 0.44(0.01) µg/L WWTP after biological treatment: 0.49(0.01) µg/L Final effluent: 0.495(0.004) µg/L North WWTP after primary treatment: 0.504 (0.002) µg/L WWTP after biological treatment: 0.55(0.02) µg/L	Aveiro (NW Portugal)	Calisto <i>et al.</i> 2011

	Final effluent: 0.54(0.01) µg/L		
	Surface water (Ria de Aveiro): 0.146(0.004) µg/L		
Carbamazepine	Set 1 River Taff -upstream: 1-27 ng/L -downstream: 71-327 ng/L WWTP Cilfynydd -influent: 709-2930 ng/L -effluent: 644-4596 ng/L  Set 2 River Ely -upstream: <0.5-495 ng/L -downstream: 9-647 ng/L WWTP Coslech -influent: 104-3110 ng/L -effluent: 152-2324 ng/L	San Francisco Bay water	Kasprzyk- Hodern <i>et al.</i> 2009
Cetirizine	<b>South</b> WWTP after primary treatment: 0.38(0.007)µg/L WWTP after biological treatment: 0.24(0.002) µg/L Final effluent: 0.23(0.004) µg/L <b>North</b> WWTP after primary treatment: 0.60(0.06) µg/L WWTP after biological treatment: 0.31(0.04) µg/L Final effluent: 0.31(0.03) µg/L  Surface water (Ria de Aveiro): 0.04(0.01) µg/L	Aveiro (NW Portugal)	Calisto <i>et al.</i> 2011
Cetirizine	157-496 ng/L	sewage treatment plant	Harman <i>et al.</i> 2011
Ibuprofen	Max: 37.9 ng/L	San Francisco Bay water	Klosterhaus <i>et al.</i> 2013
Ibuprofen	WTP1: influent: 24 317±8 ng/L effluent: 928±779 ng/L  WTP2: influent: 24 033±7 7 ng/L Effluent: 2 600±na  Surface water: 8±3 ng/L	Charleston Harbor, South Carolina	Hedgespeth <i>et al.</i> 2012
Ibuprofen	Mersey: <8-386 ng/L Tyne: <8-698 ng/L Thames: <8-928 ng/L Belfast Lough: <8-376 ng/L Tees: <8-88 ng/L	UK estuaries	Thomas and Hilton 2004
Ibuprofen	Howdown WTW: Raw: 7741-33746 ng/L Pre-UV: 8771-15778 ng/L Final: 1979-4239 ng/L	lower Tyne catchment	Roberts and Thomas 2005

	River Tyne : 144- 2370 ng/L		
Ibuprofen	Influent: 18600-26200 ng/L Lagoon1: 1840-13900 ng/L Lagoon 2: 184-5480 ng/L Effluent: 146-5030 ng/L Upstream: 1.77-4.65 ng/L Downstream: 43.6-1210 ng/L Mackinaw River:n.a.-4.75 ng/L	Mackinaw River, Illinois, USA.	Li <i>et al.</i> 2013
Ibuprofen	Set 1 River Taff -upstream:5-48 ng/L -downstream: 12-62 ng/L WWTP Cilfynydd -influent: 968-2986 ng/L -effluent: 131-424 ng/L	South Wales in the UK	Kasprzyk- Hodern <i>et al.</i> 2009
	Set 2 River Ely -upstream:<0.3-56 ng/L -downstream: 4-74 ng/L WWTP Coslech -influent: 984-6328 ng/L -effluent: 65-491 ng/L		
Ibuprofen	Raw water: 81.4-230 ng/L Conventional treatment -Diox+sad filtered: 70.9-216 ng/L -Ozonated: 28.3-58.2 ng/L -GAC filtered: <LOD Advance treatment -Ultrafiltration: 78.8-202 ng/L -Reverse Osmosis: <LOD Remineralization: <LOD	Drinking water treatment plant (DWTP) located in NE, Spain	Boleda <i>et al.</i> 2009
Salbutamol (Albuterol)	Max: 1 ng/L	San Francisco Bay water	Klosterhaus <i>et al.</i> 2013
Salbutamol	Set 1 River Taff -upstream: <1 ng/L -downstream: <1-3 ng/L WWTP Cilfynydd -influent: <2-231 ng/L -effluent: <1-234 ng/L	San Francisco Bay water	Kasprzyk- Hodern <i>et al.</i> 2009
	Set 2 River Ely -upstream: <0.5 ng/L -downstream: <0.5-5 ng/L WWTP Coslech -influent: 50-150 ng/L -effluent: <1-22 ng/L		
Salbutamol	Jarama River: 12-28 ng/L Manzanares River: 26-27 ng/L Guadarrama River: <1-29 ng/L Henares River: <1 ng/L Tagus River: <1 ng/L	Spanish territory, the Madrid Region (MR)	Valcárcel <i>et al.</i> 2011

Drugs/ Metabolite	Concentration	Location	Reference
Amphetamine	Set 1 River Taff -upstream: <1-11 ng/L -downstream: 2-13 ng/L WWTP Cilfynydd -influent: 292-12020 ng/L -effluent: 19-739 ng/L  Set 2 River Ely -upstream: <1 ng/L -downstream: <1-3 ng/L WWTP Coslech -influent: 255-3225 ng/L -effluent: <1-11 ng/L	San Francisco Bay water	Kasprzyk- Hodern <i>et al.</i> 2009
Amphetamine	Olona: <0.65 ng/L Lambro: <0.65 ng/L Po: <0.65 ng/L Arno: <0.65 ng/L	Italian rivers : Po, Arno, Lambro and Olona	Zuccato <i>et al.</i> 2008
Amphetamine	74-452 ng/L	sewage treatment plant	Harman <i>et al.</i> 2011
Benzoylecgonine	2.8-7.2 ng/L	San Francisco Bay water	Klosterhaus <i>et al.</i> 2013
Benzoylecgonine	Olona: 183 ng/L Lambro: 50 ng/L Po: 2.2-5.1 ng/L Arno: 8.1-37 ng/L	Italian rivers : Po, Arno, Lambro and Olona	Zuccato <i>et al.</i> 2008
Benzoylecgonine	Raw water: 14.6-20.1 ng/L Conventional treatment -Diox+sad filtered: 12.7-20.9 ng/L -Ozonated: 2.1-9.0 ng/L -GAC filtered: 0.3-9.0 ng/L Advance treatment -Ultrafiltration: 12.1-14.3 ng/L -Reverse Osmosis: <LOD-0.9 ng/L Remineralization: <LOD	Drinking water treatment plant (DWTP) located in NE, Spain	Boleda <i>et al.</i> 2009
Benzoylecgonine	Set 1 River Taff -upstream: <1 ng/L -downstream: 3-92 ng/L WWTP Cilfynydd -influent: 126-2114 ng/L -effluent: 202-3275 ng/L  Set 2 River Ely -upstream:<1 ng/L -downstream: <1-54 ng/L WWTP Coslech -influent: 187-3715 ng/L -effluent: <1-29 ng/L	San Francisco Bay water	Kasprzyk- Hodern <i>et al.</i> 2009
Benzoylecgonine	121-669 ng/L	sewage treatment plant	Harman <i>et al.</i> 2011
Cocaine	Max: 2.4 ng/L	San Francisco Bay water	Klosterhaus <i>et</i>

			<i>al.</i> 2013
Cocaine	Set 1 River Taff -upstream: <0.3 ng/L -downstream: <0.3-4 ng/L WWTP Cilfynydd -influent: 21-1837 ng/L -effluent: 48-324 ng/L  Set 2 River Ely -upstream: <0.3 ng/L -downstream: <0.3 ng/L WWTP Coslech -influent: 54-471 ng/L -effluent: <1	San Francisco Bay water	Kasprzyk- Hodern <i>et al.</i> 2009
Cocaine	Raw water: 0.4-1.6 ng/L Conventional treatment -Diox+sad filtered: 0.4-1.6 ng/L -Ozonated: <LOQ-0.1 -GAC filtered: <LOD Advance treatment -Ultrafiltration: 0.8-1.4 ng/L -Reverse Osmosis: <LOD Remineralization: <LOD	Drinking water treatment plant (DWTP) located in NE, Spain	Boleda <i>et al.</i> 2009
Cocaine	Olona: 44 ng/L Lambro: 15 ng/L Po: 0.3-0.8 ng/L Arno: 0.3-2.9 ng/L	Italian rivers : Po, Arno, Lambro and Olona	Zuccato <i>et al.</i> 2008
Cocaine	35-166 ng/L	sewage treatment plant	Harman <i>et al.</i> 2011
MDMA	Olona: 1.7 ng/L Lambro: 1.1 ng/L Po: <0.35-0.4 Arno: 0.5-1.4 ng/L	Italian rivers : Po, Arno, Lambro and Olona	Zuccato <i>et al.</i> 2008
MDMA	Raw water: 0.4-1.3 ng/L Conventional treatment -Diox+sad filtered: <LOD -Ozonated: <LOD -GAC filtered: <LOD Advance treatment -Ultrafiltration: <LOD -Reverse Osmosis: <LOD Remineralization: <LOD	Drinking water treatment plant (DWTP) located in NE, Spain	Boleda <i>et al.</i> 2009
Methamphetamine	Olona: ng/L Lambro: ng/L Po: ng/L Arno: ng/L	Italian rivers : Po, Arno, Lambro and Olona	Zuccato <i>et al.</i> 2008
Methamphetamine	405-1487 ng/L	sewage treatment plant	Harman <i>et al.</i> 2011
THC-COOH	Olona: <0.48 ng/L Lambro: 3.7 ng/L Po: <0.48-0.5 Arno: <0.48-1 ng/L	Italian rivers : Po, Arno, Lambro and Olona	Zuccato <i>et al.</i> 2008

TP: treatment plant

The lower values in this study can be explained by the processes that the organic compounds undergo as it reach the water body. The process and reaction of the compounds while it pass through the different media before reaching the water body can influence the state fate of the compounds. Biotransformation and adsorption affect the fate of pharmaceuticals in river (Daneshvar *et al.* 2010). Horvat *et al.* (2012) explained that the organic compounds can be affected by the aqueous solution with differing pH, buffer concentration, temperature and oxidant. Also depending on the ionic interactions (most especially for organic cations), the organic compounds can bind to humus or organic matter (Kosjek and Heath 2011). Photodegradation is likely to give an impact. The river is shallow and water temperature has a range of 26°C to ~32°C. Direct photolysis is one of the pathways for abiotic transformation of the organic compounds in the water column (Kim *et al.* 2009; Ji *et al.* 2012). Photolytic reactions could produce reactions to the parent compounds such as more toxic or retains the properties or lose the toxicity and/or microbial activity (Petrovic and Barceló 2007). Or worst, photodegradation can lead to elimination of the compounds in the aquatic system (Dévier *et al.* 2011). Other than direct photodegradation, reactions can also be produced by indirect photochemical pathways include singlet oxygen reaction, hydroxyl radical, peroxy radical, photoexcited organic matters and reactive species (Zeng *et al.* 2012). Carbamazepine, however, can persist due to its resistance to natural transformation processes e.g. adsorption and photodegradation (Tixier *et al.* 2003).

Aquatic colloids is also a factor as the hydrophobic dissolved organic matter are efficient in sorbing organic compounds at pH near pKa analytes (Vignatti *et al.* 2009; Duan *et al.* 2013). Log  $K_{ow}$  (octanol-water partition coefficients) indicates the lipophilicity of the compound (Dolores Hernando *et al.* 2007). Rogers 1996 classified the Log  $K_{ow}$  with respect to the sorption potential. Low sorption has Log  $K_{ow}$  of <2.5; medium is in between 2.5 and 4; and >4 has high sorption potential. Following this, then low sorption can be expected with Atenolol, Salbutamol, Cetirizine, Benzoylcegonine, Carbamazepine and Methamphetamine, while, Ibuprofen is under medium sorption potential. Log  $K_{ow}$  of less than 3 does not normally adsorb to particles and higher (e.g. ibuprofen) dissociates in aqueous phase (Behera *et al.* 2011). Furthermore, the sampling sites might have been far from the direct sources. Being far from the discharge point and dilution factors (Letzel *et al.* 2010) affect the concentration of the organic compounds.

The sampling duration could have affected the measurement. As the POCIS needs to be immersed for at least 2 weeks, degradation (or retention life or half-life) of the organic compounds might have been reached already. For example, ibuprofen has half-time of 10h (Kunkel and Radke 2012). Again, photodegradation is likely to give an impact. Additionally, the sampling rate chosen only considered the nearest water condition that Pasig River has. But choosing a sampling rate should be the same with: (1) type of water: should it be the linear uptake using deionized water, estuary (salinity range), freshwater; (2) pH: oxic and anoxic level; (3) water temperature; (4) organic matter content; (6) water flow: stagnant or high flow. Essentially, factors such as the use, absorption, excretion, modes of disposal or transport, physico-chemical characteristics of the aqueous system and the manner of sampling can explain the level of concentration (Figure VII.3).

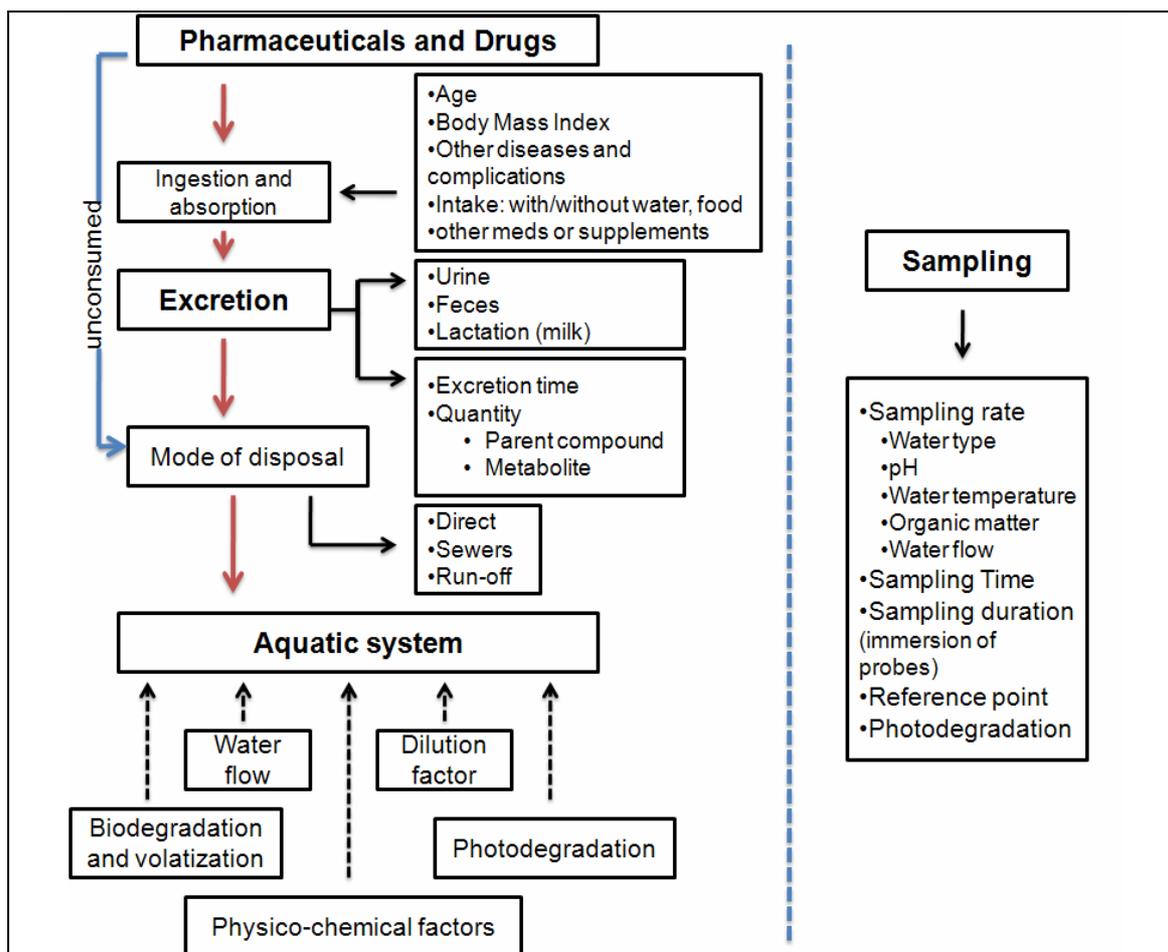


Figure VII.3. Mode of transport, fate and occurrence of the pharmaceuticals and drugs in the Pasig River

The discharge flow rates are important in explaining the variation of fluxes of the organic compounds in rivers Letzel *et al.* (2010). The water volume at the mouth of the Laguna Lake (Napindan site) is only 33% of the Manila Bay. The average residence time of the Pasig River is 3 to 5 days. The mass flow rates of each organic compound are determined by multiplying the concentrations to the water volume which gave ranges as follows (Figure VII.4): Atenolol- Period 1: 86  $\mu\text{g/s}$  to 165  $\mu\text{g/s}$ , Period 2: 153  $\mu\text{g/s}$  to 305  $\mu\text{g/s}$ ; Carbamazepine- Period 1: 12  $\mu\text{g/s}$  to 84  $\mu\text{g/s}$ , Period 2: 45  $\mu\text{g/s}$  to 196  $\mu\text{g/s}$ ; Cetirizine- Period 1: 26  $\mu\text{g/s}$  to 343  $\mu\text{g/s}$ , Period 2: 99 to 579  $\mu\text{g/s}$ ; Ibuprofen- Period 1: 13  $\mu\text{g/s}$  to 72  $\mu\text{g/s}$ , Period 2: 26  $\mu\text{g/s}$  to 288  $\mu\text{g/s}$ ; Methamphetamine- Period 1: 19  $\mu\text{g/s}$  to 447  $\mu\text{g/s}$ ; and Benzoylcegonine- Period 2: 51  $\mu\text{g/s}$  to 127  $\mu\text{g/s}$ . Manila Bay showed highest fluxes in Period 2 for Atenolol and Cetirizine. Mean daily mass flow rate is presented in Table VII.7. The water volume at the midstream (Punta, Hulo, and Guadalupe) resulted to high mass flow rates. There is apparent evidence that major (Taguig-Pateros, Marikina River, and San Juan River) and minor tributaries these areas contribute to the Pasig River.

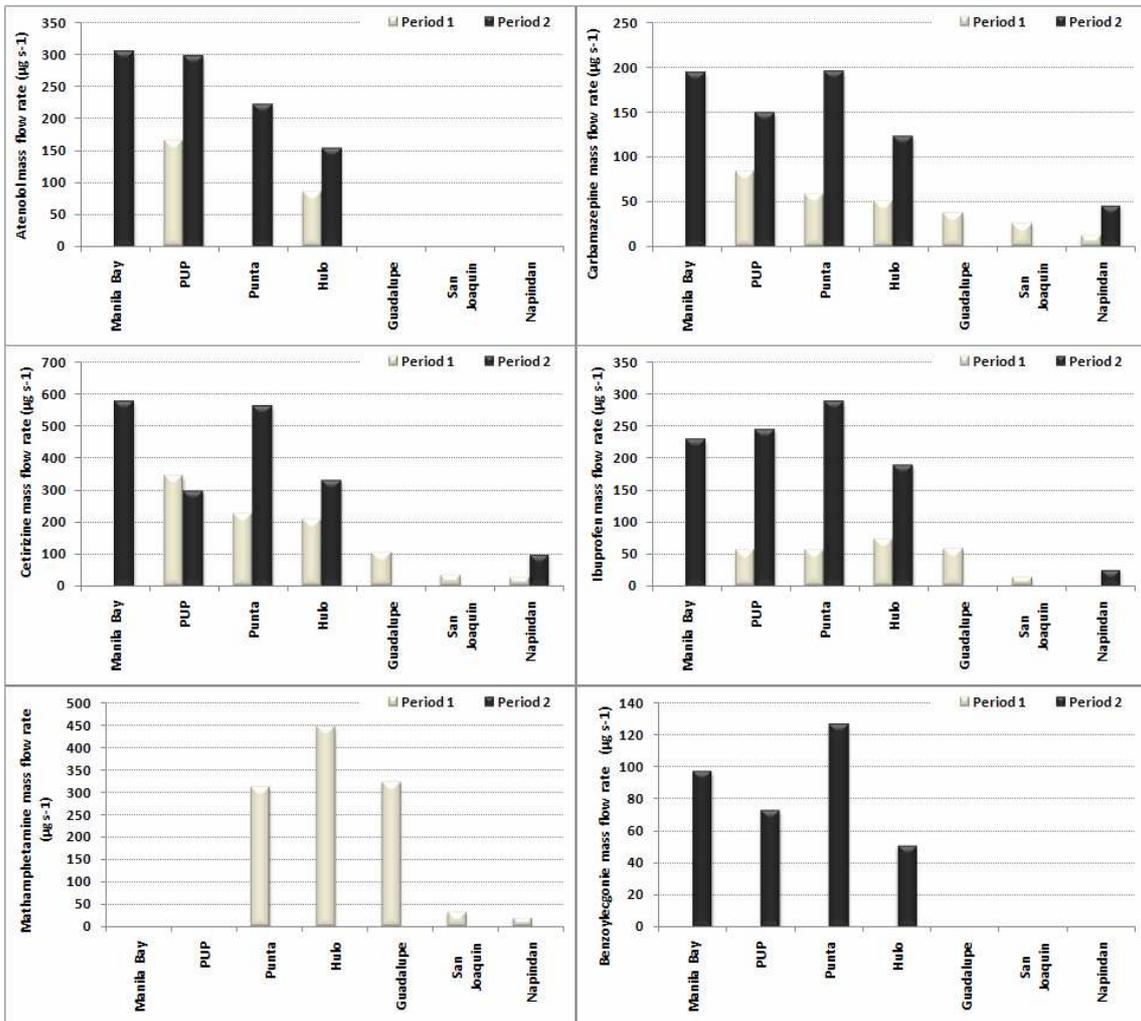


Figure VII.4. mass flow rate of Atenolol, Carbamazepine, Cetirizine, Ibuprofen, Methamphetamine, and Benzoylcegonine

Table VII.7 Mean daily mass flow rate (mg per day)

	Atenolol		Carbamazipine		Cetirizine		Ibuprofen		Methamphetamine		Benzoylcegonine	
	Period 1	Period 2	Period 1	Period 2	Period 1	Period 2	Period 1	Period 2	Period 1	Period 2	Period 1	Period 2
<b>Manila Bay</b>	*	26340	*	16826	*	50009	*	19855	*		*	8385
<b>PUP</b>	14235	25833	7262	12893	29653	25685	4832	21154				6284
<b>Punta</b>		19291	5045	16905	19553	48703	4792	24886			26905	10946
<b>Hulo</b>	7413	13251	4307	10651	18113	28565	6237	16339			38591	4391
<b>Guadalupe</b>		*	3171	*	9135	*	4990	*			27992	*
<b>San Joaquin</b>		*	2193	*	2914	*	1109	*			2854	*
<b>Napindan</b>			1020	3893	2223	8529		2183			1623	

\*POCIS samplers lost

#### **4. Conclusion**

The study tried to measure the pharmaceuticals (Salbutamol, Atenolol, Carbamazepine, Cetirizine, Ibuprofen, and Simvastatin) and drugs and metabolites (Ecgonine Methylester, Methamphetamine, Amphetamine, Ecstasy or MDMA, Cocaine, Benzoylcegonine, and THC-COOH) in a natural water system lacking wastewater treatment plants. The results indicate the presence of pharmaceuticals (Atenolol, Salbutamol or Albuterol, Carbamazepine, Cetirizine, Ibuprofen) and drugs and metabolites (Methamphetamine and Benzoylcegonine) present in the surface water of the Pasig River. Most of these compounds are found higher during Period 2. The sampling points that contribute consistently are PUP, Punta, and Hulo.

However, despite of the fact that the area lacks wastewater treatment plants, the calculated concentrations are lower compared to the other environmental occurrences from the past studies. Biotic and abiotic factors play in the level of concentration of these organic compounds (depending on the attributes). The sampling procedure such as being far from the direct source and chosen sampling rate could have affected as well. The mass fluxes, however, driven by the discharge flow rates cannot be overlooked. Manila Bay (Period 2) showed highest mass fluxes for Atenolol and Cetirizine). Hulo (Period 1) found to have highest mass fluxes for Atenolol, Ibuprofen, and Methamphetamine. Most of the mass fluxes at Punta are highest among sites such as for Carbamazepine (both Periods), Cetirizine (Period 1), Ibuprofen (Period 2), and Benzoylcegonine (Period 2). There is a substantiation that the tributaries contribute to the Pasig River as showed by the concentration and mass fluxes.

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## **CHAPTER VIII Conclusion and Perspectives**

## 1. Summary of the PhD studies

The goal of this thesis as a whole is to formulate concrete research studies that will facilitate in providing good and sound water quality basis and assessment methods. This covered complete documentation from site to laboratory to making analysis and interpretation up to how it can be applied to real water resource management strategies.

The chosen sites (Jalle River and Bordeaux Lac in France and Pasig River in the Philippines) are all influenced by the urban lifestyle but have differing natural resource characteristics considering the physico-chemical properties and milieu. The changing effect of water temperature, dissolved oxygen and salinity, for example, shows the dynamic behavior of the Pasig River. In addition, water resources management styles are distinct in each site. French site has designated wastewater treatment plants (STEP) for point sources, while, no treatment is applied for the surface run-off, rainwater/stormwater. The Philippine site, however, is a *free for all* water body. This is since the area lacks treatment plants and strict regulations to prevent the water system to be an *open wastes recipient*.

Coincidentally, the sampling campaigns corresponded to one of the specific objectives: assessing the influence of the differing climate conditions to the water system. This is as the sampling regimes encountered exceptional climate conditions while conducting the monitoring. During the year 2011, Bordeaux experienced hot and dry weather during the 1<sup>st</sup> months followed by high humidity and precipitation for the rest of the year. In the Philippines, great drought was experienced starting year 2010. Afterward, the precipitation started to be felt and increased during year 2011. This occurrence gave advantages in determining the difference of the trend of the trace elements during dry and wet periods.

In doing the water quality monitoring, the conventional method (grab or water bottle samples) is supplemented by the in-situ passive sampling technique employing the DGT and POCIS. This then lead to testing its potential and efficiency with regards to sensitivity to the natural background and to the target trace elements. Pertinence of this technique was also evaluated in terms of the capacity to give representative data covering the spatial and temporal conditions of the sampling site. Figure VIII.1 shows the aims, considerations, and approaches undertaken for this PhD studies.

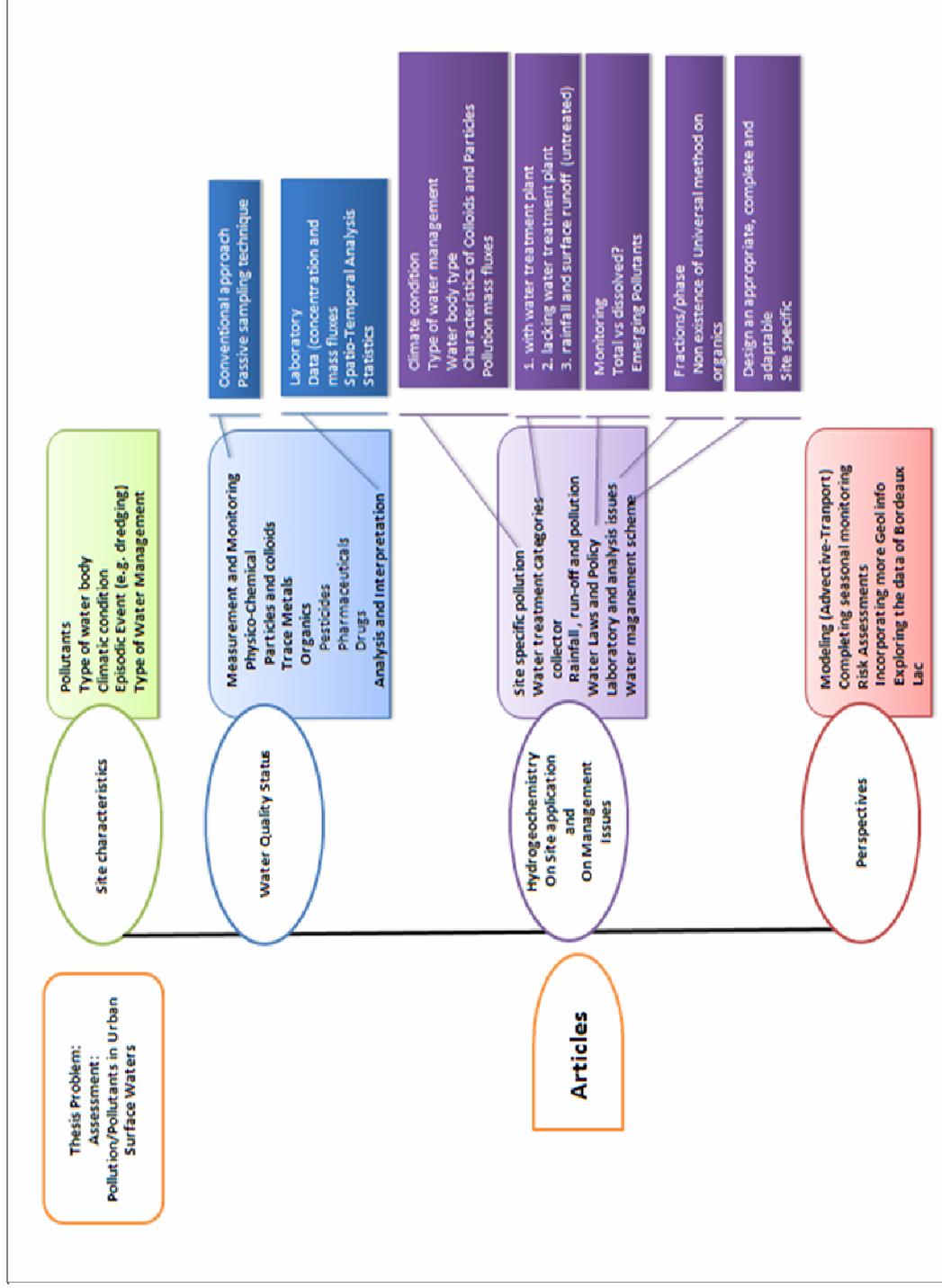
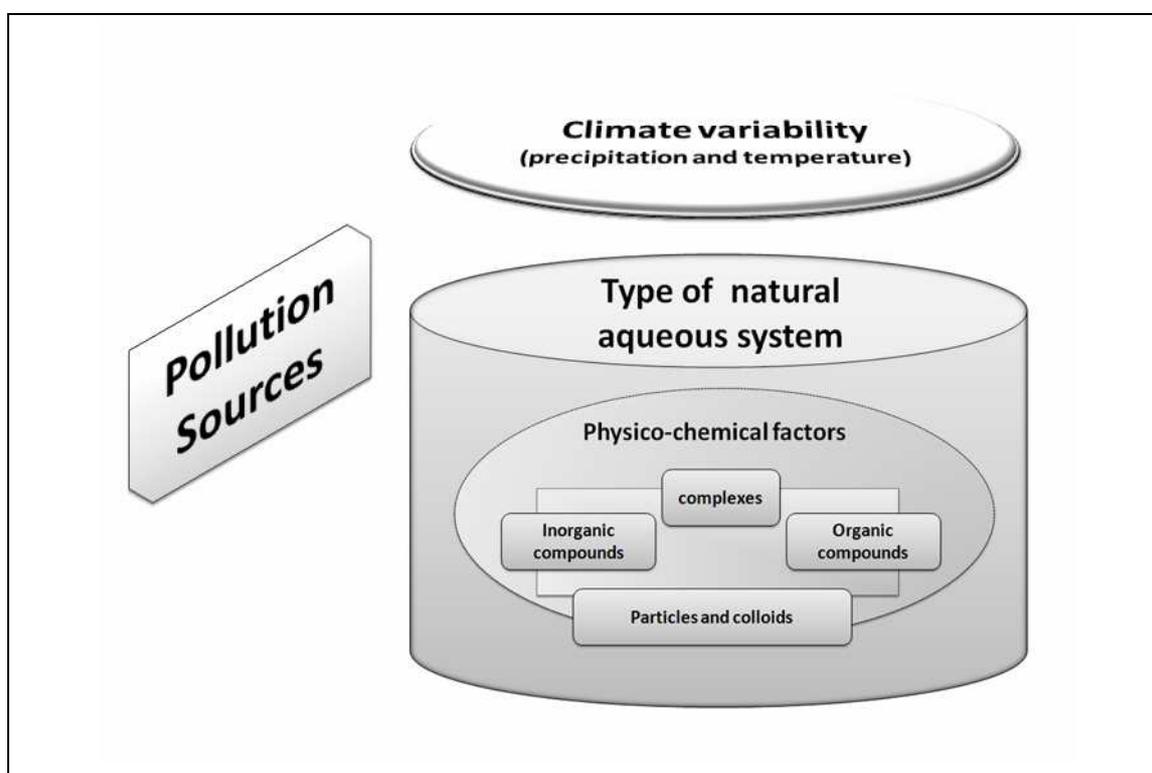


Figure VIII.1. PhD thesis structure and flow

## 2. Water Quality Assessment (Course of Action)

The elements to be considered in water quality monitoring and assessments can be divided in two parts: (1) knowing the water system and what is happening in the surrounding and in the water column and (2) analysis, interpretation and applications.

**Part I** includes the water column, pollution sources and climatic factor. These then can be divided into sub parts such as the nature of the site, climate variations and extremes, water column (inter-acting components), particles and natural aggregated tendency (Figure VIII.2).



**Figure VIII.2.** Natural aqueous system and the factors affecting the trend and behavior of the elements and compound within the water column

Site reconnaissance includes knowing the type of water system (or resources), possible sources of pollution, and possible pollution (organic or inorganic compound). The climatic trend can explain if there are existing climate extremes and variability brought about by the temperature and precipitation (anomalies). At the water column, identification of physico-chemical variations, elements and chemicals (present, fraction and concentration; Chapter 2), complexes present, and flow and water volume to be able

to determine the pollution mass fluxes. All these can facilitate in identifying the source of consistent or high concentration or fluxes (Chapters 3 to 7).

**Part II** starts after obtaining the data from Part I. This part consists of laboratory, water quality assessment and interpretation and application to water resources management. The assessments and interpretations can make use field and surrounding observation (spatio-temporal trend), evaluation of the existing water resource management (water treatment plants: point and non point sources and water use), and empirical findings. Aside from these investigatory methods (Chapters 3 and 6), the mass balance (Chapters 4 and 7) and statistical analysis (Chapter 6) give supplementary data to understand more the all the data obtained. Combination of methods and validation (Chapter 6) or comparative studies (Chapters 4 and 7) are also useful for assessing the state of the water quality. The application of the water quality assessments made is illustrated in Figure 7 of Chapter 5.

### 3. Perspectives

This manuscript is done as the objectives are already met. However, as this study is wide and the data are large, there are still on-going research papers that are currently in working (writing) progress.

There are some parts that are needed to be explored more, mostly for Chapter 3. For instance, advective-diffusion transport models are promising to give more technical results especially on evaluating how the rainwater/stormwater collectors affect the natural system (Jalle River and Bordeaux Lac). This can also help in understanding more the behavior of the trace elements in a semi-closed system, Bordeaux Lac. Also for the organic compounds, the unavailability of the sampling rates (*Rs* e.g. salbutamol) prevented to present the environmental concentration of some pharmaceuticals and drugs.

As a final point, there is a need to continue the water quality monitoring and assessments. The acquired data and information can be integrated in doing water resource formulating strategies and planning steps. Although, the trace elements can give a lot of descriptions about the natural system, the climate and physico-chemical background should never be forgotten in all the monitoring conducts. Water flow and mass volumes should be considered, hand-in-hand with the monitoring activities. These need to be carried on until it reached a point where it can comply with doing the environmental risk assessment studies.

# **APPENDICES**

## APPENDIX 1. Passive sampling protocols

### 1. Ocular site visits

1. Inspect the sites by conducting visits before installing the samplers.
2. Environmental factors such as turbulence, possible biofouling, ambient and water temperature and water pH should be checked.
3. Identify and locate the possible contributor of contaminants including the vapor-phase sources.
4. Select the sites that can best represent the system needed to be monitored.
5. Make sure that the selected sites are accessible and secure.
6. Conduct a water quality test and system examination (in the selected sites) by considering the following environmental parameters “at the very least” (additional parameters will depend on the system and the objectives):

pH (DGT works for pH 5-9)  
water flow (m/s) and depth (m)  
organic carbon: total and dissolved (mg/L)  
ionic strength (M)  
total dissolved solids (g/l)  
conductivity (mS/cm)  
turbidity (NTU)  
chlorophyll concentration ( $\mu\text{g/L}$ )  
dissolve oxygen, DO (mg/L)  
partition coefficient (e.g. POCIS works with  $\log k_{ow,s} < 3$ )  
biological oxygen demand (BOD,  $\mu\text{g/L}$ )

The abovementioned parameters *should be monitored also in parallel* during the time of passive sampler deployment.

7. If possible, particle size and characterization in the system is highly advised.
8. Consider the following:
  - a. Keep away in areas with high suspended solid discharge. If not, make sure to make or put possible obstruction.
  - b. Consider what type of canisters to be use for deployment. As samplers are so sensitive, consider using materials that will not contribute to the samplers.
  - c. For the canisters to stay immersed in the water, weights such as blocks are encouraged.

## 2. Immersing the samplers

### **Before deployment**

1. Record the following data:
  - a. GPS coordinates: in decimal degrees and with at least four decimal places
  - b. Elevation
  - a. Accurate time and date
  - b. DO
  - c. BOD
  - d. Water temperature
  - e. Ambient temperature
  - f. Salinity
  - g. pH
  - h. Conductivity
  - i. Wind direction
  - j. Turbidity
  - k. Alkalinity
  - l. TSS
2. Some other observations could be noted down. Take some photos of the site specially if there are notable observations.
3. When transporting, make sure that each passive sampler is in an air-tight container.
4. Make sure that the samplers are in cold compartments. This is before deployment, upon retrieval and when transporting.
5. Samplers should be kept sealed prior to deployment. DO NOT remove from the sealed plastic bag unless is the time for deployment.

### **Deployment**

1. The one who will deploy and collect the samplers should not smoke!
2. Hands should be clean.
3. Do not use hand lotion, perfume, colognes and other chemicals that might affect the samplers.
4. Use powder-free hand gloves.

5. White filter or the membrane (at the face of the unit) SHOULD NOT be touched. No contact on anything should be allowed.
6. Make sure that deployment of samplers is in duplicate (n=2) or triplicate (n=3) per target time and objective.
7. Do not forget the blank samplers (the same recordings should be done as well). This should be opened (i.e. opening the plastic or the case), once the 1<sup>st</sup> sampler to be immersed was open. The time that the sampler is immersed, put the blank back to its original container.
8. Samplers should be deployed immediately (minutes) right after it was removed from the plastic seal. So secure and place them in the canister as quick as possible.
9. Full immersion of the canister is needed to make sure that the water reaches the samplers.
10. If using samplers for organics, make sure that they are protected from sunlight all the time.

### **Retrieval**

1. Make sure that all the materials are all prepared.
2. The person who will get the samplers should follow again the protocol of deployment no. 1-5.
3. Immediately, remove the samplers from the canister.
4. Carefully, rinsed them with de-ionized water. Remove the surface water but do not dry them.
5. Put them in the allotted and properly labeled plastics or wrapper.
6. Place each in an air-tight plastic.
7. Put them in the cooler and keep them in the proper storage area.
8. Should be kept in the cold compartment until the time of extraction.

## APPENDIX 2. Difficulties encountered and Recommendations in using the passive sampling technique

### 1. Ocular visits and planning for the installation of the samplers

#### 1. Site selection for a better area representation

The decision should be strongly based from the objectives.

#### 2. Accessibility and security

Samplers are needed to be immersed for a period of time so this factor is very important.

#### 3. Planning for the right time to start the monitoring

Running after the rain was encountered during this sampling period. 2011 is an exceptional dry year. Since the interest of the research is on the precipitation and surface run-off, the sampling campaign was difficult to establish.

#### 4. The need to have a water collector that will consider the differing vertical gradient (depth) of the area for Bordeaux Lac for example.

At the center of the Bordeaux Lac, there is no structure to attach the canister and deploy the passive devices. A buoy (marker/floater) was used with rock at the bottom for the weight (Figure 1).

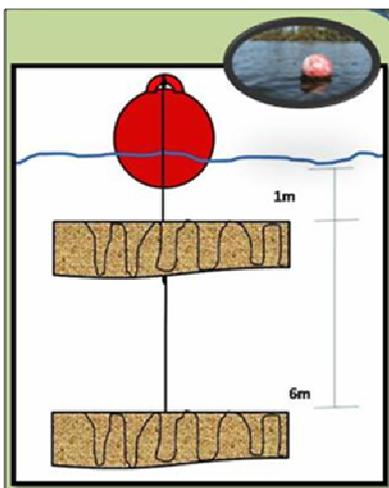
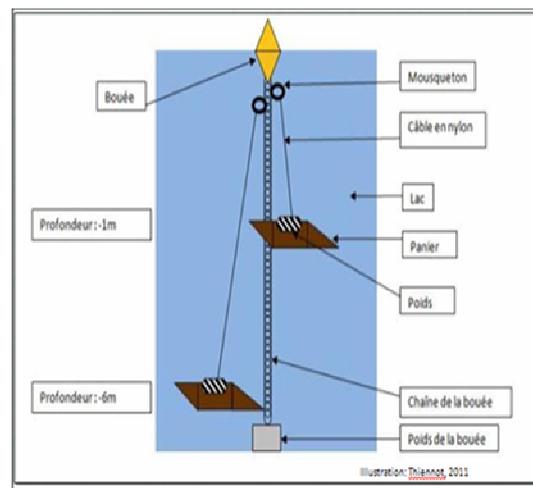


Figure 1 a The use of buoy at the site to cover the differing vertical gradient



b Using weight (poids) to keep the samplers at its proper vertical gradient

This is applicable since it is a close system; otherwise, buoy should have a stopper or should be tied to a certain structure so as not to lose the canister.

5. Type of weight (e.g. concrete blocks) needed to use in order to make sure that the canisters (with the samplers) are surely immersed.

Even the weight that will be used should not contribute to the molecules that will be captured by the passive sampler.

6. What molecules to be measured? Present or not?

Since this is the start of the monitoring program, we have no idea of what possible molecules are present in the system. Screening or preliminary measurements are necessary.

## 2. Deployment of samplers

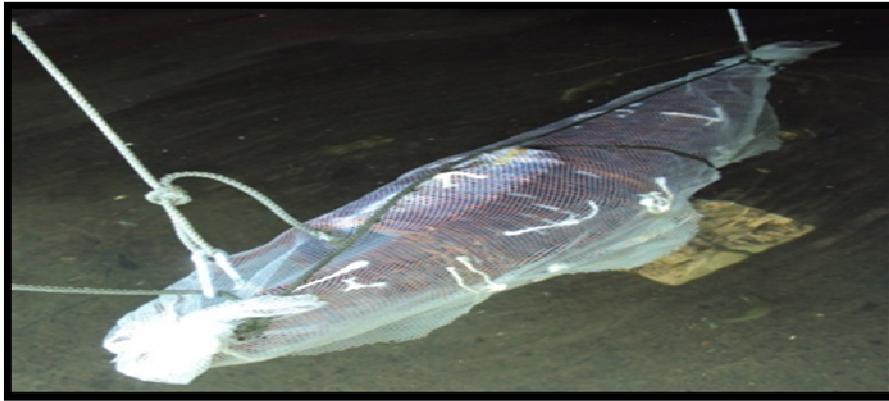
1. Choosing the right materials that will not contribute to the target molecules

- a. Canister- there might be a problem when deploying several passive samplers targeting different types of molecules/analytes. In this research, DGT and POCIS were needed to be deployed at the same time in the same canister. So a wooden basket (Figure 2) was used so that interference with the DGT will not be encountered if a metal canister will be used. Although, it should be taken into consideration that biodegradable containers are much prone to biofouling.



**Figure 2. Wooden basket used for deploying the samplers**

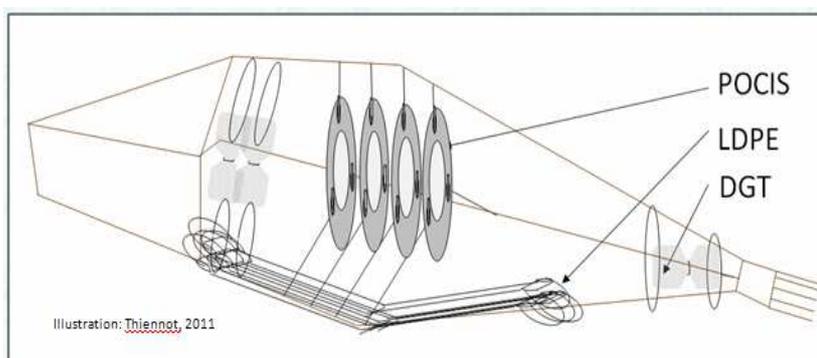
- b. Cotton threads were chosen as materials to tie the knots and holders.
- c. Fish net with fine holes were used to cover the whole basket used as canister for cover and protection (Figure 3). It helped in filtering some fine particles as well.



**Figure 3.** The use of the fish nets to cover the basket

- 2. Finding the cooling compartment might be challenging. The use of blue gel ice packs (inside a thermo container) can be used if considering a short-time period; otherwise, a thermo electric cooler is advised.
- 3. Putting the samplers in the canister

In reality, it takes more time than necessary to arrange all the samplers in a canister (Figure 4). So make sure to assemble and prepare everything before the attachment of all the samplers.



**Figure 4. a** Passive samplers inside the selected basket.



**b.** Each sampler needs to be securely attached

Consider the quickest and least possible time to be used. It is recommended that the canisters to be used be adapted to the passive devices in terms of arrangements and securely placing them. At the same time, make sure that each of the samplers is securely tied. In the figure above, same samplers where place near each other. The metal casing of the POCIS were replaced by an aluminum one (assembling of the whole POCIS was done in the lab) since DGT captures trace metals and aluminum is not part of the analytes to be measured. Screws for the POCIS are made of Teflon.

#### 4. Securing the canisters

As much as possible, make the canister unnoticeable. Attractive and interesting canisters and ropes will just put all your sampling activity at a high risk (e.g. thefts)

#### 5. Canisters being displaced

Make sure that there is proper tying. If having doubts, even if the samplers will be deployed for a long-period, have time to visit and check them from time to time.

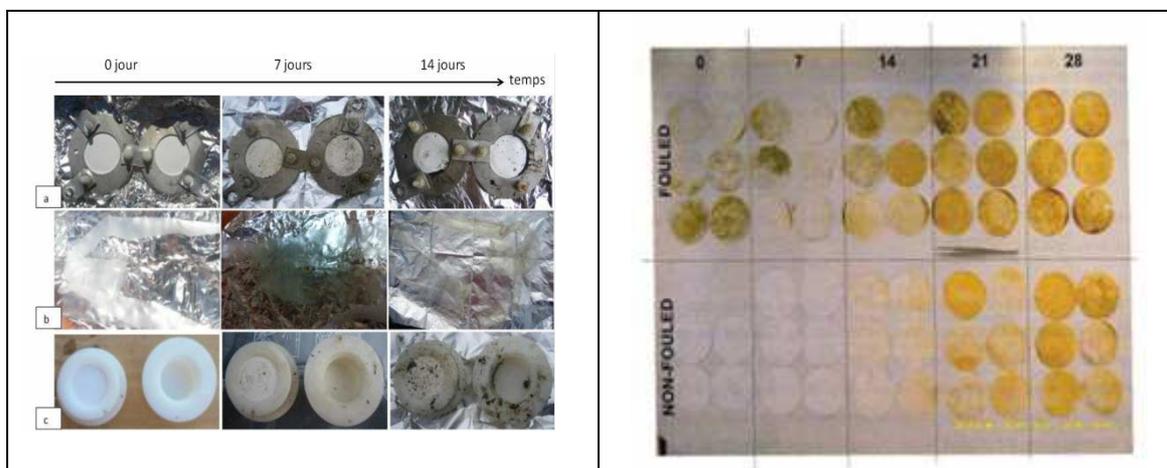
#### 6. (Un)availability of the automatic samplers

As much as possible, one should have their own automatic samplers that can monitor the physical parameters such as pH, conductivity, etc.

#### 7. Avoid heavy water flow so as not to encounter a lot of problems after.

### 3. Retrieval of sampler

1. Vandalism and theft were encountered during the sampling campaign.
2. Biofouling (Figure 5)



**Figure 5 a** Deployed samplers in the French sites (0h, 7days, 14 days)

**b.** An example of bio-fouling (Harman 2009)

- a. The canister placed at the collector is mostly likely to be prone for biofouling. The use of fish nets was helpful in sieving the unwanted macrofouling at the surface of the passive devices.
  - b. The use of the performance reference compounds (PRCs) bare recommended for POCIS and other passive samplers for organic compounds.
3. To maintain the temperature, again cooling compartment should be provided.

### 4. Laboratory

#### Extraction

Sometimes DGT gels can run dry even if temperature was meticulously kept. The use of de-ionized (DI) water might be of help then. Specific materials are necessary to comply for extraction depending on the molecules to be extracted (e.g. use materials such as vials made of Teflon for DGT extraction).

## Analysis

Contamination within the laboratory or in using the machine, etc. is highly possible in doing lab analysis. Make sure to identify the sources before doing the analysis. Provide laboratory blanks as well.

## 5. Data treatment and verification

Outliers can be encountered in terms of concentration/value. Results should be validated before applying any statistical treatment. In case of contamination, trace the sources using the field and laboratory blanks or the machine. Also you can check double check the results of the duplicate or the triplicate

## 6. Interpretation

In interpreting the results, it is important to know the characteristics of the site (physical, environmental, etc.). This will help a lot in understanding the value of the results generated and how the objective can be answered. Figure 6 best describes the importance of the site reconnaissance for the objective and results that can serve as complementary information for the analysis.

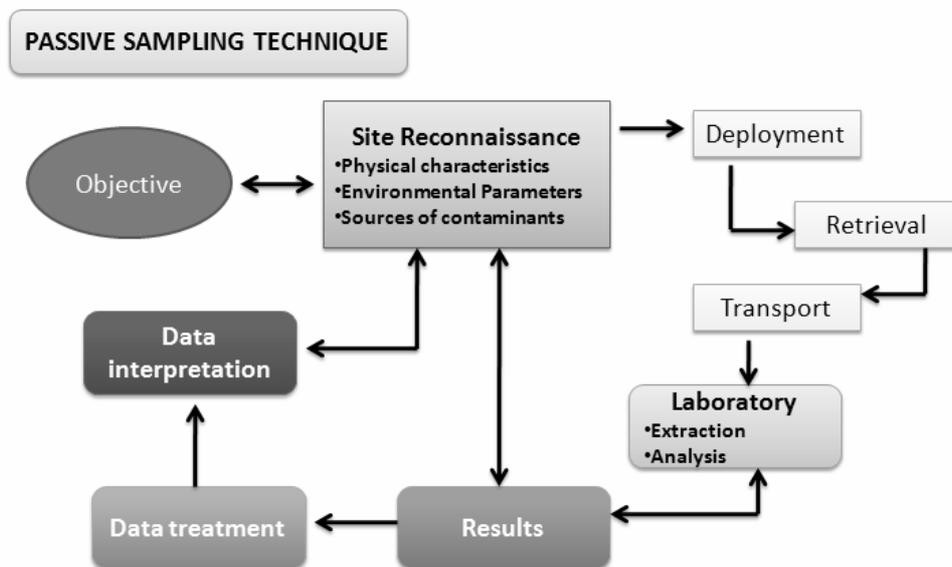


Figure 6. Schematic diagram on the operation and use of the passive sampling technique

### APPENDIX 3. Total trace metals measured with limits of detection and method used

<b>Element</b>	<b>LOD (µg/L)</b>	<b>Reference (Method)</b>
<b>Fe (Total)</b>	10.0	NF EN ISO 11885
<b>Mn (Total)</b>	10.0	NF EN ISO 11885
<b>As</b>	1.0	NF EN ISO 17294-2
<b>Ag</b>	5.0	NF EN ISO 17294-2
<b>Sb</b>	1.0	NF EN ISO 17294-2
<b>Cd</b>	0.5	NF EN ISO 17294-2
<b>Cr (Total)</b>	5.0	NF EN ISO 17294-2
<b>Co</b>	0.5	NF EN ISO 17294-2
<b>Cu</b>	10.0	NF EN ISO 11885
<b>Sn</b>	5.0	NF EN ISO 17294-2
<b>Mo</b>	0.5	NF EN ISO 17294-2
<b>Ni</b>	2.0	NF EN ISO 17294-2
<b>Pb</b>	1.0	NF EN ISO 17294-2
<b>U</b>	0.5	NF EN ISO 17294-2
<b>Ti</b>	10.0	NF EN ISO 11885
<b>Zn</b>	10.0	NF EN ISO 11885
<b>Rh</b>	0.05	NF EN ISO 17294-2
<b>Pt</b>	0.05	NF EN ISO 17294-2
<b>Zr</b>	5.0	NF EN ISO 17294-2
<b>Sr</b>	10.0	NF EN ISO 11885

## APPENDIX 4. Organics (total fraction) measured with limits of detection and method used

Substance	LOD ( $\mu\text{g/L}$ )	Internal Method
Xylène musk	0.01	Méthode interne
<b>ALKYLPHENOLS</b>		
Nonyphénols	0.03	PS n° 215 - GC/MS/MS
4-n-Nonyphénol	0.03	PS n° 215 - GC/MS/MS
4-n-Octylphénol	0.03	PS n° 215 - GC/MS/MS
Octylphénol - 4ter	0.03	PS n° 215 - GC/MS/MS
<b>ANILINES</b>		
2-Chloroaniline	0.03	PS n° 215 - GC/MS/MS
3 + 4 - Chloroaniline	0.12	PS n° 215 - GC/MS/MS
2,4-Dichloroaniline	0.03	PS n° 215 - GC/MS/MS
Diéthylaniline	0.03	PS n° 215 - GC/MS/MS
<b>CHLOROBENZENES</b>		
Pentachlorobenzène	0.01	PS n° 215 - GC/MS/MS
1,2,3,4-Tétrachlorobenzène	0.03	PS n° 215 - GC/MS/MS
1,2,3,5 + 1,2,4,5-Tétrachlorobenzène	0.06	PS n° 215 - GC/MS/MS
1,2,3-Trichlorobenzène	0.03	PS n° 215 - GC/MS/MS
1,2,4-Trichlorobenzène	0.04	PS n° 215 - GC/MS/MS
1,3,5-Trichlorobenzène	0.03	PS n° 215 - GC/MS/MS
Hexachlorobenzène	0.01	PS n° 215 - GC/MS/MS
<b>CHLORONITROBENZENES</b>		
1-Chloro-3-nitrobenzène	0.03	PS n° 215 - GC/MS/MS
2,5-Dichloronitrobenzène	0.03	PS n° 215 - GC/MS/MS
3,4-Dichloronitrobenzène	0.03	PS n° 215 - GC/MS/MS
2,3-Dichloronitrobenzène	0.03	PS n° 215 - GC/MS/MS
<b>COMP. ORG. VOLATILS ET SEMI-VOLATILS</b>		
Biphényle	0.01	PS n° 215 - GC/MS/MS
<b>DIVERS MICROPOLLUANTS ORGANIQUES</b>		
Hexachlorobutadiène	0.03	PS n° 215 - GC/MS/MS
<b>Hydrocarbures Polycycliques Aromatiques</b>		
Acénaphène	0.01	PS n° 215 - GC/MS/MS
Acénaphthylène	0.01	PS n° 215 - GC/MS/MS
Anthracène	0.01	PS n° 215 - GC/MS/MS
Benzo(a)anthracène	0.01	PS n° 215 - GC/MS/MS
Benzo(a)pyrène	0.005	PS n° 215 - GC/MS/MS
Benzo(b)fluoranthène ~	0.005	PS n° 215 - GC/MS/MS
Benzo(g,h,i)pérylène ~	0.005	PS n° 215 - GC/MS/MS
Benzo(k)fluoranthène ~	0.005	PS n° 215 - GC/MS/MS
Chrysène	0.01	PS n° 215 - GC/MS/MS
Dibenzo(a,h)anthracène	0.01	PS n° 215 - GC/MS/MS
Fluoranthène	0.01	PS n° 215 - GC/MS/MS
Fluorène	0.01	PS n° 215 - GC/MS/MS
Indéno(1,2,3-c,d)pyrène ~	0.01	PS n° 215 - GC/MS/MS
Méthyl(2)fluoranthène	0.01	PS n° 215 - GC/MS/MS
Méthyl(2)naphtalène	0.01	PS n° 215 - GC/MS/MS
Naphtalène	0.02	PS n° 215 - GC/MS/MS
Pérylène	0.01	PS n° 215 - GC/MS/MS
Phénanthrène	0.01	PS n° 215 - GC/MS/MS
Pyrène	0.01	PS n° 215 - GC/MS/MS
<b>METABOLITES DES TRIAZINES</b>		
Atrazine déisopropyl	0.02	PS/13/14/11 - LC/MS/MS

Atrazine deséthyl	0.02	PS/13/14/11 - LC/MS/MS
Atrazine-2-hydroxy	0.06	PS/13/14/11 - LC/MS/MS
Terbutylazine deséthyl	0.02	PS/13/14/11 - LC/MS/MS
<b>PESTICIDES AMIDES</b>		
Diméthénamide	0.02	PS/13/14/11 - LC/MS/MS
Isoxaben	0.02	PS/13/14/11 - LC/MS/MS
Métolachlore	0.02	PS/13/14/11 - LC/MS/MS
Napropamide	0.02	PS/13/14/11 - LC/MS/MS
Propachlore	0.02	PS/13/14/11 - LC/MS/MS
Tébutam	0.02	PS/13/14/11 - LC/MS/MS
Oryzalin	0.02	PS/13/14/11 - LC/MS/MS
Alachlore	0.01	PS n° 215 - GC/MS/MS
Propyzamide	0.01	PS n° 215 - GC/MS/MS
<b>PESTICIDES ARYLOXYACIDES</b>		
Fluazifop butyl	0.02	PS/13/14/11 - LC/MS/MS
2,4-D (sous forme de sels)	0.02	PS/13/14/11 - LC/MS/MS
2,4-MCPA (sous forme de sels)	0.02	PS/13/14/11 - LC/MS/MS
2,4-MCPB (sous forme de sels)	0.02	PS/13/14/11 - LC/MS/MS
2,4,5-T (sous forme de sels)	0.02	PS/13/14/11 - LC/MS/MS
Dichloroprop (sous forme de sels)	0.02	PS/13/14/11 - LC/MS/MS
Dichloroprop-P (sous forme de sel de DMA)	0.02	PS/13/14/11 - LC/MS/MS
Mécoprop (sous forme de sels)	0.02	PS/13/14/11 - LC/MS/MS
Triclopyr (sous forme de sels)	0.02	PS/13/14/11 - LC/MS/MS
<b>PESTICIDES CARBAMATES</b>		
Carbaryl	0.04	PS/13/14/11 - LC/MS/MS
Carbendazime	0.02	PS/13/14/11 - LC/MS/MS
Fénoxycarbe	0.02	PS/13/14/11 - LC/MS/MS
Pyrimicarbe	0.02	PS/13/14/11 - LC/MS/MS
Prosulfocarbe	0.02	PS/13/14/11 - LC/MS/MS
Triazamate	0.02	PS/13/14/11 - LC/MS/MS
Aldicarb	0.06	PS/13/14/11 - LC/MS/MS
Carbofuran	0.01	PS n° 215 - GC/MS/MS
Chlorpropham	0.01	PS n° 215 - GC/MS/MS
Propham	0.01	PS n° 215 - GC/MS/MS
<b>PESTICIDES DIVERS</b>		
Chloridazon	0.02	PS/13/14/11 - LC/MS/MS
Cloquintocet-1-méthylhexyl ester	0.02	PS/13/14/11 - LC/MS/MS
Dichlormid	0.02	PS/13/14/11 - LC/MS/MS
Diflufénicanil	0.02	PS/13/14/11 - LC/MS/MS
Diméthomorphe	0.02	PS/13/14/11 - LC/MS/MS
Fénoxaprop-éthyl	0.02	PS/13/14/11 - LC/MS/MS
Fenpropidine	0.02	PS/13/14/11 - LC/MS/MS
Fenpropimorphe	0.02	PS/13/14/11 - LC/MS/MS
Flurtamone	0.02	PS/13/14/11 - LC/MS/MS
Imidaclopride	0.02	PS/13/14/11 - LC/MS/MS
Krésoxym-méthyl	0.02	PS/13/14/11 - LC/MS/MS
Métalaxyl	0.04	PS/13/14/11 - LC/MS/MS
Métazachlore	0.02	PS/13/14/11 - LC/MS/MS
Norflurazon	0.04	PS/13/14/11 - LC/MS/MS
Oxadixyl	0.02	PS/13/14/11 - LC/MS/MS
Prochloraze	0.04	PS/13/14/11 - LC/MS/MS
Phoxim	0.02	PS/13/14/11 - LC/MS/MS
Méthomyl	0.02	PS/13/14/11 - LC/MS/MS
Prétilachlore	0.02	PS/13/14/11 - LC/MS/MS
Isoxaflutole	0.02	PS/13/14/11 - LC/MS/MS
Metsulfuron méthyl	0.02	PS/13/14/11 - LC/MS/MS
Bromacil (sous forme de sels)	0.02	PS/13/14/11 - LC/MS/MS

Fludioxonil (sous forme de sels)	0.02	PS/13/14/11 - LC/MS/MS
Fluroxypyr (sous forme de sels)	0.02	PS/13/14/11 - LC/MS/MS
Aclonifen	0.03	PS n° 215 - GC/MS/MS
Benoxacor	0.01	PS n° 215 - GC/MS/MS
Bromoxynil octanoate	0.03	PS n° 215 - GC/MS/MS
Butralin	0.01	PS n° 215 - GC/MS/MS
Clomazone	0.01	PS n° 215 - GC/MS/MS
Cyprodinil	0.03	PS n° 215 - GC/MS/MS
Dicofol	0.01	PS n° 215 - GC/MS/MS
Diméthénamid-P	0.01	PS n° 215 - GC/MS/MS
Ethofumesate	0.01	PS n° 215 - GC/MS/MS
Procymidone	0.01	PS n° 215 - GC/MS/MS
Quinoxifène	0.01	PS n° 215 - GC/MS/MS
Trifuraline	0.01	PS n° 215 - GC/MS/MS
Anthraquinone	0.01	PS n° 215 - GC/MS/MS
Crimidine	0.03	PS n° 215 - GC/MS/MS
<b>PESTICIDES NITROPHENOLS ET ALCOOLS</b>		
Bromoxynil (sous forme de sels)	0.02	PS/13/14/11 - LC/MS/MS
Ioxynil (sous forme de sels)	0.02	PS/13/14/11 - LC/MS/MS
Ioxynil octanoate	0.01	PS n° 215 - GC/MS/MS
<b>PESTICIDES ORGANOCHLORES</b>		
Dimétachlore	0.02	PS/13/14/11 - LC/MS/MS
Acétochlore	0.01	PS n° 215 - GC/MS/MS
Aldrine	0.01	PS n° 215 - GC/MS/MS
Chlordane cis	0.01	PS n° 215 - GC/MS/MS
Chlordane trans	0.01	PS n° 215 - GC/MS/MS
2,4' - DDD	0.01	PS n° 215 - GC/MS/MS
4,4' - DDD	0.01	PS n° 215 - GC/MS/MS
2,4' - DDE	0.01	PS n° 215 - GC/MS/MS
4,4' - DDE	0.01	PS n° 215 - GC/MS/MS
2,4' - DDT	0.01	PS n° 215 - GC/MS/MS
4,4' - DDT	0.01	PS n° 215 - GC/MS/MS
Dieldrine	0.01	PS n° 215 - GC/MS/MS
Endosulfan alpha	0.01	PS n° 215 - GC/MS/MS
Endosulfan beta	0.01	PS n° 215 - GC/MS/MS
Endrine	0.01	PS n° 215 - GC/MS/MS
Fluorochloridone	0.01	PS n° 215 - GC/MS/MS
HCH alpha	0.01	PS n° 215 - GC/MS/MS
HCH bêta	0.01	PS n° 215 - GC/MS/MS
HCH delta	0.01	PS n° 215 - GC/MS/MS
HCH epsilon	0.01	PS n° 215 - GC/MS/MS
HCH gamma (lindane)	0.005	PS n° 215 - GC/MS/MS
Heptachlore	0.01	PS n° 215 - GC/MS/MS
Isodrine	0.01	PS n° 215 - GC/MS/MS
Oxadiazon	0.01	PS n° 215 - GC/MS/MS
Heptachlore époxide	0.01	PS n° 215 - GC/MS/MS
<b>PESTICIDES ORGANOPHOSPHORES</b>		
Oxydéméton-méthyl	0.04	PS/13/14/11 - LC/MS/MS
Vamidotion	0.02	PS/13/14/11 - LC/MS/MS
Bromophos éthyl	0.01	PS n° 215 - GC/MS/MS
Bromophos méthyl	0.01	PS n° 215 - GC/MS/MS
Carbophénotion	0.01	PS n° 215 - GC/MS/MS
Chlorfenvinphos	0.01	PS n° 215 - GC/MS/MS
Chlormephos	0.01	PS n° 215 - GC/MS/MS
Chlorpyriphos éthyl	0.01	PS n° 215 - GC/MS/MS
Chlorpyriphos méthyl	0.01	PS n° 215 - GC/MS/MS
Diazinon	0.01	PS n° 215 - GC/MS/MS
Dichlorvos	0.03	PS n° 215 - GC/MS/MS

Fenitrothion	0.01	PS n° 215 - GC/MS/MS
Fenthion	0.01	PS n° 215 - GC/MS/MS
Malathion	0.01	PS n° 215 - GC/MS/MS
Parathion éthyl	0.03	PS n° 215 - GC/MS/MS
Parathion méthyl	0.01	PS n° 215 - GC/MS/MS
Phosalone	0.01	PS n° 215 - GC/MS/MS
Terbufos	0.01	PS n° 215 - GC/MS/MS
<b>PESTICIDES PYRETHRINOIDES</b>		
Fenpropathrine	0.01	PS n° 215 - GC/MS/MS
Lambda cyhalotrine	0.01	PS n° 215 - GC/MS/MS
<b>PESTICIDES STROBILURINES</b>		
Azoxystrobine	0.02	PS/13/14/11 - LC/MS/MS
Picoxystrobine	0.02	PS/13/14/11 - LC/MS/MS
Pyraclostrobin	0.02	PS/13/14/11 - LC/MS/MS
Trifloxystrobine	0.02	PS/13/14/11 - LC/MS/MS
<b>PESTICIDES SULFONYLUREES</b>		
Nicosulfuron	0.02	PS/13/14/11 - LC/MS/MS
<b>PESTICIDES TRIAZINES</b>		
Amétryne	0.02	PS/13/14/11 - LC/MS/MS
Atrazine	0.02	PS/13/14/11 - LC/MS/MS
Cyanazine	0.02	PS/13/14/11 - LC/MS/MS
Hexazinone	0.02	PS/13/14/11 - LC/MS/MS
Hydroxyterbuthylazine	0.02	PS/13/14/11 - LC/MS/MS
Métamitron	0.02	PS/13/14/11 - LC/MS/MS
Métribuzine	0.04	PS/13/14/11 - LC/MS/MS
Prométryne	0.02	PS/13/14/11 - LC/MS/MS
Propazine	0.02	PS/13/14/11 - LC/MS/MS
Sebuthylazine	0.02	PS/13/14/11 - LC/MS/MS
Simazine	0.02	PS/13/14/11 - LC/MS/MS
Terbuméon	0.02	PS/13/14/11 - LC/MS/MS
Terbuthylazine	0.02	PS/13/14/11 - LC/MS/MS
Terbutryne	0.02	PS/13/14/11 - LC/MS/MS
Bentazone (sous forme de sels)	0.02	PS/13/14/11 - LC/MS/MS
Pendiméthaline	0.01	PS n° 215 - GC/MS/MS
<b>PESTICIDES TRIAZOLES</b>		
Bitertanol	0.02	PS/13/14/11 - LC/MS/MS
Cyproconazole	0.02	PS/13/14/11 - LC/MS/MS
Difénoconazole	0.02	PS/13/14/11 - LC/MS/MS
Epoxyconazole	0.02	PS/13/14/11 - LC/MS/MS
Fenbuconazole	0.02	PS/13/14/11 - LC/MS/MS
Flusilazole	0.02	PS/13/14/11 - LC/MS/MS
Hexaconazole	0.02	PS/13/14/11 - LC/MS/MS
Metaconazole	0.02	PS/13/14/11 - LC/MS/MS
Penconazole	0.02	PS/13/14/11 - LC/MS/MS
Propiconazole	0.04	PS/13/14/11 - LC/MS/MS
Tébuconazole	0.02	PS/13/14/11 - LC/MS/MS
Tétraconazole	0.02	PS/13/14/11 - LC/MS/MS
<b>PESTICIDES UREES SUBSTITUEES</b>		
Chloroxuron	0.02	PS/13/14/11 - LC/MS/MS
Chlortoluron	0.02	PS/13/14/11 - LC/MS/MS
Diméfuron	0.02	PS/13/14/11 - LC/MS/MS
Diuron	0.02	PS/13/14/11 - LC/MS/MS
Ethidimuron	0.02	PS/13/14/11 - LC/MS/MS
Fénuron	0.02	PS/13/14/11 - LC/MS/MS
Fluoméfuron	0.02	PS/13/14/11 - LC/MS/MS
Iodosulfuron-méthyl sodium	0.02	PS/13/14/11 - LC/MS/MS
Isoproturon	0.02	PS/13/14/11 - LC/MS/MS
Linuron	0.02	PS/13/14/11 - LC/MS/MS

<b>Métabenzthiazuron</b>	0.02	<i>PS/13/14/11 - LC/MS/MS</i>
<b>Métobromuron</b>	0.02	<i>PS/13/14/11 - LC/MS/MS</i>
<b>Métoxuron</b>	0.02	<i>PS/13/14/11 - LC/MS/MS</i>
<b>Monolinuron</b>	0.02	<i>PS/13/14/11 - LC/MS/MS</i>
<b>Monuron</b>	0.02	<i>PS/13/14/11 - LC/MS/MS</i>
<b>Mésosulfuron-méthyl</b>	0.02	<i>PS/13/14/11 - LC/MS/MS</i>
<b>Thifensulfuron méthyl</b>	0.02	<i>PS/13/14/11 - LC/MS/MS</i>
<b>Néburon</b>	0.06	<i>PS/13/14/11 - LC/MS/MS</i>
<b><i>Plastifiants</i></b>		
<b>PCB 101</b>	0.01	<i>PS n° 215 - GC/MS/MS</i>
<b>PCB 118</b>	0.01	<i>PS n° 215 - GC/MS/MS</i>
<b>PCB 138</b>	0.01	<i>PS n° 215 - GC/MS/MS</i>
<b>PCB 153</b>	0.01	<i>PS n° 215 - GC/MS/MS</i>
<b>PCB 180</b>	0.01	<i>PS n° 215 - GC/MS/MS</i>
<b>PCB 194</b>	0.01	<i>PS n° 215 - GC/MS/MS</i>
<b>PCB 28</b>	0.01	<i>PS n° 215 - GC/MS/MS</i>
<b>PCB 52</b>	0.01	<i>PS n° 215 - GC/MS/MS</i>
<b><i>PESTICIDES PYRETHRINOIDES</i></b>		
<b>Beta cyfluthrine</b>	0.02	<i>PS n° 215 - GC/MS/MS</i>
<b>Bifenthrine</b>	0.01	<i>PS n° 215 - GC/MS/MS</i>
<b>Deltaméthrine</b>	0.03	<i>PS n° 215 - GC/MS/MS</i>
<b>Perméthrine</b>	0.01	<i>PS n° 215 - GC/MS/MS</i>
<b>Phénothrine</b>	0.01	<i>PS n° 215 - GC/MS/MS</i>

## **Suivi par capteurs passifs des polluants émergents dans les eaux de surface en contexte urbain**

### **RÉSUMÉ :**

L'étude a pour objectif de déterminer la qualité des eaux de surface sous différentes conditions climatiques et pratiques de gestion des eaux de surface. Trois sites ont été choisis pour: (1) la rivière Jalle de Blanquefort, (2) le lac de Bordeaux, France et (3) la rivière Pasig aux Philippines. Les sites français présentent des collecteurs d'eau qui se déversent directement dans les eaux de surface. La rivière Pasig sert de collecteur d'eaux usées en l'absence de stations de traitement des eaux usées et collectées. Au cours des campagnes de mesure, il a été possible de suivre l'impact de la variabilité climatique (pluviométrie) et d'évènements aléatoires sur la qualité chimiques (éléments traces métalliques et polluants organiques) des eaux ; en combinant échantillonnage classique et par capteurs passifs. Les propriétés physico-chimiques de l'eau ainsi que les caractéristiques des particules et l'utilisation d'analyses statistiques permettent de préciser le comportement des molécules détectées et de décrire l'évolution hydrochimique des eaux de surface urbaines et estuariennes vis-à-vis d'aléas climatiques contrastés.

### **ABSTRACT:**

The study aimed to assess the water quality of the surface water in differing climate conditions and management practices. Three interesting sites were chosen, (1) Jalle River and (2) Bordeaux Lac both in France and the (3) Pasig River in the Philippines. The French sites have rainfall and run-off collectors that directly discharge water to the water bodies. Pasig River, on the other hand, becomes a waste collector as waste management and treatment plant are lacking. Trace metals and organics (pesticides, herbicides, pharmaceuticals and drugs) were measured. Conventional and passive sampling approaches were employed. The mass fluxes were obtained in order to calculate the pollution transport. Physico-chemical properties and the particle characteristics, integrating statistical analyses, facilitated in explaining the behavior of the measured molecules and describing the hydrological system in relation to climate variability.

**Keywords :** passive sampling techniques, hydrogeochemistry, trace elements, organic pollutants, run-off, urban collectors, urban hydrology, France, Philippines