Étude de la contamination et de l'écotoxicité associée des sédiments de surface en zone littorale lacustre

Nathalie Lécrivain

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Étude de la contamination et de l'écotoxicité associée des sédiments de surface en zone littorale lacustre

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Proverbe chinois

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Résumé

La zone littorale, de grande importance pour le fonctionnement écologique du lac, est souvent la première zone réceptrice de la contamination provenant du bassin versant. Cette pollution est majoritairement piégée dans les sédiments de surface. Pour autant, les conditions environnementales variables qui règnent en zone littorale sont susceptibles de favoriser la biodisponibilité des contaminants par le jeu des réactions physico-chimiques et biologiques. Cette thèse s'appuie sur l'étude de deux grands lacs péri-alpins, le Lac du Bourget et le Lac d'Annecy, pour mieux comprendre le comportement des polluants sédimentaires (ETM, HAP et PCB) en zone littorale lacustre. Nos travaux visent notamment (1) à **caractériser la contamination littorale et l'influence des sources locales dans cette contamination**, (2) à **évaluer l'écotoxicité des sédiments littoraux et les changements de mobilité et de biodisponibilité des polluants sédimentaires sous l'influence de changements abiotiques de la zone littorale tels que ceux induits par le marnage lacustre**. Nos résultats montrent que la contamination des sédiments et organismes autochtones présente une hétérogénéité spatiale significative sur le littoral des deux lacs, tant en intensité qu'en composition (i.e. profil de contamination). L'implication de sources locales (e.g. eaux pluviales drainées sur le bassin-versant) dans cette hétérogénéité spatiale a été mise en évidence. L'écotoxicité des sédiments de la zone littorale, évaluée via la réponse de biomarqueurs enzymatiques (AChE, GST), physiologiques (e.g. taux d'ingestion chez *D. magna*) et des traits de vie (e.g. taux de croissance, reproduction et survie) présente également une hétérogénéité spatiale significative. La biodisponibilité des ETM sédimentaires a été plus spécifiquement étudiée aux interfaces sédiment-eau-biote. Elle varie selon l'élément, le biote exposé (benthique ou pélagique) et sous l'effet du marnage. L'assèchement et remise en eau du sédiment littoral s'accompagnent d'une réduction de la fraction biodisponible des ETM. L'abaissement de la hauteur d'eau, en revanche, entraîne une accentuation de la remise en suspension de particules sédimentaires susceptibles d'exercer un risque écotoxicologique sur le biote littoral. Nos résultats soulignent la complexité de la contamination littorale et de son transfert dans les grands lacs péri-alpins et encouragent les approches écotoxicologiques dans l'évaluation de l'état écologique.

Mots clés : Zone littorale lacustre, micropolluant, sédiment, biodisponibilité, marnage.

Abstract

The littoral zone of lakes is of great ecological importance and yet receives a large array of contaminants from the watershed. This pollution is mainly trapped by the surface sediment, but its bioavailability may be allowed by physico-chemical and biological reactions in this zone of high environmental fluctuations. This work aims at improving knowledge about the behavior of sediment-borne contaminants (trace metals, PAHs and PCBs) in the lake littoral zone by using two large perialpine lakes; Lake Bourget and Lake Annecy. More precisely, our goals were to **(1) characterize the littoral contamination and the influence of local sources in this contamination, (2) assess the ecotoxicity of the sediment-borne contamination and the main changes in its mobility and bioavailability under abiotic changes in the littoral zone, such as those related to water-level fluctuations in lakes.** The contamination of the sediments and native organisms exhibited a significant spatial heterogeneity along the lake littoral, in both intensity and profile's composition. The involvement of local sources of contamination (e.g. stormwater runoff) as drivers of this spatial heterogeneity has been highlighted. The ecotoxicity of littoral sediments was assessed through the responses of enzymatic biomarkers (AChE and GST), physiological traits (e.g. ingestion rates in *D. magna*) and life-history traits (e.g. growth, reproduction and survival rates). Our results also underscored a significant spatial heterogeneity of the littoral sediment ecotoxicity. A greater focus on the bioavailability of trace metals at the sediment-water-biota interfaces showed that bioavailability depends on the metal, the exposed biota (benthic vs pelagic) and fluctuate under water-level fluctuations. Drought and re-immersion of surface sediments were followed with a reduction of the bioavailable fractions of the trace metals. However, decreases in the water-level led to increase suspended sediments in the water column, which may exert an ecotoxicological risk for the littoral biota. Our results underline how complex the littoral contamination and bioavailability are and promote ecotoxicological approaches in the assessment of the ecological status of large lakes.

Keywords: Lake Littoral zone, micropollutant, sediment, bioavailability, water-level fluctuations.

Valorisation des travaux

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- Lécrivain, N., Aurenche, V., Cottin, N., Frossard, V. & Clément, B. (2018). Multi-contamination (heavy metals, polychlorinated biphenyls and polycyclic aromatic hydrocarbons) of littoral sediments and the associated ecological risk assessment in a large lake in France (Lake Bourget). Science of The Total Environment, 619, 854-865.

- Lécrivain, N., Frossard, V. & Clément B. (*sous presse*). Contribution of trace metallic elements to weakly contaminated lacustrine sediments: effects on benthic and pelagic organisms through multi-species laboratory bioassays. Ectotoxicology, 10.1007/s10646-018-2008-3.

- Lécrivain, N., Frossard, V., Naffrechoux, E. & Clément, B. (*Soumis à Polycyclic Aromatic Compounds*). Dissecting organic pollutants (OPs) signatures in littoral sediments to assess the influence of a local urban source at the whole lake scale.

- Lécrivain, N., Frossard, V. & Clément B. (*En révision à Environmental Science and Pollution Research*). Simulating lake water level fluctuations in the laboratory: what is the fate of sediment-borne trace metals?

- Lécrivain, N., Duparc, A., Clément, B., Naffrechoux, E. & Frossard, V. (*en préparation pour soumission à Chemosphere*). Tracking sources and transfer of contamination according to pollutants variety at the sediment-biota interface using a clam as bioindicator in peri-alpine lakes.

- Lécrivain, N., Clément, B., Seigle-Ferrand, J., Bouffard, D. & Frossard, V. (*en préparation pour soumission à Hydrobiologia*). Effects of water-level fluctuations on the littoral aquatic environment and metallic contamination of a large peri-Alpine lake (Lake Bourget).

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- Lécrivain, N., Frossard, V. & Clément, B. Contribution des éléments traces metalliques (ETM) à la toxicité de sédiments littoraux lacustres testés en microcosmes multi-espèces. *Colloque 2018 de la Société d'Ecotoxicology Fondamentale et Appliquée (SEFA)*, Montpellier, France, 27-28 juin 2018.

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- Frossard, V., Lécrivain, N., Duparc A., Clément B. & Naffrechoux E. Contamination littorale du lac d'Annecy par les hydrocarbures aromatiques polycycliques (HAP) et les éléments traces métalliques (ETM) : Origines, risques et transfert biologique. ALP-FDAAPPMA74. 39p.

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Liste des abréviations

Ace	Acénaphtène
AChE	Acétylcholine estérase
Acy	Acénaphtylène
Ant	Anthracène
As	Arsenic
BaA	Benzo(a)anthracène
BaP	Benzo(a)pyrène
BbF	Benzo(b)fluoranthène
BghiP	Benzo(g,h,i)pérylène
BkF	Benzo(k)fluoranthène
Cd	Cadmium
Chr	Chrysène
Cr	Chrome
Cu	Cuivre
DbahA	Dibenzo(a,h)anthracène
DCE	Directive Cadre sur l'Eau
ETM	Elément Trace Métallique
Fla	Fluoranthène
Flu	Fluorène
GST	Glutathion S-transférase
HAP	Hydrocarbure Aromatique Polycyclique
Ip	Indeno(1,2,3,c,d)pyrène
MES	Matières En Suspension
MO	Matière Organique
MS	Matière Sèche
Nap	Naphtalène
Ni	Nickel
NQE	Norme de Qualité Environnementale
PAF	Perte Au Feu
Pb	Plomb
PCB	Polychlorobiphényle
Phe	Phénanthrène
Pyr	Pyrène
Sn	Etain
ZL	Zone Littorale
Zn	Zinc

AAS	Atomic Absorption Spectrophotometry
DM	Dry Mass
ERA	Ecological Risk Assessment
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
Koa	Octanol-Air partioning coefficient
Kow	Octanol-Water partioning coefficient
LOI	Loss on Ignition
NA	Non-Available value
ND	Non-Detectable value
OC	Organic Carbon
OM	Organic Matter
PAH	Polycyclic Aromatic Hydrocarbon
PCA	Principal Components Analysis
PCB	Polychlorinated Biphenyl
PEC	Probable Effect Concentration
PEL	Probable Effect Level
PNEC	Predicted No Effect Concentration
SQG	Sediment Quality Guideline
TEC	Threshold Effect Concentration
TM	Trace metal
TOC	Total Organic Carbon
WLF	Water-Level Fluctuation
WM	Wet mass

Introduction

I. Contexte général

I.1. Les grandes familles de micropolluants

Selon Ramade (1998), « un micropolluant est un polluant présent à faible concentration [de l'ordre du mg L^{-1} ou mg kg^{-1}] dans l'environnement. La plupart des micropolluants appartiennent au groupe des polluants xénobiotiques [substance étrangère à un organisme ou écosystème] caractérisés par des effets toxicologiques importants même s'ils sont à des concentrations très faibles ».

Avec l'industrialisation, la diversité et le nombre de micropolluants extraits des ressources naturelles (e.g. métaux) ou artificiellement produits et rejetés dans l'environnement ont considérablement augmenté à l'échelle mondiale depuis la fin du 19ème siècle. Aujourd'hui, l'ubiquité de certaines familles de micropolluants est à la fois expliquée par leur rôle dans la production de nombreux produits industriels, domestiques, agricoles, par des échanges commerciaux internationaux et des transports non intentionnels par voie atmosphérique, hydrologique et biologique (Bernhardt et al., 2017). C'est notamment le cas des éléments traces métalliques (ETM), hydrocarbures aromatiques polycycliques (HAP) et polychlorobiphényles (PCB). Leur production (e.g. Figure 1.A) et leur utilisation (e.g. Figure 1.B) largement répandues depuis le début du 20ème siècle ont entraîné la contamination des milieux aquatiques à l'échelle planétaire (e.g Figure 1.C). Ils sont aujourd'hui des contaminants à forts enjeux à la fois sanitaires (Adams et al., 2000; Järup, 2003; Kim et al., 2013; Schwarzenbach et al., 2010) et environnementaux (Bjerregaard et al., 2015; Malaj et al., 2014). Ils apparaissent pour la plupart dans la liste des substances prioritaires à analyser dans le cadre de la DCE (Commission Européenne, 2013).

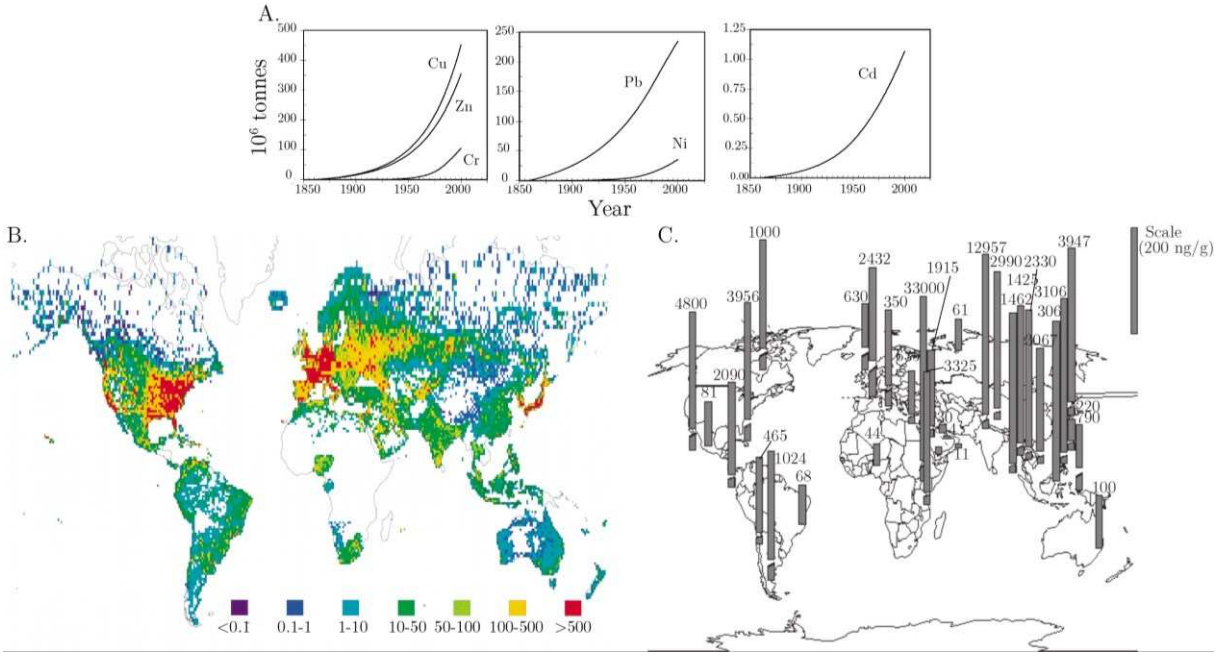

Figure 1. Exemples de grandes tendances temporelles et spatiales de la production, utilisation et émissions dans les milieux aquatiques des micropolluants avec (A) l'évolution temporelle cumulée de la production mondiale estimée en ETM (Cd, Cr, Cu, Ni, Pb, Zn) depuis 1850 à 2002 (modifiée d'après Han et al. (2002)), (B) la répartition mondiale estimée de l'usage mondial historique cumulé des PCB en tonnes à une résolution de 1° longitude x 1° latitude depuis leur création (modifiée d'après Breivik et al. (2002)), et (C) la répartition spatiale des concentrations sédimentaires de surface de la somme de 16 HAP (ng g^{-1}) mesurées en mer, estuaires et rivières principalement (modifié d'après Ramesh et al. (2011)).

Les **ETM**, longtemps appelés métaux lourds, regroupent la plupart des métaux et métalloïdes, présents à l'état dit de « trace » dans l'environnement du point de vue géochimique (fréquemment < 1000 mg kg^{-1}) et du point de vue biologique (fréquemment < 100 mg kg^{-1} matière sèche) (Alloway, 2013). Les ETM sont des micropolluants inorganiques par nature hydrophobes, non biodégradables et donc persistants dans l'environnement. Parmi les ETM, l'arsenic (As), le cadmium (Cd), le chrome (Cr), le cuivre (Cu), le nickel (Ni), le plomb (Pb), l'étain (Sn) et le zinc (Zn) sont classiquement étudiés pour leur occurrence dans l'environnement et plus particulièrement les milieux aquatiques (Bourrier et al., 2010) (Fechner et al., 2011; Lebrun et al., 2015, 2014; Thévenot et al., 2009; Tusseau-Vuillemin et al., 2007).

Les **HAP** sont des micropolluants organiques dont la structure moléculaire consiste en l'agencement d'au moins deux cycles benzéniques (Di Toro et al., 1991). Ils sont ubiquistes, volatiles, hydrophobes et lipophiles, ce qui leur confère une affinité forte pour les particules solides et notamment la matière organique particulaire (Zhou et al., 2004). Ils ont une stabilité chimique forte bien qu'inférieure à celle des ETM, puisqu'ils peuvent être soumis à des dégradations biologiques et physico-chimiques (e.g. hydrolyse, photo-oxydation). Parmi les 130 HAP référencés à ce jour, 16 – Naphtalène (Nap), Acénaphtylène (Acy), Acénaphtène (Ace), Fluorène (Flu),

Phénanthrène (Phe), Anthracène (Ant), Fluoranthène (Fla), Pyrène (Pyr), Benzo(a)anthracène (BaA), Chrysène (Chr), Benzo(b)fluoranthène (BbF), Benzo(k)fluoranthène (BkF), Benzo(a)pyrène (BaP), Benzo(g,h,i)pérylène (BghiP), Dibenzo(a,h)anthracène (DbahA), Indeno(1,2,3,c,d)pyrène (Ip) – sont classés prioritaires par l'agence américaine de protection de l'environnement (US EPA) pour leur abondance dans l'environnement et leur toxicité avérée (Keith, 2015; Pozo et al., 2012).

Les **PCB** sont des micropolluants organiques persistants (POPs) composés de deux noyaux phényles pouvant comporter chacun jusqu'à 5 atomes de chlore en substitution des atomes d'hydrogène. Ils sont volatiles, persistants, lipophiles et hydrophobes. Ces composés peuvent être transportés sur de longues distances par voie atmosphérique. Parmi les 209 congénères, 7 PCB indicateurs référencés par le Bureau des Références de la Communauté Européenne – PCB 28, 52, 101, 118, 138, 153 et 180 – sont couramment étudiés en lien avec leur occurrence dans l'environnement. Ils représentent, en concentration, jusqu'à 43 % de la composition des principaux mélanges commerciaux (i.e. Aroclors) (Dargnat et Fisson, 2010; Wyrzykowska et al., 2006) et jusqu'à 50 % (hors PCB 118) de la totalité des PCB quantifiés dans les matrices biologiques et tissus humains (EFSA, 2005).

I.2. Origines et émissions des micropolluants

Les **ETM** peuvent avoir une origine naturelle lithogénique. Néanmoins, sauf rares exceptions, ces émissions représentent moins de 10 % des émissions totales (Pacyna et al., 2016). Ainsi, les rejets anthropiques sont la plupart du temps responsables de leur présence dans les milieux aquatiques avec des flux annuels mondiaux estimés à $9{,}4.10^3$ t pour le Cd et à 226.10^3 t pour le Zn (Järup, 2003; Pacyna et al., 2016) (Figure 2). Certains ETM sont utilisés dans l'industrie métallurgique dans les alliages avec d'autres métaux comme l'acier, le fer ou le cobalt pour conférer une meilleure résistance mécanique ou lutter contre la corrosion ; c'est le cas du Cd, Cr et Zn. Ils entrent également dans la fabrication des piles et batteries (Cd, Cr, Ni, Pb), peuvent être utilisés comme agents stabilisants (Cd, Pb, Sn), agents blanchissants (As) ou entrer dans la composition de pigments et colorants (Cd, Cr, Cu, Pb, Zn) ou agents détergents (Cr, Zn). Le Cr entre dans la composition de certains ciments alors que le Zn est utilisé dans le caoutchouc. De par leurs propriétés toxiques, ils sont utilisés dans l'industrie pharmaceutique (As, Zn) ou dans certains produits phytosanitaires (Bisson et al., 2006), dans la conservation du bois (As, Cu) ou dans des revêtements antisalissure des coques de bateaux (Cu, Sn) (Hoch, 2001). En 2016, l'INERIS publiait un rapport faisant état de la présence de divers micropolluants en sortie de 760 stations de traitement des eaux usées urbaines entre 2011 et 2013 et relevait les ETM comme la famille de micropolluants la plus quantifiée (INERIS, 2016).

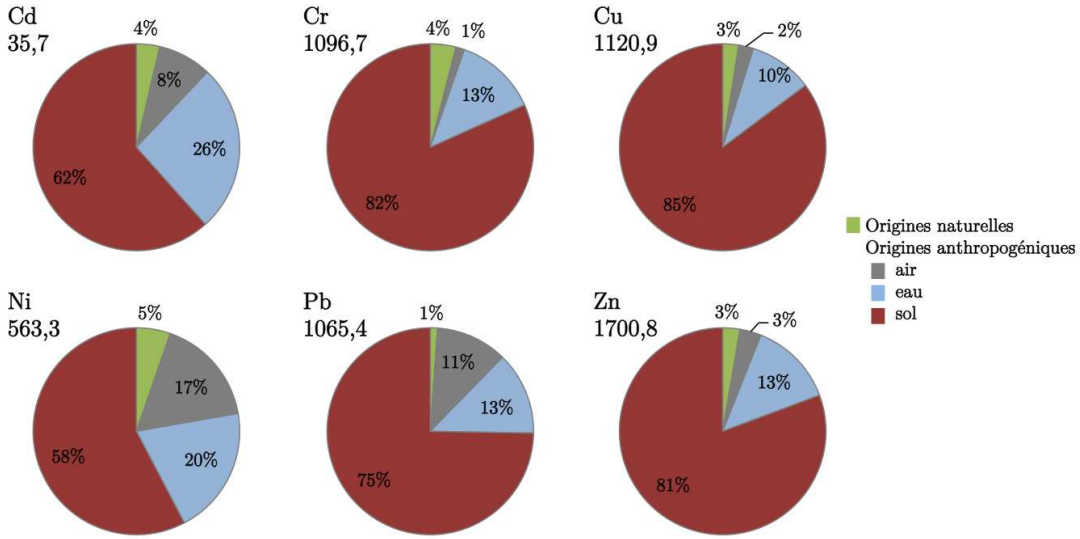

Figure 2. Répartition (%) des émissions mondiales en Cd, Cr, Cu, Ni, Pb et Zn d'origine naturelle et anthropogénique et distribution des émissions anthropogéniques dans les milieux récepteurs air, eau et sol. Les valeurs à côté des diagrammes correspondent aux flux annuels mondiaux (10^3 tonnes an^{-1}) (d'après Pacyna et al. (2016)).

Les **HAP** peuvent être d'origine naturelle, biogénique et diagénétique (Wakeham et al., 1980; Wakeham et Canuel, 2016), synthétisés par des végétaux et bactéries ou formés durant des processus de dégradation de la matière organique. Ils peuvent également être émis lors de feux de forêt (Vergnoux et al., 2011) et éruptions volcaniques (Ilnitsky et al., 1975). Ces émissions sont néanmoins d'un ordre de grandeur inférieur à celles d'origines anthropiques (Lima et al., 2005). Ces dernières peuvent être de nature pyrogénique et véhiculées par voie atmosphérique ; combustion incomplète de produits pétroliers et de bois, processus industriel de transformation de la houille et du charbon. En 2007, ces émissions atmosphériques à l'échelle mondiale étaient de l'ordre de 504 Gg provenant en majorité des secteurs commercial et résidentiel (60,5 %), de la combustion de matière végétale (déforestation, agriculture) (13,6 %) et de la combustion de pétrole liée au transport (12,8 %) (Shen et al., 2013). Les émissions anthropiques peuvent également être d'origine pétrogénique et véhiculées en grande majorité par ruissellement ; fuite et déversement durant le transport, le stockage et l'utilisation de pétrole brut (Abdel-Shafy et Mansour, 2016).

Les **PCB** sont des molécules de synthèse utilisées en mélange pour leurs propriétés physiques : stables et peu réactives. Ils ont été massivement utilisés entre 1930 et 1970 dans la fabrication de transformateurs électriques, condensateurs, fluides caloporteurs et peintures notamment. Même si leur production et utilisation nouvelle sont interdites depuis 1987 en France et 1993 à l'échelle mondiale, leur ubiquité tient à leur grande persistance dans l'environnement et leur propension à être transportés par voie atmosphériques sur de très longues distances, mais également aux échanges commerciaux internationaux actuels de produits anciens et déchets

incluant des PCB (Breivik et al., 2016). En 2015, Li et Wania (2016) estimaient à 87,6 kt la masse en 6 PCB (PCB 28, 52, 118, 153 et 180) répartie dans le monde par le biais d'échanges internationaux de substances techniques, transformateurs, condensateurs et déchets électriques et électroniques. Selon cette même étude, 31,4 tonnes de ces PCB ont directement atteint l'hydrosphère. De fait, les PCB sont encore aujourd'hui dosés dans les sols, sédiments (Desmet et al., 2012) et biotes (Jepson et al., 2016). Les PCB sont particulièrement persistants dans les matrices biologiques du fait de leur lipophilie. En France, plus de 60 départements étaient encore concernés par des interdictions de consommation et de commercialisation (totales ou partielles) de poissons en 2014 suite à la modification le 01/01/2012 du règlement européen 1881/2006 en ce qui concerne les teneurs maximales en dioxines, en PCB de type dioxine et en PCB autres que ceux de type dioxine des denrées alimentaires (Ministère de la Transition Ecologique et Solidaire, 2016).

I.3. Devenir et effets des polluants dans les milieux aquatiques

I.3.1. Voies d'entrée des polluants et mobilité aux interfaces sédiment-eau-biote

Les milieux aquatiques constituent des réceptacles de la contamination en micropolluants provenant des compartiments terrestre et atmosphérique (Schwarzenbach et al., 2010).
Les voies d'entrée dans le milieu aquatique de ces micropolluants peuvent se faire (Figure 3) :

(1) directement par les activités au sein du milieu (e.g. contamination par le Sn des coques de bateau ou de HAP par fuites d'essence).

(2) par voie atmosphérique, par échanges gazeux et retombées particulaires, sèches ou humides, des émanations lors de la combustion de divers produits fossiles (charbon et pétrole notamment) liées aux activités industrielles, domestiques (chauffage) et de transport (Cu, Zn, HAP). Les usines d'incinération d'ordures ménagères participent également pour une large part à l'émission d'ETM, HAP et PCB dans l'atmosphère. Les PCB peuvent être remobilisés dans l'atmosphère à température ambiante, faisant des points fortement contaminés (e.g. décharges) des sources potentielles d'émissions.

(3) via le compartiment terrestre, par ruissellement puis rejets par des buses ou les tributaires. Les eaux de ruissellement sont alors chargées en substances accumulées sur les surfaces de ruissellement. Les contaminations véhiculées par ruissellement peuvent être domestiques (e.g. corrosion des toitures (Zn, Cu)), liées aux véhicules (e.g. corrosion de la carrosserie, abrasion des freins (Cu) et pneumatiques (Zn, Pb), fuites d'essence (HAP)), industrielles (e.g. surfaces imperméables non décontaminées, rejets sans traitement) et agricoles (e.g. intrants (Cu, Cd, As) et par épandages (Zn, Ni) (Tóth et al., 2016)). Des échanges de polluants entre eaux souterraines et eaux de surface peuvent également être facilités dans la zone hyporhéique (Rosenberry et al., 2015).

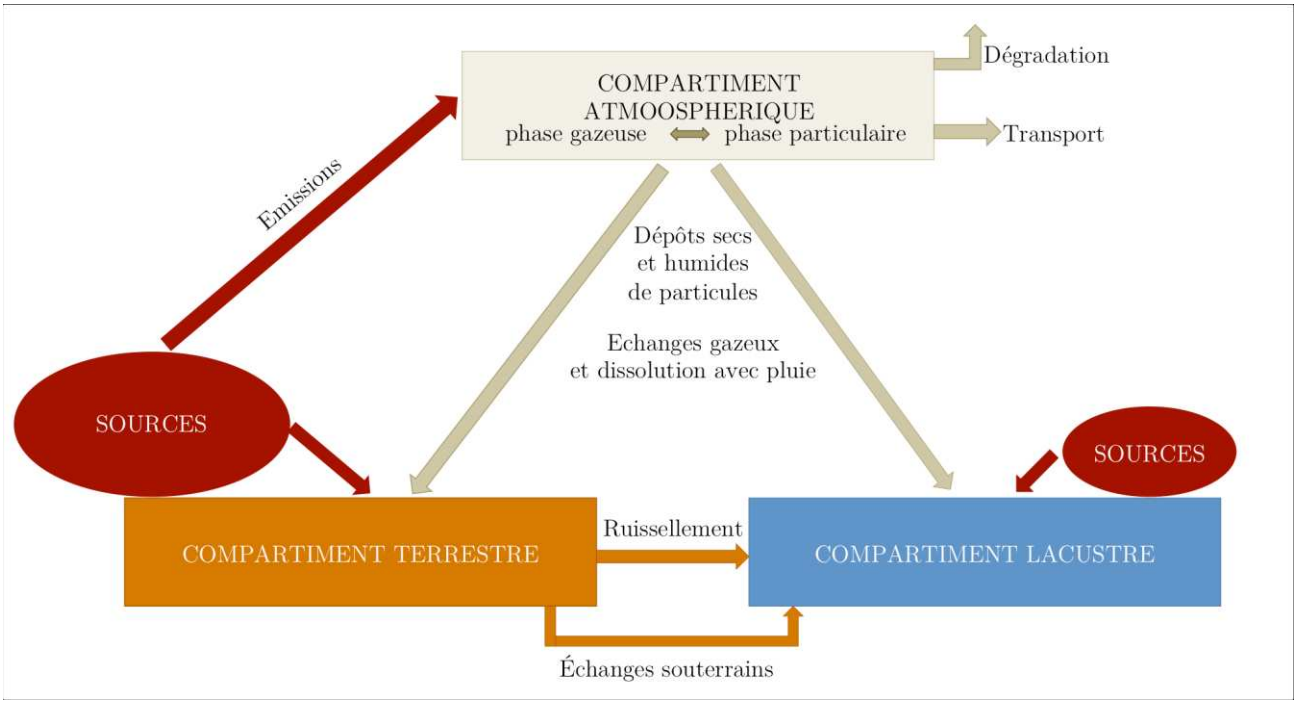

Figure 3. Schématisation des principales voies d'entrée des polluants dans les milieux aquatiques (modifié d'après Prevedouros et al. (2004)). Les chiffres (1) à (3) font référence aux points abordés dans le texte ci-dessus.

Les différences de structure moléculaire entre familles de polluants, mais également au sein-même de ces familles, leur confèrent des propriétés variées de mobilité et liaison avec le compartiment sédimentaire et biologique. Néanmoins, les principaux mécanismes physiques, chimiques et biologiques, communs à l'ensemble des polluants, qui régissent leur mobilité aux interfaces eau-sédiment-biote sont les suivants (Figure 4) :

- réactions de précipitation sous la forme d'hydroxydes et de carbonates. La réaction inverse est la dissolution,
- réactions d'adsorption physique non spécifique et réversible (forces de Van der Waals) ou chimique par la création de liaisons chimiques, le plus souvent sous forme de complexe avec des oxydes hydratés, des minéraux argileux (Curtis et al., 1986) ou la matière organique (Ahangar et al., 2010; Sigg et al., 1992),
- échanges ioniques de l'élément chargé avec un composé solide, majoritairement la matière organique ou les argiles.
- diffusion, absorption (Krauskopf et Bird, 1995) et advection de la fraction dissoute (Boudreau, 1996),
- transport par des particules colloïdales à grande surface spécifique (Lions, 2004; Vignati et al., 2005),
- sédimentation de particules (Bloesch, 1995) et organismes morts ou rejets biologiques dont la décomposition peut permettre une incorporation au biote et sédiment,

- sorption et désorption biologiques aboutissant à la bioconcentration de l'élément (Romera et al., 2007), ingestion aboutissant à la bioaccumulation de l'élément jusqu'à la bioamplification du polluant dans le réseau trophique,
- bioturbation par les organismes endobenthiques permettant un enfouissement des polluants dans les strates inférieures du sédiment ou au contraire une remobilisation dans la colonne d'eau des polluants souvent plus mobiles des couches anoxiques (Meysman et al., 2005).

Ces réactions sont principalement contrôlées par :

- les propriétés intrinsèques aux molécules. La masse moléculaire des HAP est positivement corrélée au coefficient de partage octanol/eau (K_{ow}) et négativement à celui de l'octanol/air (K_{oa}), ce qui conditionne en partie l'affinité des éléments pour la matière organique,
- les propriétés structurales du sédiment telles que la granulométrie des particules, car celle-ci rend compte de la surface spécifique disponible pour les liaisons avec les polluants ainsi que les volumes d'eau interstitielle disponible, la quantité et qualité de la matière organique et la composition en anions/cations susceptibles d'entrer en compétition sur les sites de liaison avec les éléments chargés (Wang et al., 1997),
- les conditions physico-chimiques du milieu telles que le pH, le potentiel d'oxydoréduction (De Jonge et al., 2012), la force ionique (Audry, 2003) ou la température (qui conditionne surtout la productivité biotique),
- les paramètres biotiques du milieu tels que l'abondance microbienne susceptible d'agir sur les paramètres abiotiques évoqués, sur les substances complexantes ou directement sur les polluants.

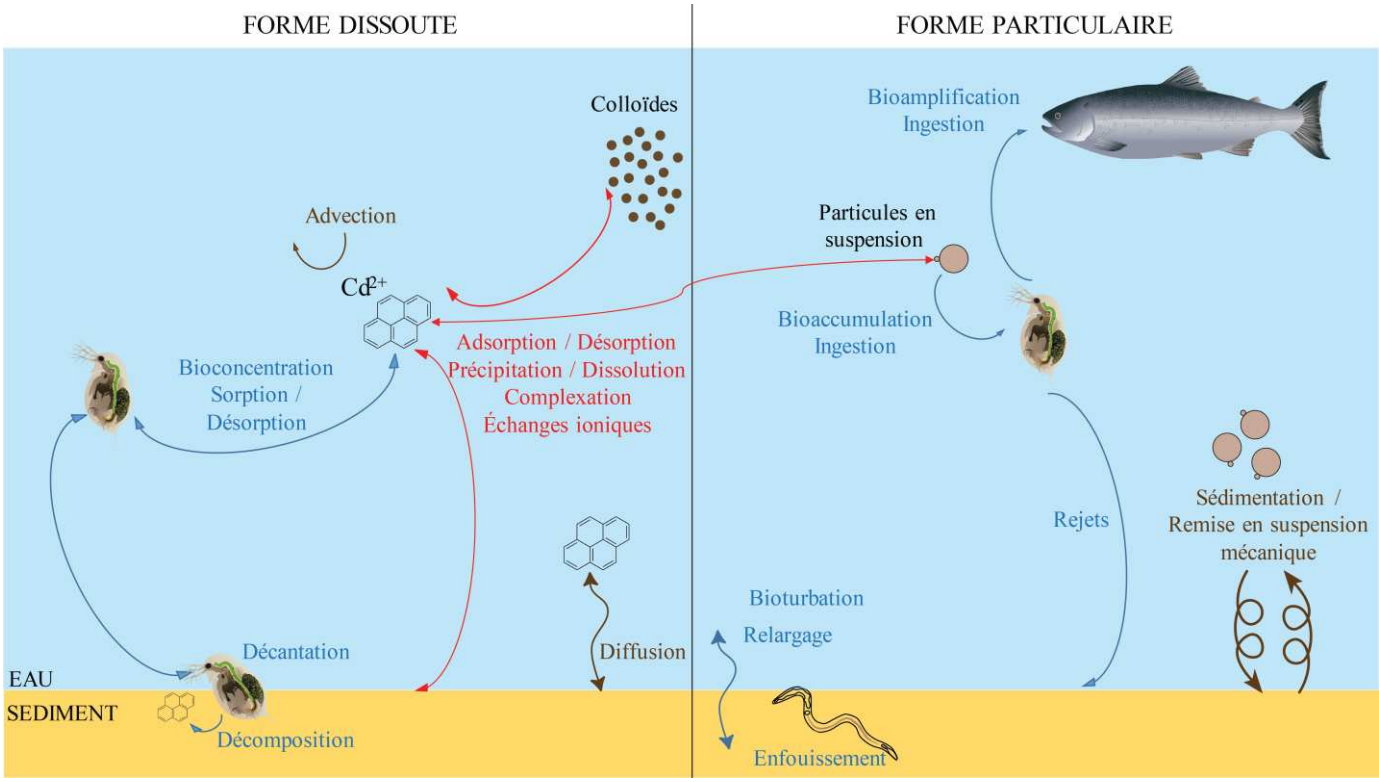

Figure 4. Schématisation des principaux mécanismes physiques (marron), chimiques (rouge) et biologiques (bleu) régissant la mobilité des polluants aux interfaces sédiment-eau-biote (d'après Westrich et Förstner (2007)).

I.3.2. Toxicité des micropolluants dans les milieux aquatiques

Les ETM peuvent s'avérer toxiques, y compris les oligo-éléments Ni, Cu et Zn à des concentrations anormalement élevées pour l'organisme exposé (Järup, 2003). Ils peuvent être à l'origine de dommages subcellulaires sur les membranes et noyaux cellulaires (altération de l'ADN pouvant conduire à de la carcinogénèse ou apoptose (Beyersmann et Hartwig, 2008)), mitochondries, lysosomes, réticulum endoplasmique. Les métaux peuvent également altérer le fonctionnement d'enzymes impliquées dans des mécanismes de détoxication et de réparation cellulaire et être à l'origine de la formation de dérivés réactifs de l'oxygène et de stress oxydatif (Wang et Shi, 2001).

Les HAP et les PCB sont neurotoxiques, immunotoxiques, hépatotoxiques, reprotoxiques et cancérigènes (Baird et al., 2005; Kim et al., 2013). De par leur caractère lipophile, ils peuvent être à l'origine de perturbations du fonctionnement membranaire des cellules (Sikkema et al., 1995; Sverdrup et al., 2002). Ils peuvent être bioconcentrés et, en ce qui concerne les PCB notamment, facilement bioamplifiés dans les réseaux trophiques car difficilement dégradés, éliminés ou biotransformés (Gray, 2002).

Les effets toxiques mesurés à l'échelle individuelle peuvent être d'ordre comportemental (e.g. réduction de la mobilité ou augmentation de l'évitement), se traduire au niveau de la croissance,

de la reproduction ou de la survie. Ces effets sont soit le résultat d'une action toxique directement sur des processus métaboliques susceptibles d'impacter les traits d'histoire de vie, soit celui d'une modification de l'allocation énergétique en réaction au stress causé par l'exposition au toxique (Amiard-Triquet et al., 2011).
Ces effets toxiques apparaissent lorsque la concentration du contaminant dans l'organisme est telle que le taux d'internalisation excède les taux combinés d'excrétion et de détoxication du contaminant par cet organisme (Figure 5).

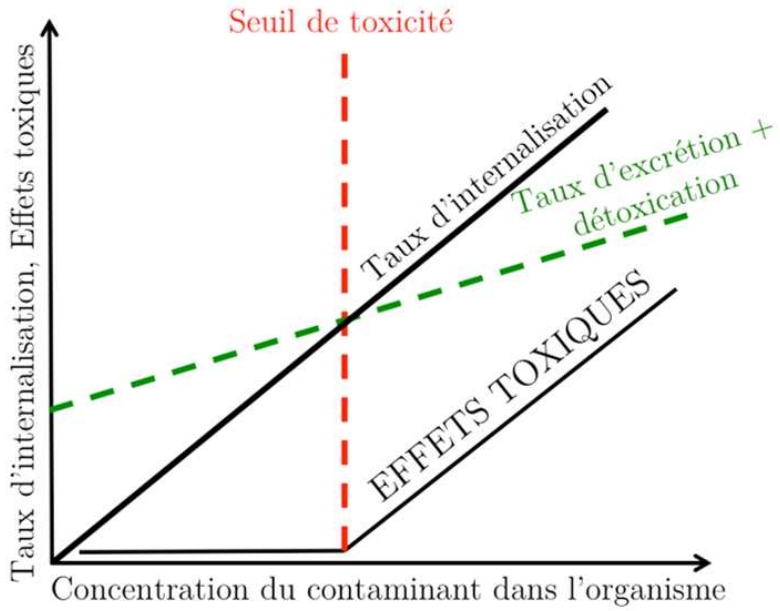

Figure 5. Représentation schématique des processus rentrant en jeu dans l'apparition de la toxicité d'une substance, puis de sa toxicité croissante avec l'augmentation de sa concentration (traduite d'après Rainbow et Luoma (2011)).

Ce seuil de toxicité dépend donc de la capacité de la substance à être internalisée et interagir avec des systèmes biologiques de l'organisme, c'est à dire de sa **biodisponibilité** (Rand, 1995; Semple et al., 2007).

La biodisponibilité d'un élément est d'une part conditionnée par les caractéristiques structurales et la spéciation du xénobiotique. A titre d'exemple, l'ion divalent Cd^{2+} ressemble en taille et charge à l'ion essentiel Ca^{2+} et peut facilement pénétrer le compartiment biotique par les transporteurs de cet ion essentiel (Wang et al., 1997). En revanche, un changement de spéciation de cet ETM, en se complexant avec la matière organique par exemple, empêchera ce transport facilité vers les matrices biologiques (Adams et al., 2011). De même, les modifications de la structure des HAP par bio- ou photo-dégradation peuvent conduire à des changements de biodisponibilité (McConkey et al., 1997). Enfin, le dernier exemple porte sur les PCB dont la position des atomes de chlore conditionne en partie l'agencement des cycles phényles, agencement à l'origine d'un encombrement stérique limitant la diffusion passive de la molécule à travers les

membranes (Shaw et Connell, 1984). Il est à noter que parmi les 7 PCB indicateurs, seul le PCB 118 possède une conformation similaire aux dioxines, ce qui augmente sa toxicité (INERIS, 2005). De plus, des effets additifs, synergiques ou au contraire antagonistes peuvent apparaître en présence d'une combinaison de contaminants (Beyer et al., 2014; Gauthier et al., 2014; Norwood et al., 2003).

La biodisponibilité, d'autre part, dépend de l'organisme exposé et de sa capacité à internaliser le toxique. La guilde trophique de l'espèce peut jouer sur les voies d'exposition au toxique, son état physiologique (e.g. âge, sexe) et son efficacité d'incorporation (Eggleton et Thomas, 2004; Safe and Hutzinger, 1984; Tchounwou et al., 2012).

Enfin, l'efficacité d'excrétion et de détoxication est également susceptible de varier, influant ainsi sur le seuil de toxicité du xénobiotique (Figure 5). Cette efficacité dépend de l'organisme, de son état physiologique lui-même influencé par l'environnement (e.g. effets multi-stress lumière et xénobiotique chez les organismes autothrophes (Cheloni et Slaveykova, 2018)), et à son histoire d'exposition (e.g. mécanisme de défense et d'acclimatation) notamment.

I.4. Les lacs et leur zone littorale réceptacles des micropolluants

Parmi les différents milieux aquatiques, les lacs constituent des milieux d'une grande valeur écologique et socio-économique. Eau potable, irrigation, énergie hydroélectrique, pêche, lieux de récréation et sport sont autant de ressources supportant la forte croissance démographique autour des grands lacs dans le monde depuis la seconde moitié du 20ème siècle (Beeton, 2002). L'intensification du tissu urbain et des activités industrielles autour de ces plans d'eau s'est accompagnée d'une transformation du fonctionnement hydrologique du bassin versant (imperméabilisation des sols, chenalisation des tributaires, stabilisation du niveau d'eau) (Ostendorp et al., 2004; Reyjol et al., 2014) et d'un accroissement des rejets de pollution (Carpenter et al., 2007). Ces pressions anthropiques ont affecté l'intégrité écologique des grands lacs, notamment par la dégradation de la qualité chimique des masses d'eau et de leur état trophique allant jusqu'à l'eutrophisation dans un grand nombre de cas (Ashley et al., 2011; Jenny et al., 2016).

En Europe, des mesures de réduction des rejets en azote et phosphore conjointement à un suivi scientifique du statut trophique des grands lacs ont permis d'endiguer ce phénomène d'eutrophisation (Hobæk et al., 2012; Jacquet et al., 2005; Schindler et al., 2016). Cependant, les réactions ont été plus lentes vis-à-vis de la contamination des écosystèmes lacustres par les micropolluants, probablement à cause des difficultés analytiques et financières propres à l'étude de ces substances. Avec la Directive Cadre sur l'Eau (DCE) de 2000 (Directive 2000/60/CE), des programmes de surveillance de l'état chimique des masses d'eau des états membres se mettent en place et priorisent le suivi de 33 substances chimiques (Commission Européenne, 2000; Kallis

et Butler, 2001). A ces substances sont d'abord attribuées des concentrations seuils (Normes de Qualité Environnementale) à ne pas dépasser dans la colonne d'eau, mesurées en un point central et profond du lac. La zone littorale (ZL), en revanche, ne fait pas l'objet d'une surveillance réglementaire de sa contamination (Ostendorp, 2004).

On dénombre autour de 500 000 lacs naturels (dont la surface excède 0,01 km^2 par définition) en Europe (Kristensen et Hansen, 1994). La surface cumulée des 164 lacs européens référencés dans la base de données mondiale des lacs[1] est de 542 475 km^2, soit une surface approximative en ZL de 97 650 km^2 (18 % de la surface totale selon Vadeboncoeur et al. (2011)). On peut donc imaginer le rôle quantitatif, mais également qualitatif que jouent les ZL des grands lacs dans le maintien de la biodiversité. En effet, les franges littorales sont le siège de variations abiotiques et d'une complexité structurale qui abrite une grande diversité de faune et flore et dont l'Homme a su tirer les avantages économiques, culturels et récréationnels (Carpenter et Cottingham, 1997). Leur rôle écologique au sein du lac est multiple ; elles abritent 93 % des espèces vivantes des lacs, dont 72 % endémiques (Vadeboncoeur et al., 2011), elles jouent le rôle de zone tampon entre milieux terrestre et aquatique et sont le siège d'importants cycles biogéochimiques (Wetzel, 2001) pour le fonctionnement écologique du lac (Schmieder, 2004) (Figure 6).

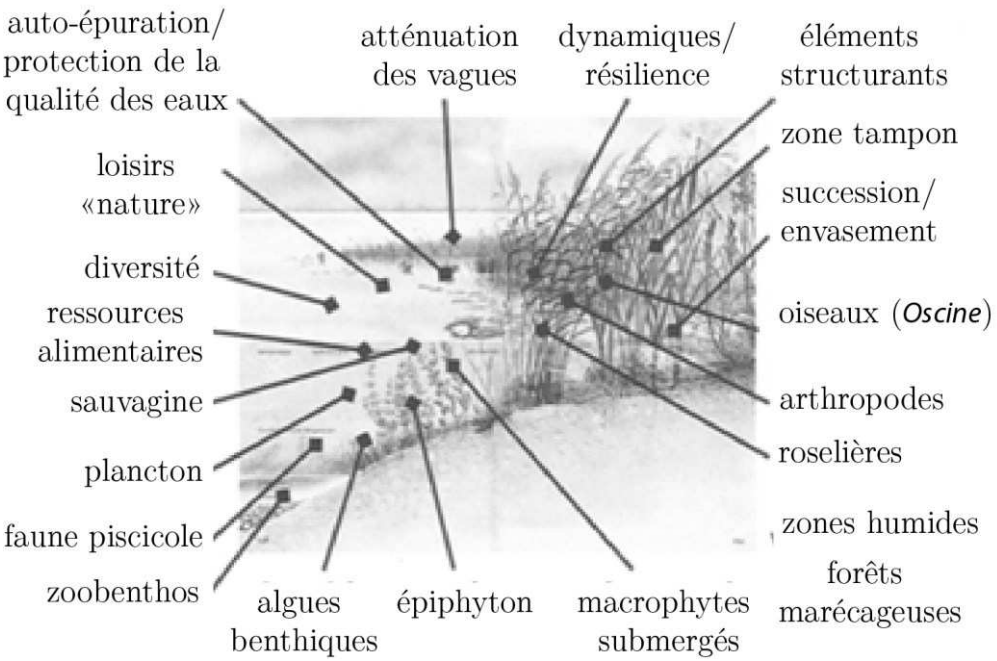

Figure 6. Exemples de fonctions écologiques et communautés animales et végétales des ZL lacustres (traduite d'après Schmieder (2004)).

[1] http://wldb.ilec.or.jp/Search/LakeListRegionCode/EUR

La biocénose et la connexion entre habitats terrestres et aquatiques peuvent être altérées par des usages anthropiques intensifs de cette zone comme l'aménagement artificiel des berges ou l'apport excessif de polluants (Bragg et al., 2003; Salmaso et al., 2018). La frange littorale est en effet la première zone réceptrice de la plupart des contaminants provenant du bassin versant et véhiculés au lac par les tributaires, des buses de rejet, ou directement des activités en bordure de lac (zones récréatives type plages et ports) (Ostendorp et al., 2004; Xing et al., 2018) (cf section I.3.1). Dans cette zone, le sédiment de surface joue le rôle de compartiment de stockage des micropolluants hydrophobes (Atkinson et al., 2007; Bryan et Langston, 1992; Burton, 2018). Néanmoins, les échanges aux interfaces sédiment-eau-biote sont supposés nombreux et facilités par les fluctuations des variables environnementales (e.g. régime hydrodynamique, pH, température, luminosité, bioturbation) plus importantes que nulle part ailleurs dans le lac (Hofmann et al., 2008; Matisoff, 2018; Precht et al., 2004; Strayer et Findlay, 2010; Zoumis et al., 2001) (cf section I.3.1). Ces fluctuations environnementales sont susceptibles de favoriser les changements de mobilité des micropolluants et d'impacter le biote benthique et pélagique augmentant ainsi le risque écotoxicologique au niveau des sédiments de la zone littorale (cf section I.3.2) (Nedrich and Burton, 2017). On retrouve souvent dans la littérature la notion de rôle de « stockage » et de « source » de contamination que joue le compartiment sédimentaire en ZL (Davis et Fox, 2009; Simcik et al., 1999; Weisener et al., 2017).

La régulation des fluctuations de niveau d'eau est également une menace pour l'intégrité écologique des ZL (Evtimova et Donohue, 2016; Hofmann et al., 2008). Ces fluctuations naturelles, à l'échelle de l'ensemble du lac, sont générées par un bilan hydrique en déséquilibre entre apports et sorties d'eau, issus de processus météorologiques et hydrologiques (e.g. fonte des neiges, précipitations, évaporation)(Hofmann et al., 2008). La fenêtre de fluctuations au cours de l'année du niveau d'eau résultant de ces processus est appelée « marnage ». Le marnage de la plupart des grands lacs européens a été artificiellement maîtrisé et réduit dès les années 80 pour principalement permettre la production d'hydroélectricité ou la prévention des inondations (e.g. lac Vänern en Suède (Marttunen et al., 2006), lac Léman en France et Suisse[2], plus de 300 lacs en Finlande (Aroviita et Hämäläinen, 2008)), la principale exception à ce jour étant le Lac de Constance. La stabilisation artificielle du niveau d'eau peut avoir des effets néfastes sur le fonctionnement écologique des berges en altérant notamment la succession écologique de différents processus abiotiques (e.g. cycles géochimiques (Wantzen et al., 2008)), et biotiques (e.g. croissance des roselières (Miquet, 1997), cycle de vies des producteurs primaires et consommateurs benthiques et pélagiques (Evtimova et Donohue, 2016)).

Devant les enjeux écologiques, économiques et sociétaux de la ZL lacustre, les connaissances portant sur le comportement biotique et abiotique de cet écotone face aux altérations

[2] http://www.donnees.rhone-alpes.developpement-durable.gouv.fr/lacs_rha/lacs_leman.htm

anthropiques (comme référencées dans les quelques lignes précédentes) sont nécessaires pour entreprendre des mesures de restauration à l'échelle du lac dans son intégralité et atteindre l'objectif de bon état écologique visé par la DCE à l'échelle européenne (Ostendorp, 2004; Schmieder, 2004). L'impact des pollutions sur le biote de la ZL, notamment, est un sujet encore peu abordé dans la littérature scientifique ; 4 % des 2137 études publiées depuis 1990 (96,7 % articles, 4,3% revues) sont du domaine de la toxicologie environnementale[3]. Approfondir les connaissances sur le fonctionnement de la zone littorale en matière de prise en charge, de devenir et d'impacts des contaminants est donc primordial.

II. Problématiques

Ce travail de thèse s'attache à améliorer l'état des connaissances sur le comportement des polluants en zone littorale lacustre de grands lacs, et proposer des outils d'évaluation de la toxicité dans cette frange littorale au travers des questionnements suivants :

Comment se caractérise la variabilité spatiale de la multi-contamination littorale ? Celle-ci présente-elle un risque écotoxicologique variable à l'échelle de la zone littorale lacustre ?
Aujourd'hui, les niveaux de contamination des lacs sont en majorité évalués *via* l'étude d'échantillons pélagiques et sédimentaires en zone profonde, jugés intégrateurs des pressions chimiques de l'ensemble du lac. Nous pouvons supposer que la contamination littorale, davantage impactée localement par des sources ponctuelles, varie spatialement, donnant ainsi une estimation de l'état de contamination et du risque écotoxicologique associé plus fine qu'à partir de suivis réglementaires.

L'étude de la composition de la contamination sédimentaire et du biote autochtone peut-elle nous renseigner sur la contribution de sources locales à la contamination littorale?
Face au besoin de caractériser l'évolution sur le long terme de l'état chimique des lacs, la Directive fille de 2008 (2008/105/CE) impose des contrôles de la contamination en micropolluants hydrophobes dans le sédiment et/ou le biote (Commission Européenne, 2008). Ces compartiments sont en effet considérés comme davantage intégrateurs de la pollution que la colonne d'eau où elle se trouve plus variable dans le temps et moins concentrée (i.e. moins détectée). Pour l'heure, ces échantillonnages ne sont pas effectués en zone littorale. Néanmoins, tout comme la variabilité temporelle des niveaux de contamination au sein d'une carotte sédimentaire permet de remonter aux sources de pollution majeures, la variabilité spatiale des sédiments de surface du littoral ne

[3] Recherche sur Web of Sciences sur les articles et revues selon les mots clés «littoral» OR «shore» AND «lake» NOT «marine» en excluant le domaine de l'océanographie dans les résultats.

pourrait-elle pas nous renseigner sur l'influence locale de sources de pollution sur la contamination du sédiment ? Dans le cas où les organismes autochtones seraient différemment contaminés le long du littoral, leurs profils de contamination peuvent-ils nous renseigner sur la nature des sources qui les contaminent ? Ces données pourraient être de nature à aider les gestionnaires à prioriser leurs actions le long de la zone littorale.

Les variables environnementales propres à la zone littorale telles que les fluctuations du niveau d'eau et les changements abiotiques ainsi que leurs fluctuations sont-elles impliquées dans la mobilité et la biodisponibilité des contaminants ?

Le marnage lacustre, qu'il soit artificiel (e.g. vidange de barrage) ou naturel (i.e. fluctuations du niveau d'eau selon la balance hydrique), engendre des variations abiotiques en zone littorale potentiellement à l'origine d'impacts sur le biote. Alors que les impacts écologiques tels que le stress hydrique pour les organismes peu mobiles font l'objet de régulières évaluations (Wantzen et al., 2008), seuls 12 % des sujets d'études intègrent l'étude des polluants (Leira et Cantonati, 2008). Nous pouvons néanmoins supposer que les changements abiotiques liés au marnage (e.g. assèchement, réduction de la colonne d'eau) sont susceptibles d'impacter la mobilité et la biodisponibilité des micropolluants sédimentaires.

III. Choix méthodologiques et démarche générale

Pour comprendre les processus d'impacts écotoxiques des contaminants en ZL littorale, une évaluation du risque rétrospective de la contamination présente est nécessaire. Elle passe par la quantification des polluants dans la matrice sédimentaire et l'observation d'altérations au niveau biologique, de l'individu à l'écosystème. Ce chapitre détaille les principaux outils d'évaluation de l'écotoxicité du sédiment de surface.

III.1. Choix des micropolluants d'étude

Les critères de sélection des familles de micropolluants pour ces travaux ont été les suivants :

- polluants ubiquistes et notamment largement répandus dans les milieux lacustres,
- polluants issus des activités anthropiques urbaines et industrielles,
- polluants hydrophobes à fort potentiel d'adsorption sur les sédiments,
- toxicité avérée et disponible dans la littérature.

Sur la base de ces critères, notre choix s'est porté sur :

- les 8 ETM précédemment évoqués : As, Cd, Cr, Cu, Ni, Pb, Sn et Zn,

- 15 des 16 HAP de l'USEPA : Acy, Ace, Flu, Phe, Ant, Fla, Pyr, BaA, Chr, BbF, BkF, BaP, BghiP, DbahA, Ip. Il a été choisi d'exclure le Nap, considéré comme très volatil et pouvant être à l'origine de biais dans le dosage sur matrice.
- les 7 PCB indicateurs : les congénères 28, 52, 101, 118, 138, 153, 180.

Par leur diversité structurale, ces polluants présentent des comportements variés en termes d'affinité pour le sédiment (e.g. log K_{ow} de 3,9 pour Ace à 7 pour PCB 180) permettant d'étudier des processus de mobilité, biodisponibilité et toxicité différents.

III.2. Choix des sites d'étude

III.2.1. Lacs d'étude

Les grands lacs péri-alpins français, le lac du Bourget et le lac d'Annecy (Tableau 1), sont les deux plus grands lacs naturels français. Ils constituent des plans d'eau d'une grande valeur écologique mais aussi sociale et économique (Balvay et al., 2012; Salmaso et al., 2018). A eux deux, ils approvisionnent annuellement près de 230 000 personnes en eau potable. Du fait de leurs attraits touristiques, la population des bassins-versants tend à doubler durant la période estivale. La préservation de la bonne qualité des eaux est donc un enjeu de taille pour les gestionnaires de ces lacs, à savoir le Syndicat Mixte du Lac d'Annecy (SILA) et le Comité Intersyndical pour l'Assainissement du Lac du Bourget (CISALB).

Tableau 1. Fiche signalétique des lacs du Bourget et d'Annecy.

	lac du Bourget	**lac d'Annecy**
Coordonnées GPS	45°43′N, 5°52′E	45°51'N, 6°10'E
Formation	Surcreusement glaciaire	Surcreusement glaciaire
Etat trophique	oligo à mésotrophique	oligotrophique
Stratification	méromitique	monomictique
Temps moyen de séjour des eaux	8,5 ans	3,8 ans
Superficie	42 km^2	27 km^2
Volume	3,6 km^3	1,127 km^3
Périmètre	44 km	45,4 km
Profondeur maximale	145 m	65 m*
Profondeur moyenne	81 m	41 m
Noms des principaux tributaires et contribution en apports au lac (%)[1]	Leysse (68 %), Tillet (6,5 %), Sierroz (25,5 %)	Eau Morte (40 %) Ire (15 %), Laudon (12 %)
Noms des exutoires	Canal de Savière	Thiou
Altitude	231,5 m	447 m
Climat	continental	continental
Directions majoritaires (contribution en %) des vents[2]	N (26,5 %), NO (21,4 %)	SO (13,1 %), NNE (10,8 %)

Tableau 1. Suite et fin.

		Lac du Bourget	Lac d'Annecy
Superficie du BV		560 km²	250 km²
Population du BV		170000 hbts	125000 hbts
Nombre de plages[3]		9	13
nombre de ports[3]		14	11
Occupation des sols du BV[3]	Forêts	45 %	56 %
	terres agricoles et prairies	34 %	21 %
	aires urbaines et industrielles	13 %	17 %
	eaux de surface	8 %	6 %

* hors source sous-lacustre du Boudioz d'une profondeur de 82 m très localement.
[1] CISALB et Nicoud et Manalt, (2001)
[2] https://fr.windfinder.com/windstatistics/aix-les-bains_lac_bourget
[3] http://www.grand-lac.fr/tourisme/ports/ et https://www.lac-annecy.com/bouger/ports.html
[4] Corinne Land Cover (2000)

Ces lacs ont suivi la trajectoire historique des grands lacs européens quant au développement anthropique de leur bassin-versant. A titre d'exemple, la surface urbaine a quadruplé depuis 1945 (Figure 7).

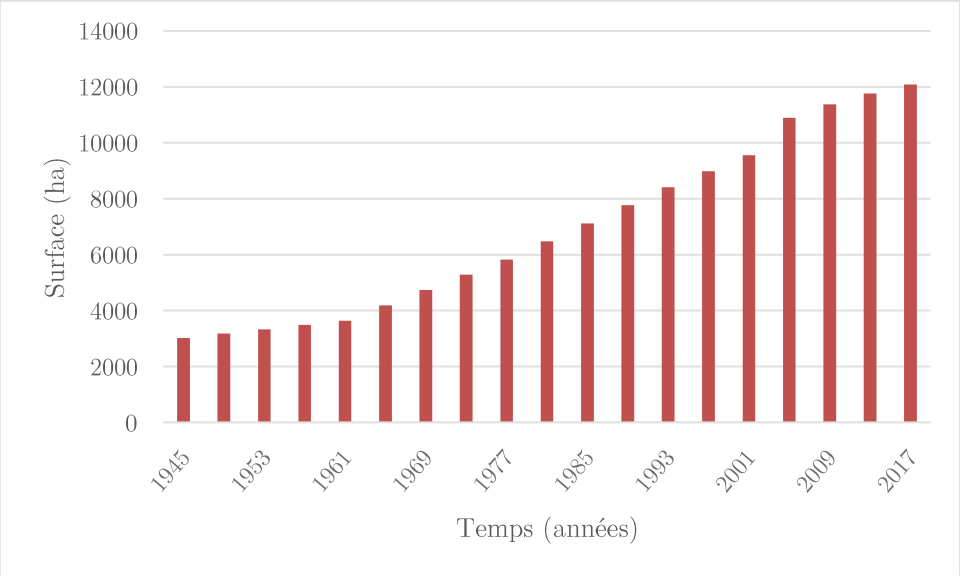

Figure 7. Evolution cumulée de la surface (hectares) de l'enveloppe urbaine de 1945 à 2017 sur la Métropole de Savoie d'après la DDT Savoie 2018[4]. L'enveloppe urbaine correspond à l'urbanisation totale incluant le secteur du résidentiel, économique et les infrastructures de transport.

[4] SCoT Métropole Savoie : http://www.observatoire.savoie.equipement-agriculture.gouv.fr/Communes/scot.php?SIREN=200000003#Paragraphe21

Les symptômes d'eutrophisation dès les années 50 ont poussé les gestionnaires des lacs à mettre en œuvre des mesures de restauration visant notamment à réduire les apports en phosphore et azote. Par ailleurs, d'importants travaux d'assainissement, comme la dérivation des eaux usées traitées de Chambéry et d'Aix-les-Bains au Rhône par la galerie souterraine sous la chaîne de l'Epine dès 1974 pour le lac du Bourget (Darcy, 1979) ou encore la création d'un réseau collecteur d'eaux usées ceinturant le lac d'Annecy et se déversant en son aval dès 1962 (Rulliere et al., 1972), ont permis, conjointement à une surveillance scientifique accrue, de rétablir un régime méso à oligotrophe pour ces lacs.

Si les réseaux d'assainissement des eaux usées font encore aujourd'hui l'objet de travaux de réhabilitation, notamment vis-à-vis de la construction de bassins de stockage/restitution sur les réseaux unitaires (CISALB, 2012), l'apport en N et P est en grande partie maîtrisé. En revanche, les apports en micropolluants via les eaux de ruissellement ou encore par voie atmosphérique restent encore difficilement qualifiables et quantifiables. Jung (2009) a mis en évidence l'implication de la Leysse dans l'apport en micropolluants au lac du Bourget sur une période de près d'un siècle au travers de l'étude de carottes sédimentaires profondes. De plus, ces dernières décennies, l'état chimique des eaux des tributaires des lacs du Bourget et d'Annecy a fait l'objet d'un déclassement de bon à mauvais état, à cause notamment de concentrations élevées en HAP lourds (Eaufrance[5]). La diversité de l'occupation des sols des bassin-versants de ces lacs et plus finement à l'échelle littorale (e.g. plages, ports, Tableau 1) laisse supposer autant de sources potentielles de contamination de la zone littorale, faisant ainsi de ces lacs des cas d'études appropriés pour aborder les problématiques de cette thèse. Au contraire du lac d'Annecy, pour lequel le tissu urbain le plus dense se situe à l'aval du lac, l'agglomération d'Aix-les-Bains-Chambéry est localisée en amont du lac du Bourget, ajoutant une composante intéressante à l'étude de la contamination littorale de ce lac. Enfin, la volonté du CISALB d'appliquer un marnage artificiel d'octobre à décembre 2017 de 70 cm au lieu des 30 cm classiquement imposés par la régulation du niveau du lac du Bourget depuis les années 80 a permis la réalisation d'une étude terrain de l'influence des variables environnementales telles que les fluctuations du niveau d'eau sur la mobilité des contaminants de la zone littorale. Du fait de ces deux dernières caractéristiques, propres au lac du Bourget, ce dernier a fait l'objet de la plupart des études menées dans cette thèse.

[5] http://sierm.eaurmc.fr/surveillance/eaux-superficielles/index.php?donnees=etat&codeRegion=84&codeDept=74&codeCommune=&bassin=&sousBassinVersant=&coursdeau=#selection

III.2.2. Contamination générale des lacs d'étude

Les données récentes de contamination sédimentaire en zone centrale des lacs du Bourget et d'Annecy rendues disponibles par l'Agence de l'Eau dans le cadre de la surveillance DCE (Agence de l'Eau Rhône Méditerranée Corse, 2017a, 2017b) ont été comparées à des niveaux de concentration en ETM, HAP et PCB de sédiments de surface des lacs à l'échelle planétaire dans la Figure 8 (voir ANNEXE I pour le détail des méthodologies et résultats de la sélection des articles de cette brève revue de la littérature). Les bassins-versants des lacs issus de cette recherche bibliographique ont des degrés d'anthropisation variables allant du lac d'altitude au bassin-versant exempt de source locale de contamination au lac urbain ou impacté par des sources industrielles identifiées. Néanmoins, cette comparaison vise à donner un aperçu du niveau de contamination général des lacs d'étude par rapport à un panel large de contamination à l'échelle mondiale.

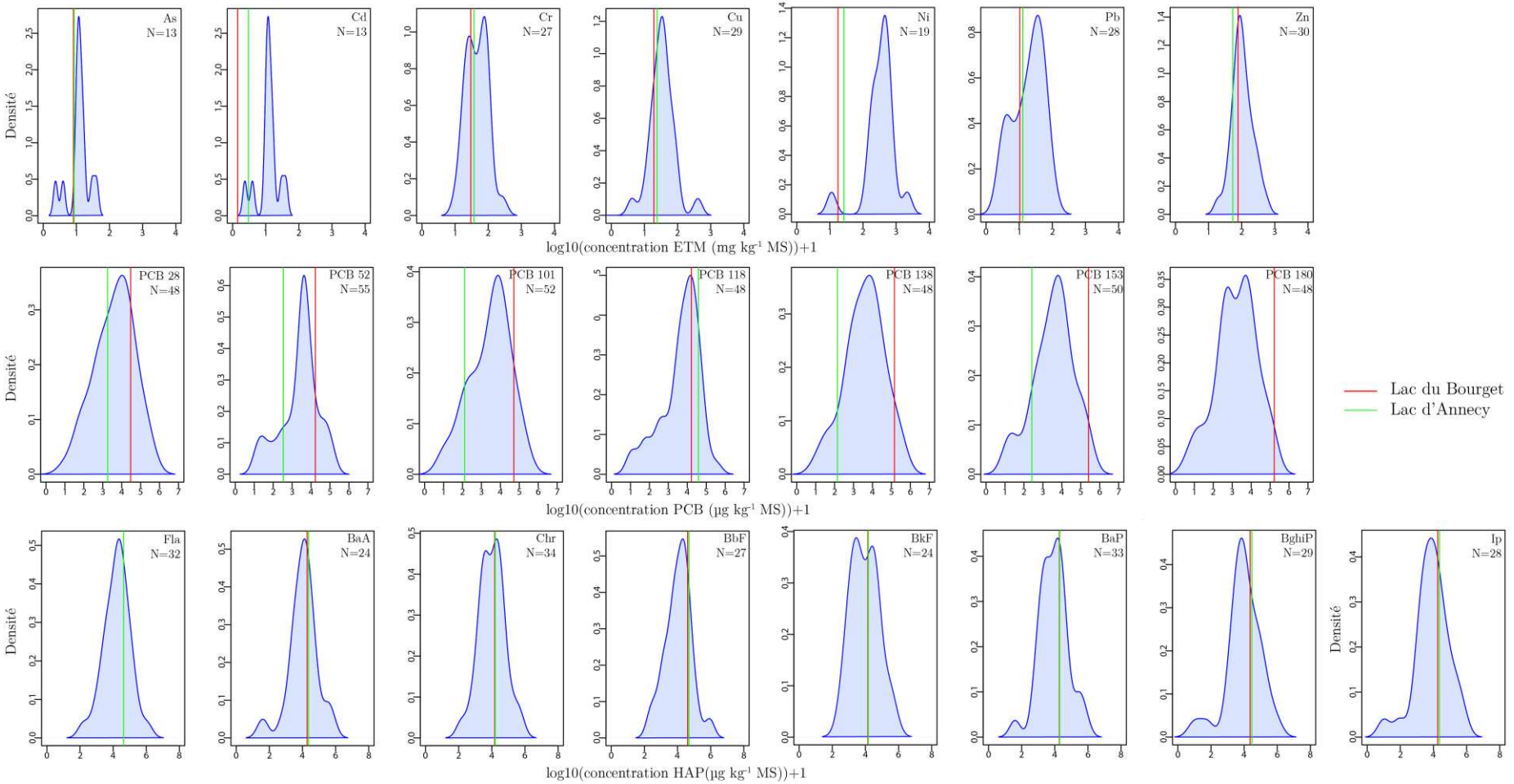

Figure 8. Histogrammes représentatifs de la distribution de la contamination sédimentaire en ETM (log_{10}(concentration(mg kg^{-1}))), PCB (log_{10}(concentration(µg kg^{-1}))+1) et HAP (log_{10}(concentration(µg kg^{-1}))) de lacs dans le monde et représentation du niveau de contamination sédimentaire des lacs d'Annecy (vert) et Bourget (rouge) d'après les données disponibles de la campagne 2016 de l'Agence de l'Eau dans le cadre de la surveillance DCE (Agence de l'Eau Rhône Méditerranée Corse, 2017a, 2017b). Pour chaque contaminant, «N» indique le nombre de résultats disponibles sur les 31 lacs en ETM, les 62 en PCB et les 34 en HAP. NB : les données absentes pour les lacs du Bourget et d'Annecy correspondent à des concentrations non détectées par l'Agence de l'Eau. Seuls 8 des 15 HAP d'étude figurent ici, les autres n'ayant pas été détectés dans les lacs du Bourget et d'Annecy. Le Sn ne figure pas dans ces résultats puisque non relevé dans les articles de cette revue de la littérature.

A l'exception de l'As non détecté dans les sédiments du lac du Bourget, la contamination en ETM des deux lacs d'étude est similaire, bien que légèrement supérieure dans le lac d'Annecy sauf pour le Zn. L'intensité des contaminations est généralement plus faible pour ces deux lacs que la contamination moyenne mondiale issue de cette revue de la littérature. En effet, la proportion de lacs dont la contamination est inférieure à celle du lac du Bourget et d'Annecy est toujours inférieure à 50 % pour les ETM considérés.
Le lac d'Annecy semble faiblement contaminé en PCB ; le PCB 180 n'est pas détecté et la proportion de lacs dont la contamination est inférieure à la sienne varie entre 10 (PCB 138) et 33 % (PCB 28), sauf pour le PCB 118 pour lequel 83 % des lacs en sont plus faiblement contaminés. En revanche, le lac du Bourget semble fortement contaminé en PCB puisque 65 (PCB 118) à 100 % (PCB 180) des 63 lacs étudiés ont une contamination inférieure à la sienne. Les rejets passés d'une usine de condensateurs et transformateurs implantée à 700 m du lac dès 1921 pourraient expliquer ces fortes teneurs en PCB (Jung, 2009).
Les contaminations en HAP des lacs d'Annecy et du Bourget sont globalement similaires dans les HAP détectés et importantes comparées aux données de la littérature puisqu'elles se situent dans la moyenne haute.
De façon générale, les sédiments en zone profonde des lacs du Bourget et d'Annecy semblent présenter des teneurs moyennes à élevées en ETM, HAP et PCB au regard du niveau de contamination mondial des lacs que laisse entrevoir cet échantillon de la littérature. Par conséquent, ces résultats justifient le choix de ces lacs et familles de contaminants comme cas d'étude pour l'évaluation de l'écotoxicité de sédiments littoraux lacustres.

III.2.3. Délimitation de la zone littorale et choix des sites littoraux

Il n'existe pas de définition claire et universelle de la ZL lacustre dans la réglementation internationale (voir l'Appendix de Ostendorp, (2004) sur le sujet).
Dans un contexte scientifique, les définitions de la ZL lacustre varient en fonction de la discipline (Provencher et Dubois, 2008). Ainsi, la nomenclature géomorphologique de la ZL se base sur les processus d'action des vagues à l'origine de la formation de la beine et du mont (e.g. Figure 9.A) alors que les limnologues effectuent un découpage de la ZL par type de végétation régi principalement par la pénétration de la lumière (e.g. Figure 9.B) (Hutchinson, 1967; Ostendorp et al., 2004; Wetzel, 2001). Selon cette dernière définition, la ZL se compose de l'eulittoral et l'infralittoral. La zone eulittorale est la frange la plus exposée au marnage lacustre et aux variations des paramètres environnementaux qui accompagnent ces fluctuations du niveau d'eau (Cantonati et al., 2009). Selon cette définition, les délimitations de la ZL varient au sein d'un même lac selon sa bathymétrie littorale (Lake, 2011; Wantzen et al., 2008), son exposition aux vagues et panache des tributaires, mais dans tous les cas séparent clairement la zone pélagique définie comme calme d'un point de vue régime hydrodynamique et dont la pénétration limitée de lumière proscrit l'établissement à long terme de macrophytes.

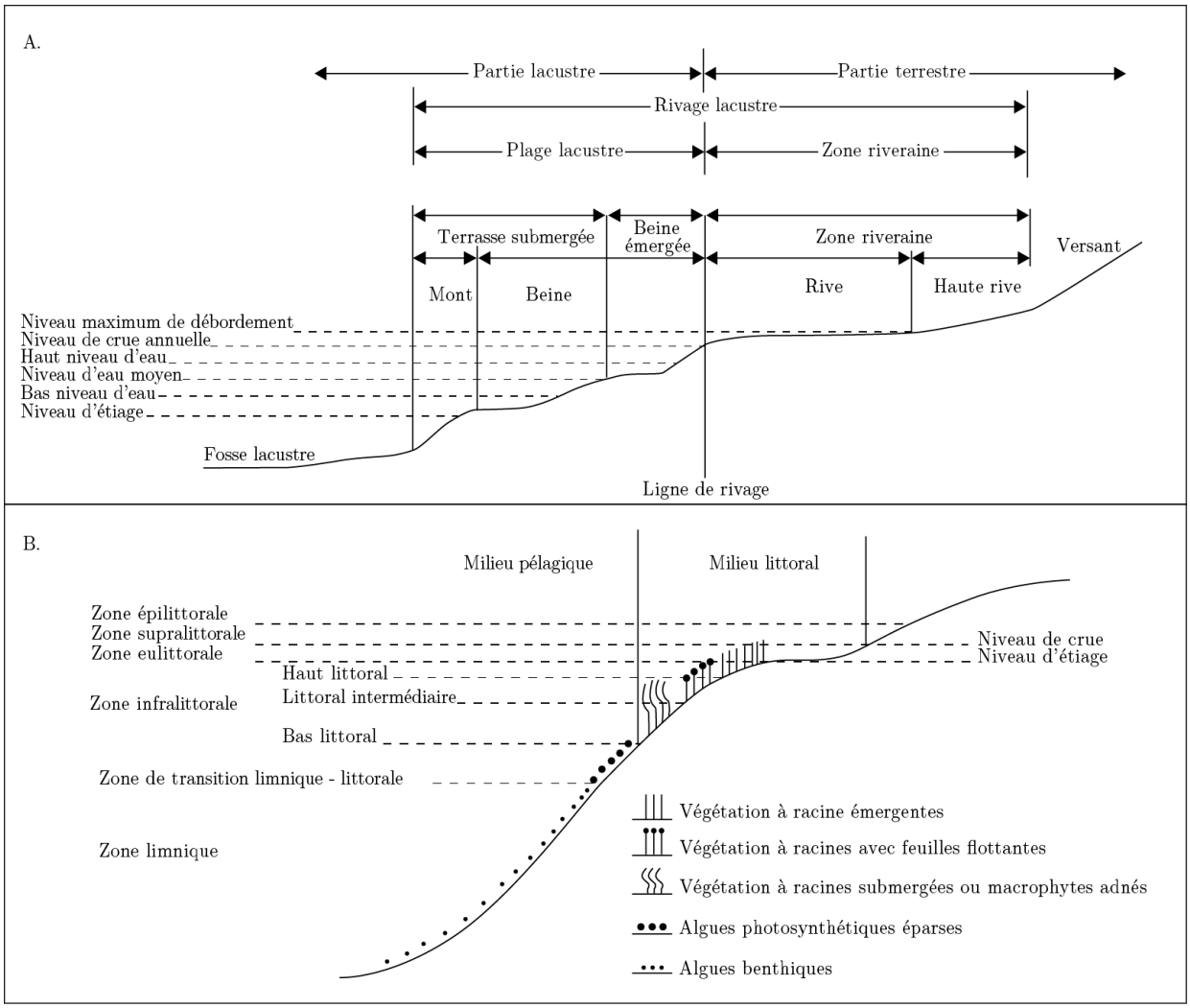

Figure 9. Exemples de deux classifications différentes de la zone littorale selon la discipline ; (A) géomorphologie et (B) limologie (modifié d'après Provencher et Dubois (2008))

De plus, il est évident que la question scientifique conditionne l'échelle d'observation et ainsi le périmètre, la forme et l'hétérogénéité de la zone littorale considérée (Heino, 2000; Stoffels et al., 2005; Strayer et Findlay, 2010). Dans cette thèse, l'objectif étant d'évaluer le niveau de contamination des sédiments littoraux et l'influence de perturbations abiotiques comme celles que pourrait provoquer un marnage, la profondeur à laquelle les sédiments ne sont *a priori* plus impactés par ces perturbations fixe le périmètre de ce que nous définissons comme la zone littorale lacustre. Elle est représentée dans la Figure 9 comme la zone eulittorale. .

Les sites littoraux d'étude ont été sélectionnés en fonction de :

- la nature de l'activité anthropique à proximité (port, plage, voie ferrée, route), ou *a contrario* l'absence d'activité anthropique (roselières, littoral non occupé),
- la proximité des principaux tributaires,
- leur bathymétrie (pente douce entre 1 et 5 %),

- la nature du substrat sédimentaire la plus homogène possible entre les sites,
- leur accessibilité sur le terrain.

Ces sites font l'objet de descriptions détaillées dans les chapitres de cette thèse.

III.3. Evaluation de l'écotoxicité des sédiments de la zone littorale

III.3.1. Les outils d'évaluation de l'écotoxicité

a. Evaluer l'exposition et le potentiel toxique à partir de la matrice abiotique

Les méthodes analytiques (e.g. spectroscopie, diffraction ou fluorescence à rayons X, microscopie) permettent de quantifier le niveau de contamination en dosant directement dans la matrice sédimentaire la concentration totale en polluants. Souvent exprimée en $mg.kg^{-1}$ de masse sèche (MS) de sédiment, cette valeur peut ensuite faire l'objet d'une normalisation par le taux de matière organique (MO) du sédiment. Cette normalisation facilite l'analyse comparative de la contamination entre différents sites littoraux aux taux de MO différents, tout en excluant un biais de concentration lié à une affinité des contaminant à cette MO (Eggleton et Thomas, 2004; Reid et al., 2000; Zhang et al., 2014).

Une première évaluation du potentiel toxique des sédiments peut être apportée par la comparaison de ces valeurs à des seuils de toxicité réglementaires. Avec la volonté d'augmenter la surveillance du compartiment sédimentaire depuis la Directive fille de 2008 (2008/105/CE), des valeurs seuils de toxicité propres au sédiment sont aujourd'hui disponibles dans la réglementation européenne et sur le portail INERIS[6]. Ainsi, les Qsed (Norme de qualité pour le sédiment d'eau douce) sont déterminées soit par le calcul en utilisant l'approche d'équilibre de partage ou par extrapolation en appliquant un facteur de division sur les données biologiques (CL/CE50 ou NOEC/CE10 pour organismes benthiques) (Chochois et Migné-Fouillen, 2011). En parallèle, sont proposées dans la littérature des concentrations sédimentaires seuils issues de résultats de tests d'écotoxicité en laboratoire et validées sur le terrain. Sans être exhaustif, citons par exemple les PNEC (Predicted No Effect Concentration), les LEL / SEL (Lowest / Severe Effect levels) (Persaud et al., 1992), les TEL / PEL (Threshold / Probable Effect Levels) (Smith et al., 1996) et les ERL / ERM (Effect range Low / Medium) (Long et Morgan, 1990). **Devant le nombre important de seuils disponibles dans la littérature, notre choix s'est porté sur les seuils consensuels proposés par MacDonald et al. (2000), à savoir les TEC (Threshold Effect Concentration) et PEC (Probable Effect Concentration).** Une concentration sédimentaire en dessous de la TEC est supposée ne pas avoir d'effet néfaste pour l'organisme benthique alors qu'un dépassement de la PEC laisse prévoir des effets nocifs probables. Dans un contexte de multi-contamination sédimentaire, MacDonald et al. (2000) proposent également de calculer un

[6] https://substances.ineris.fr/fr/page/9

quotient de risque (quotient de PEC moyen) égal la moyenne des ratios des concentrations sédimentaires des polluants avec leur PEC respective. D'après la relation (1) obtenue des résultats de tests d'écotoxicité, une PEC moyenne inférieure à 0,1 indique un risque écotoxique inférieur à 10 % alors qu'une PEC moyenne supérieure à 0,5 présente un risque supérieur à 50 %.

$$fréquence\ de\ toxicité\ (\%) = 101{,}48\ (1 - 0{,}36^{quotient\ de\ PEC\ moyen}) \quad (1)$$

b. Evaluer la biodisponibilité

Doser les substances totales de la matrice sédimentaire permet de quantifier et qualifier la contamination à laquelle est exposé le biote. En revanche, le degré de liaison des contaminants avec la matrice sédimentaire donne une indication sur leur mobilité aux interfaces sédiment-eau-biote et donc d'une certaine façon sur leur biodisponibilité.

La mobilité des contaminants peut s'évaluer expérimentalement au moyen de tests de lixiviation. La lixiviation consiste en l'extraction par voie liquide (e.g. eau, acides ou bases) sous l'influence de réactions physiques, chimiques ou biologiques d'une ou plusieurs fractions des contaminants initialement contenus dans la matrice sédimentaire (Blanchard, 2000). Ces tests peuvent se faire à l'équilibre ou en dynamique, en batch ou en colonne et peuvent être simples ou multiples (i.e. extractions séquentielles) (voir Blanchard (2000) pour le détail de ces tests). **Dans ces travaux, nous avons choisi d'effectuer des tests de lixiviation simple en batch avec ratio liquide/solide de 10 l/kg en agitation rotative 24 h (EN 12457-2, 2002) et des tests d'extractions séquentielles inspirés de Tessier et al. (1979). Le premier test permet d'accéder à la fraction de la contamination sédimentaire la plus facilement mobilisable sous l'effet d'agitation avec l'eau comme cela pourrait être le cas à l'interface eau-sédiment en ZL et le second test donne les proportions des quatre formes de liaisons avec le sédiment (i.e. du plus au moins mobilisable) dans lesquelles se trouvent les ETM.**
La modélisation à partir de certaines données physico-chimiques du sédiment et de sa contamination totale peut également donner des informations sur la mobilité de cette contamination (e.g. Biotic Ligand Model BLM ; (Di Toro et al., 2005)).

Enfin, la connaissance des concentrations totales en contaminants dans l'eau interstitielle peut être utile dans la mesure où la contamination dans ce compartiment du sédiment est jugée davantage biodisponible pour les organismes benthiques (Di Toro et al., 1991) mais également plus facilement re-mobilisable dans la colonne d'eau (Knezovich et al., 1987). Cette connaissance peut s'acquérir par extraction mécanique de l'eau interstitielle (e.g. filtration, centrifugation) ou au travers de capteurs passifs (Cleveland et al., 2017). Le fonctionnement de ces derniers repose sur la diffusion et la sorption des contaminants à travers un jeu de membranes cumulant ainsi

une fraction assimilable à celle biodisponible par absorption pour les organismes exposés (Cornelissen et al., 2008).

Les concentrations en polluants mesurées dans les organismes exposés apportent des informations sur la biodisponibilité des contaminants sédimentaires, notamment lorsqu'ils sont mis en relation avec la contamination du sédiment à travers le facteur de bioconcentration (BCF). Dans la littérature, le BCF peut être défini comme la concentration interne de l'organisme, qu'importe le mode d'intégration des polluants dans l'organisme, sur la concentration du même polluant dans la matrice à laquelle il est exposé (Adams et al., 2011). Dans certains cas, le numérateur correspond en revanche à la concentration interne résultant uniquement d'un transfert passif (diffusion) (van der Oost et al., 2003), par opposition au facteur de bioaccumulation qui intègre en supplément la fraction ingérée par l'organisme (Mackay et Fraser, 2000). **Dans cette thèse, le BCF a été calculé comme le ratio entre la concentration interne en contaminants et la concentration du même contaminant dans la matrice sédimentaire totale, puisque c'est la biodisponibilité de la contamination sédimentaire qui nous intéressait ici.**

Les biomarqueurs d'exposition sont définis comme des mesures dans les fluides, cellules ou tissus d'un organisme susceptibles de révéler des modifications biochimiques ou cellulaires liées à la présence et l'intensité de substances toxiques (Depledge, 1994; Henderson et al., 1987). Ils mettent en évidence l'interaction entre un agent toxique et des cellules/molécules cibles. Au-dessus d'un certain seuil, lié à la dose de polluant ou au temps d'exposition par exemple, le signal du biomarqueur (e.g. activité enzymatique) dévie de son activité classique naturelle, souvent en réaction de défense à la présence du xénobiotique (van der Oost et al., 2003). Par conséquent, les biomarqueurs d'exposition apportent une indication sur le niveau de biodisponibilité des contaminants auxquels les organismes sont exposés. **Dans notre cas, l'acetylcholine esterase (AChE) et la glutathion S-transférase (GST) ont été sélectionnées.** L'AChE est une enzyme impliquée dans le passage de l'influx nerveux dont l'activité peut être inhibée par des polluants à l'action neurotoxique (Payne et al., 1996). La GST, en revanche, joue un rôle dans la détoxication des toxiques à l'origine d'un stress oxydatif (Habig et al., 1974).
Les biomarqueurs d'exposition présentent un intérêt majeur dans la détection précoce de perturbations des écosystèmes en lien avec des pressions chimiques (Vasseur et Cossu-Leguille, 2003). Néanmoins, dans le but d'évaluer l'impact écotoxique des sédiments littoraux, des mesures d'effet biologique en lien avec cette exposition deviennent nécessaires.

c. Evaluer l'effet biologique

L'étude du stress peut se faire à différentes échelles biologiques (i.e. du moléculaire à l'écosystème) (Figure 10). De manière générale, plus la pertinence écologique augmente, plus la compréhension mécanistique des processus de toxicité des contaminants est complexe et la réponse tardive

puisqu'elle résulte généralement d'un effet cascade à partir des niveaux d'organisation biologiques inférieurs (Bettinetti et al., 2012).

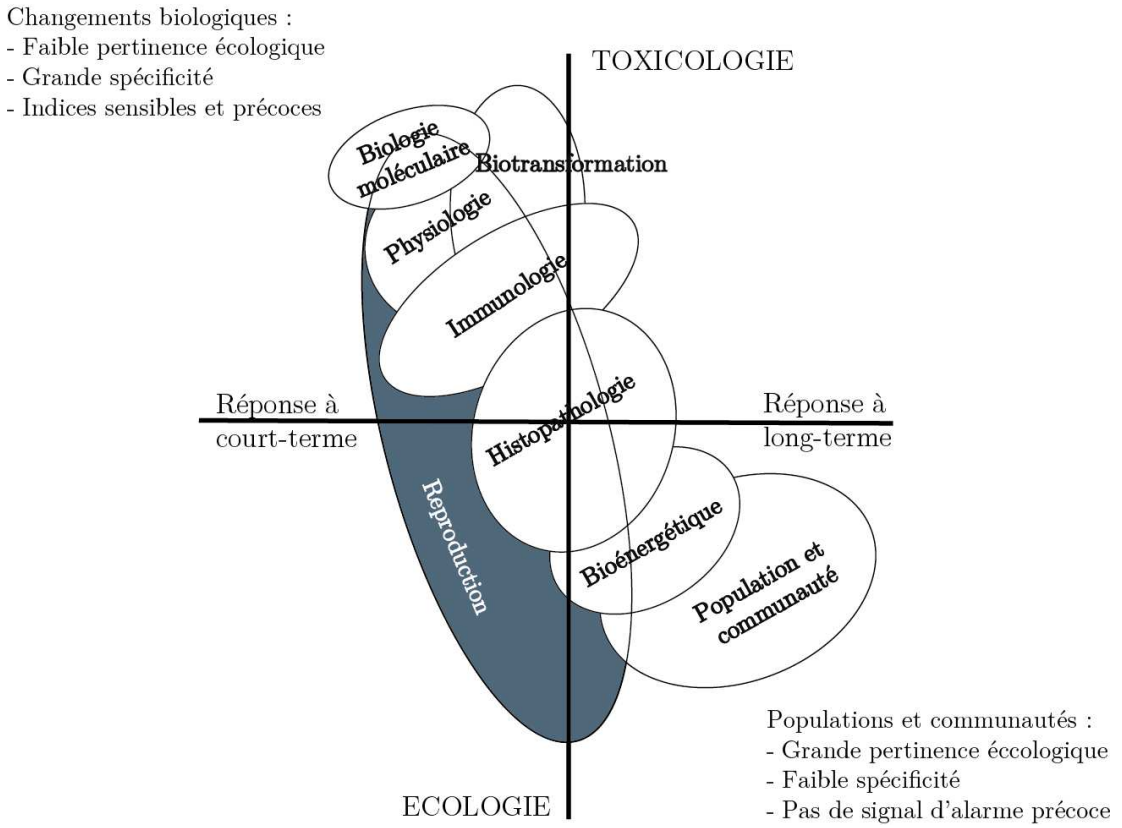

Figure 10. Les différents niveaux de réponses biologiques à une exposition à la contamination (traduite d'après Amiard-Triquet et al. (2015))

Aux échelles sub-individuelle et individuelle, les biomarqueurs d'effets sont définis comme des mesures biochimiques, physiologiques ou des traits d'histoire de vie dont l'état et le fonctionnement sont impactés par l'action du ou des xénobiotiques. Certains biomarqueurs d'exposition, comme l'AChE par exemple, sont également considérés comme des biomarqueurs d'effets. Dans le cas de l'AChE en effet, son activité est perturbée sous l'effet de substances neurotoxiques (Garric et al., 2010). Des mesures de comportement telles que le taux d'alimentation, de mobilité et des traits de vie (i.e. taux de croissance, reproduction, survie) peuvent témoigner d'altérations biologiques. Mis en relation avec la contamination interne ou celle du sédiment, ils permettent de mettre en évidence un probable effet stressant de la pollution à l'échelle de l'individu. **Les réponses biologiques sélectionnées pour cette thèse sont d'origine biochimique (i.e. activité de l'AChE), physiologique (i.e. taux d'ingestion chez *D. magna*) et plus largement propres aux traits d'histoire de vie (i.e. taux de reproduction, croissance individuelle et survie).**

Les effets sur les populations et communautés peuvent être discutés, modélisés au regard de certains résultats au niveau de la reproduction (population) (Forbes et Calow, 2002) et des

concentrations internes en contaminants potentiellement bio-amplifiables dans le réseau trophique (communauté) (Geiszinger et al., 2009). De plus, l'étude des compositions des communautés peut mettre en évidence des changements progressifs de communautés, des plus sensibles aux plus résistantes aux pressions chimiques (Sabater et al., 2007; Tlili et al., 2016). Néanmoins, comme évoqué précédemment, les relations robustes de causes à effets des contaminants sont plus délicates à identifier sur ces processus biologiques que sur ceux à plus court terme comme les effets individuels.

Il est primordial d'opter pour une approche à plusieurs niveaux combinant quantification de la contamination dans le sédiment, information sur sa biodisponibilité et réponse biologique pour une bonne compréhension de l'impact écotoxique de la multi-contamination des sédiments en ZL, tout comme il est important de coupler des approches de laboratoire et de terrain. En effet, lorsqu'elles sont effectuées en laboratoire, les mesures sur le biote ne permettent pas d'anticiper des effets environnementaux modulatoires sur l'exposition et l'effet de la contamination du sédiment, alors que, mesurées sur le terrain, il devient délicat de discerner avec précision l'effet lié à une exposition aux contaminants et les effets liés à d'autres stress sur la réponse biologique. Pour ces raisons, il peut être pertinent de coupler mesures en laboratoire et mesures sur le terrain.

III.3.2. Les démarches d'évaluation de l'écotoxicité

a. Essais en laboratoire

Ils permettent de mettre en évidence des potentiels impacts écotoxiques sous paramètres abiotiques (e.g. température, luminosité, oxygène) et biotiques (e.g. organismes, première exposition ou non à la contamination) contrôlés. **L'écotoxicité des sédiments littoraux a été évaluée dans ce travail au travers d'essais en microcosme de laboratoire selon une approche matrice, par le prélèvement de sédiments naturels multi-contaminés sur le terrain et l'exposition d'une ou plusieurs espèces aquatiques** (AFNOR, 2014a, 2014b; Clément, 2006) (Figure 11.A). Ils peuvent également se faire à plus large échelle sous forme de mésocosmes (Caquet et al., 2000). Les tests en laboratoire peuvent être conçus pour évaluer la toxicité ou mettre en lumière des mécanismes simples d'impact des polluants des sédiments. Malgré tous les efforts mis en œuvre dans certaines études pour simuler les conditions réelles, la diversité des paramètres entrant en jeu *in situ* dans l'impact de la contamination de la ZL sur l'écosystème ne peut être reproduite en laboratoire (Fetters et al., 2016; Mayer-Pinto et al., 2010).

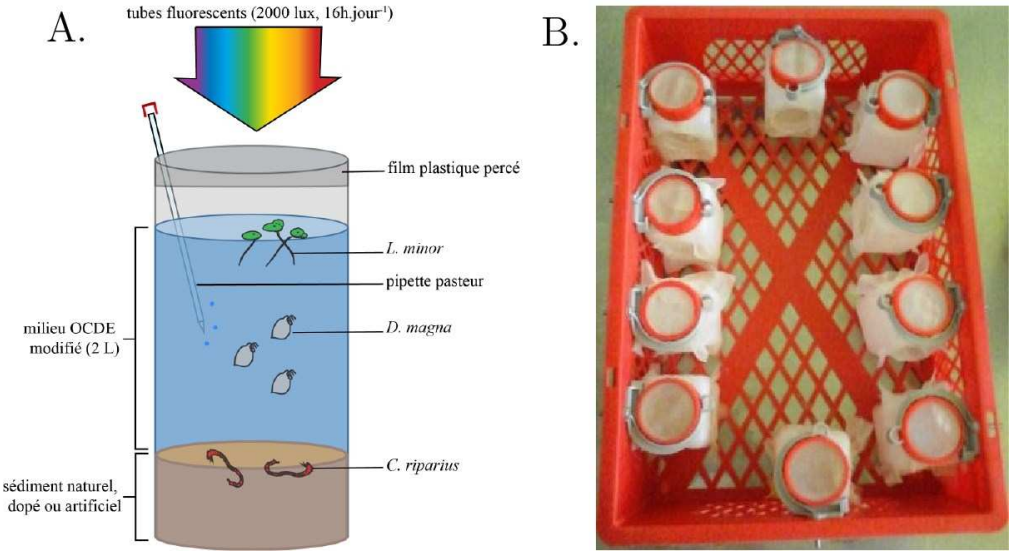

Figure 11. Dispositifs d'exposition des organismes de laboratoire à la contamination sédimentaire, en bioessais de laboratoire (A) et par encagement in situ *(B).*

b. Expérimentations et suivis in situ

Les travaux *in situ* pour l'évaluation de l'écotoxicité des sédiments littoraux ont consisté dans cette thèse en l'exposition d'organismes de laboratoire par encagement (Figure 11.B) **ou le prélèvement de matrices biotiques et abiotiques autochtones.** L'encagement a pour avantage d'exposer des organismes indemnes de contamination significative et dont on peut maîtriser le temps d'exposition par rapport au cycle de vie (e.g. émergence, reproduction) susceptibles d'influencer l'impact écotoxique du milieu d'étude. En revanche, l'analogie des réponses observées chez ces organismes avec celles du biote autochtone doit se faire avec précaution puisque le temps et l'historique d'exposition ne permettent pas toujours de mettre en évidence des effets d'acclimatation que l'on pourrait observer sur des organismes exposés en permanence à la contamination. L'étude d'organismes autochtones comme bio-indicateurs de la contamination et de l'écotoxicité de la zone littorale peut alors s'avérer pertinente, mais nécessite, comme pour l'exposition en laboratoire, un choix judicieux des organismes d'étude.

c. Choix des organismes d'étude

Une espèce est considérée comme bioindicatrice de la pollution d'un milieu si elle reflète le niveau de contamination d'un environnement et représente l'impact de cette pollution sur un habitat, une communauté ou un écosystème au sein du milieu (Gerhardt, 2002). Les indices biologiques lacustres utilisant les macro-invertébrés se basent sur l'abondance d'espèces indicatrices pour évaluer l'impact des pressions anthropiques sur la ZL lacustre (Lang, 2009; Verneaux et al., 2004). Entre autres, les bivalves peuvent également s'avérer de bons bioindicateurs de la contamination du milieu aquatique puisqu'ils sont 1) sédentaires, 2) faciles à identifier, 3) souvent présents en forte densité en zone littorale, 4) largement distribués sur des aires géographiques étendues, 5) caractérisés par une masse relativement importante (~0.5 g MS / ind) et d'une durée

de vie suffisamment longue (> 1 an) permettant d'être intégrateurs de la contamination. Pour ces raisons, les bivalves ont été utilisés dans la biosurveillance de grands projets internationaux tels que le Mussel Watch Program (Goldberg, 1986; Krishnakumar et al., 2018). **Dans nos travaux, la contamination de l'espèce autochtone et invasive *Corbicula fluminea* (Figure 12-A) a été étudiée.** Ce filtreur microphage est exposé aux polluants, dissous ou particulaires, à l'interface eau-sédiment.

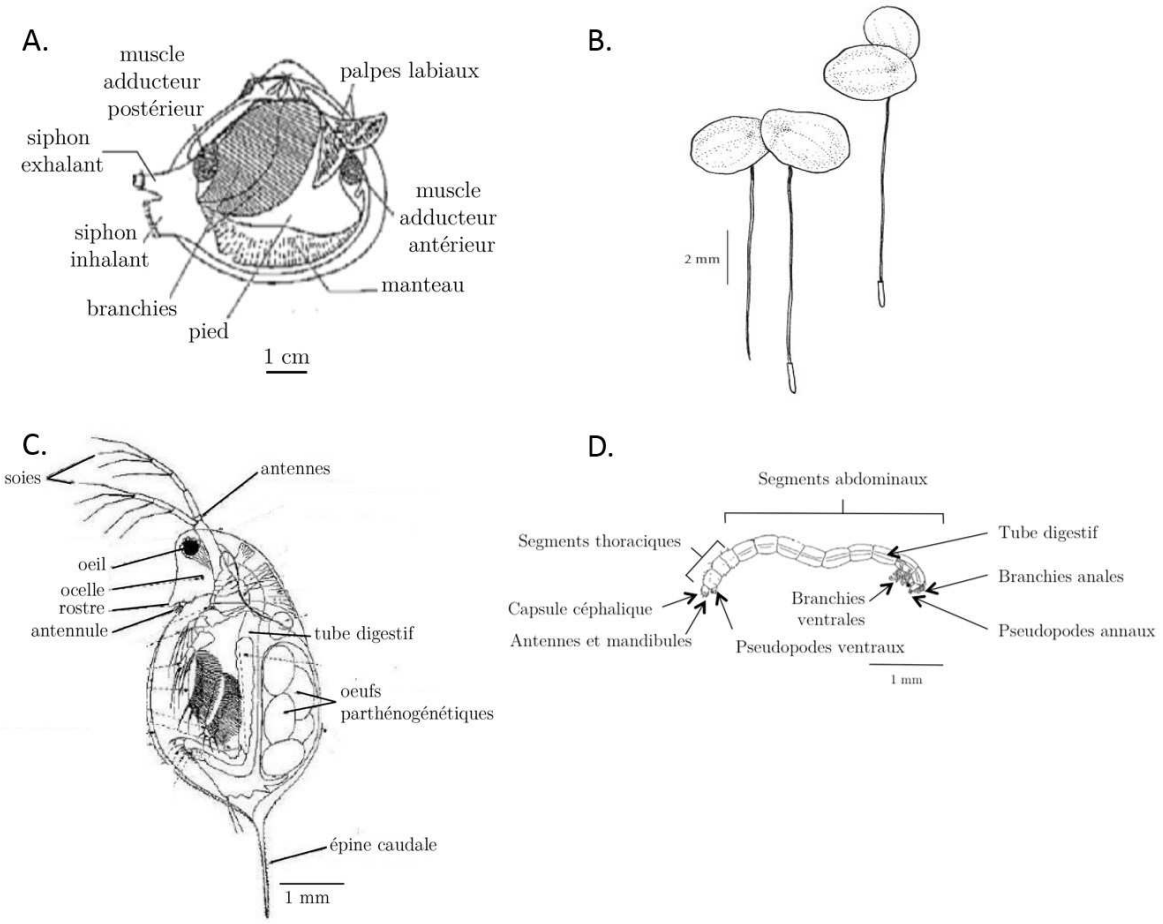

Figure 12. Schémas des organismes sélectionnés dans ces travaux ; (A) Anatomie des principaux organes de C. fluminea *après ablation du lobe droit du manteau (modifié d'après Ciutat (2003)), (B) colonie de L. minor (modifié d'après "E-Flora BC Atlas Page,"), (C) anatomie de* D. magna *(modifié d'après Amoros (1984)) et (D) larve de* C. riparius *(modifié d'après Bonnet (2000)).*

Des organismes de laboratoire peuvent également être utilisés pour des encagements *in situ,* tels que *Daphnia magna* (pélagique) ou *Chironomus* sp. (benthique). Ces derniers sont également utilisés comme macro-invertébrés modèles dans les tests de laboratoire, normés (AFNOR, 2010, 2014a) ou non (Clément, 2006; Lamonica et al., 2016). Les principaux critères selon lesquels un organisme est un modèle biologique approprié pour un test écotoxicologique sont les suivants (Amiard-Triquet et al., 2015) :

- grande répartition géographique et à un niveau clé des réseaux tropiques pour une grande pertinence écologique,
- durée du cycle de vie adaptée à la durée d'exposition du test (e.g. tests d'émergence ou de reproduction),
- grande capacité à accumuler les polluants,
- voie d'exposition permettant d'informer sur la toxicité d'un compartiment ou d'une fraction de la contamination (e.g. compartiment pélagique ou fraction dissoute de la contamination),
- facilité d'élevage.

Pour ces travaux, trois organismes de laboratoire ont été sélectionnés ; *Lemna minor, Daphnia magna* et *Chironomus riparius*. *L. minor* (Figure 12.B) est un macrophyte flottant permettant l'étude de la toxicité de la fraction dissoute de la contamination sédimentaire transférée à la colonne d'eau et susceptible d'impacter la flore aquatique. La sélection de *D. magna* (Figure 12.C) donne lieu à un éventail conséquent de mesures sur l'individu telles que la survie, la croissance, la reproduction et l'ingestion algale. L'exposition de ce microcrustacé zooplanctonique aux contaminants se fait principalement *via* la colonne d'eau, sous forme dissoute ou particulaire, bien qu'il lui arrive d'ingérer des particules à la surface sédimentaire. Les larves de *C. riparius* (Figure 12.D) sont utiles pour évaluer la toxicité du sédiment brute par contact direct, ingestion de l'eau interstitielle (Adams, 1985) et de l'eau de surface chargée en particules sédimentaires (Baker et Ball 1995). A eux trois, ces organismes représentent des niveaux trophiques différents : producteurs, consommateurs primaires et détritivores.

L'ensemble des démarches et outils d'évaluation de l'écotoxicité des sédiments littoraux utilisés dans cette thèse sont résumés dans la Figure 13.

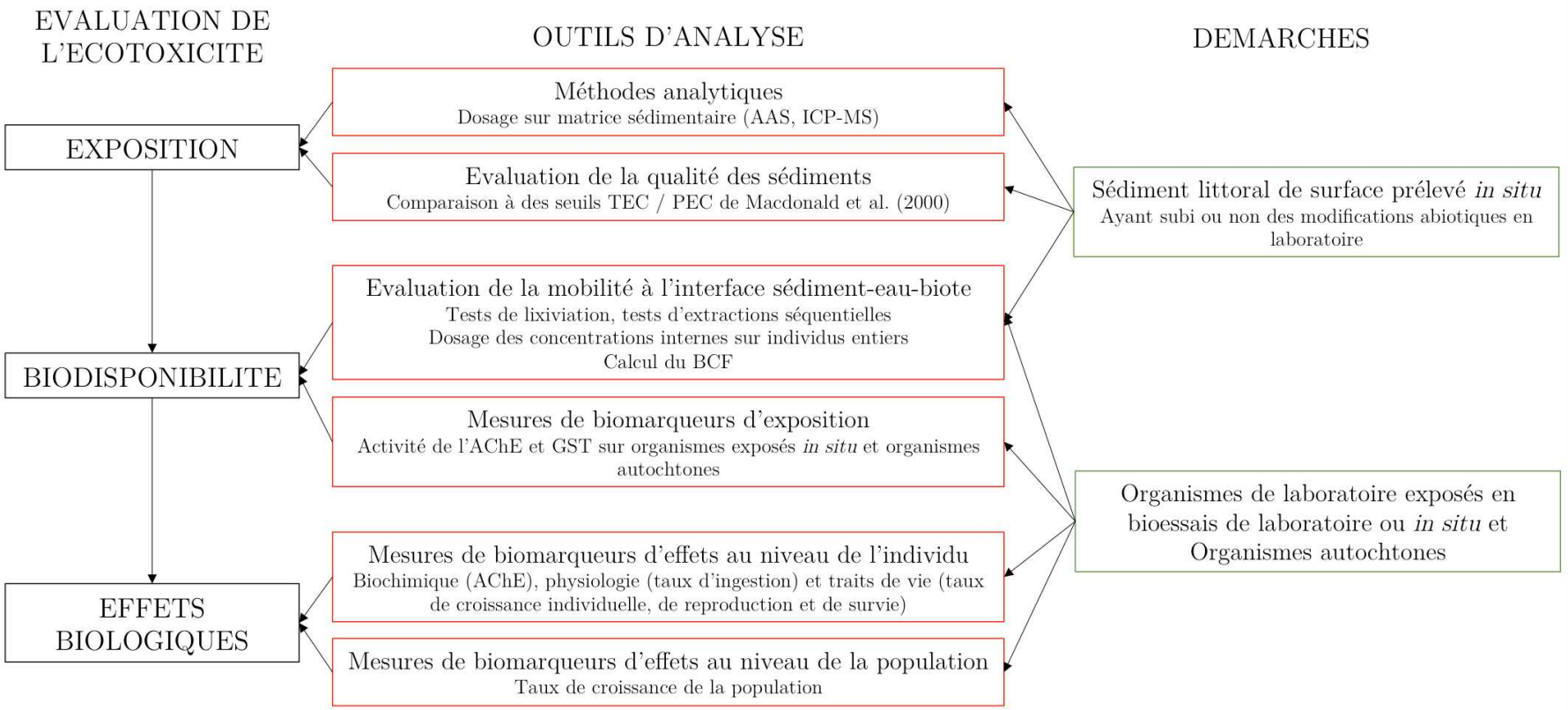

Figure 13. Schéma des démarches et outils d'analyse de l'écotoxicité des sédiments littoraux utilisés dans cette thèse.

IV. Structuration du manuscrit

Ce manuscrit se divise en deux parties principales, elles-mêmes décomposées en Chapitres construits sur la base d'articles scientifiques (Figure 14).

La **Première Partie** porte sur l'évaluation de la contamination et de son écotoxicité sur l'ensemble de la zone littorale lacustre. Le **Chapitre 1** évalue l'hétérogénéité spatiale de la contamination sédimentaire littorale et des réponses du biote exposé. Ces résultats soulèvent ainsi les enjeux d'étudier la contamination littorale lacustre. Les **Chapitres 2 et 3**, portant respectivement sur les lacs du Bourget et d'Annecy, utilisent des outils d'analyses différents pour mettre en lumière l'influence des sources locales dans la contamination du sédiment (Chapitre 2) et du biote (Chapitre 3) littoral. Ils apportent des clés d'explication à l'hétérogénéité spatiale de la contamination à l'échelle littorale.

La **Seconde Partie** de thèse est consacrée à une échelle plus fine, celle de l'interface eau-sédiment, pour approfondir la notion de mobilité et de biodisponibilité des polluants dans la zone littorale. Le **Chapitre 4** évalue la réponse conjointe des organismes du compartiment benthique et pélagique à un gradient naturel de contamination des sédiments littoraux. Les derniers chapitres portent sur l'étude des changements de mobilité des contaminants sédimentaires sous l'influence du marnage en zone littorale. Le **Chapitre 5** traite de l'influence de l'assèchement et remise en eau du sédiment de surface en conditions contrôlées de laboratoire sur la mobilité des contaminants, alors que le **Chapitre 6** évalue *in situ* les effets des fluctuations du niveau d'eau sur la mobilité particulaire et dissoute des contaminants.

Ces deux parties sont suivies d'une discussion générale et de perspectives liées aux travaux réalisés.

En annexe sont présentées différentes fonctions en langage R destinées à faciliter l'analyse des données de contamination.

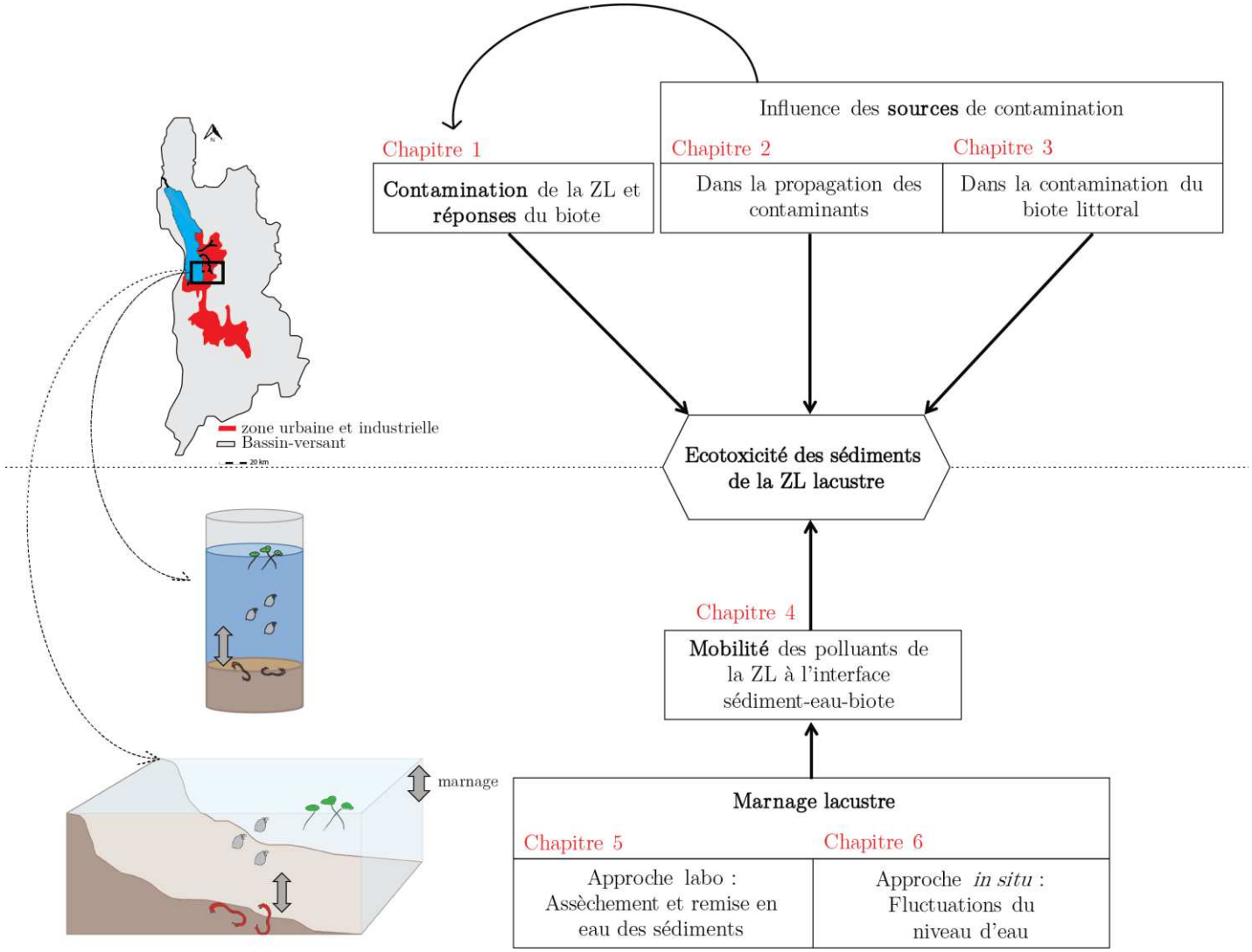

Figure 14. Schéma synoptique de la structuration de la thèse avec l'agencement des chapitres.

V. Littérature

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PARTIE I

Evaluation de la contamination et de l'écotoxicité des sédiments à l'échelle du littoral lacustre

La vision du « lac microcosme » de Forbes (1926) selon laquelle le lac est une entité isolée de son environnement a aujourd'hui évolué (Hansson et al., 2013). Les lacs sont directement impactés par les modalités de gestion de leur bassin-versant en termes de flux en nutriments et micropolluants. Le périmètre d'étude du fonctionnement lacustre s'est par conséquent progressivement élargi à l'échelle du bassin versant (Jennings et al., 2003; Liu et al., 2015; Pace et al., 2004; Whitman et al., 2006). Pour améliorer la qualité écologique des masses d'eau, des gestions intégrées des rejets en azote et phosphore au lac par le bassin-versant s'opèrent pour les grands lacs (Schindler, 2006). La maîtrise des rejets en micropolluants néanmoins est plus délicate compte tenu de la multiplicité des sources et des modalités d'entrée au lac.

L'objectif de cette première partie est de caractériser la multi-contamination sédimentaire de la zone littorale lacustre du lac du Bourget afin d'évaluer dans un premier temps si son hétérogénéité spatiale conduit à un risque écotoxicologique variable (Chapitre 1).
Puis la variabilité des profils de contamination du sédiment (Chapitre 2) et du biote autochtone (Chapitre 3) le long du littoral du lac du Bourget et d'Annecy est étudiée dans le but d'améliorer la compréhension sur l'implication des sources locales dans l'hétérogénéité de la pollution littorale.

Chapitre 1

Evaluation de la multi-contamination et de l'écotoxicité associée des sédiments littoraux lacustre ; le cas du Lac du Bourget

1. Démarche générale

Ce chapitre fait état de la multi-contamination des sédiments de surface du littoral du lac du Bourget et de leur écotoxicité. Ce travail s'est concentré sur 10 sites et 3 familles de contaminants ; 6 ETM, 15 HAP et 7 PCB. L'évaluation de l'écotoxicité s'est faite au travers d'une évaluation du risque écologique dite « rétrospective », c'est-à-dire qu'elle évalue la toxicité de la multi-contamination existante pour les organismes de la ZL (Suter II, 2016; van der Oost et al., 2003).

Dans cette étude, l'approche d'évaluation du risque écotoxicologique intègre à la fois (Figure 15) :

- la comparaison des concentrations sédimentaires aux PEC de MacDonald et al. (2000),
- des mesures d'exposition *via* l'évaluation des activités AChE et GST d'organismes de laboratoire exposés par encagement (*D. magna*) et d'organismes benthiques autochtones (*C. fluminea* et chironomes),
- des mesures d'effets *via* une exposition de *D. magna* en microcosme de laboratoire aux sédiments littoraux prélevés.

Pour chaque site, un quotient de PEC moyen (mean PEC quotient) a été calculé, donnant une première indication sur le degré de toxicité de la multi-contamination. L'exposition et les effets observés/mesurés sont susceptibles d'être influencés par d'autres paramètres que cette multi-contamination sédimentaire, surtout sur le terrain (e.g. variables environnementales abiotiques, stress lié à la ressource alimentaire, compétition ou prédation). Afin d'expliquer au mieux les relations entre contamination du sédiment et réponses biologiques observées, des régressions linéaires ont été effectuées entre les quotients de PEC moyens et les réponses enzymatiques d'une part, les réponses des traits de vie de *D. magna* exposées au laboratoire d'autre part. Dans ce chapitre, il s'agit donc (1) d'évaluer d'une part la différence inter-sites de la contamination sédimentaire ainsi que des réponses biologiques entre les sites littoraux et (2) de préciser le lien entre contamination sédimentaire et réponses biologiques sur des gradients croissants de contamination (Figure 15).

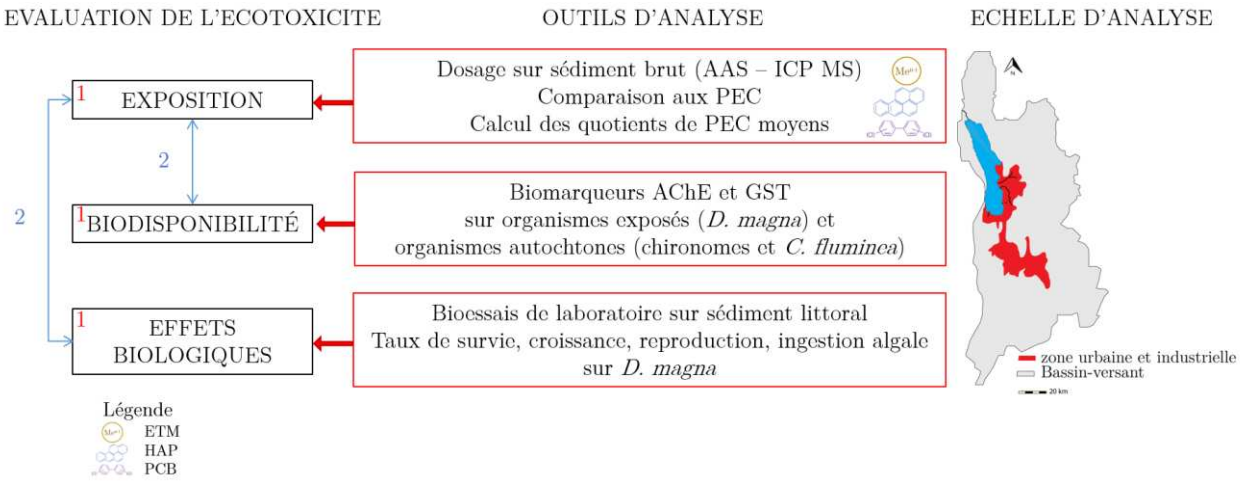

Figure 15. Schéma récapitulatif des outils et de l'échelle d'analyse pour l'évaluation de l'écotoxicité dans l'Article 1. Les chiffres 1 et 2 font référence aux deux étapes d'analyses abordées dans le texte ci-dessus.

2. Article 1 - Multi-contamination (heavy metals, polychlorinated biphenyls and polycyclic aromatic hydrocarbons) of littoral sediments and the associated ecological risk assessment in a large lake in France (Lake Bourget)

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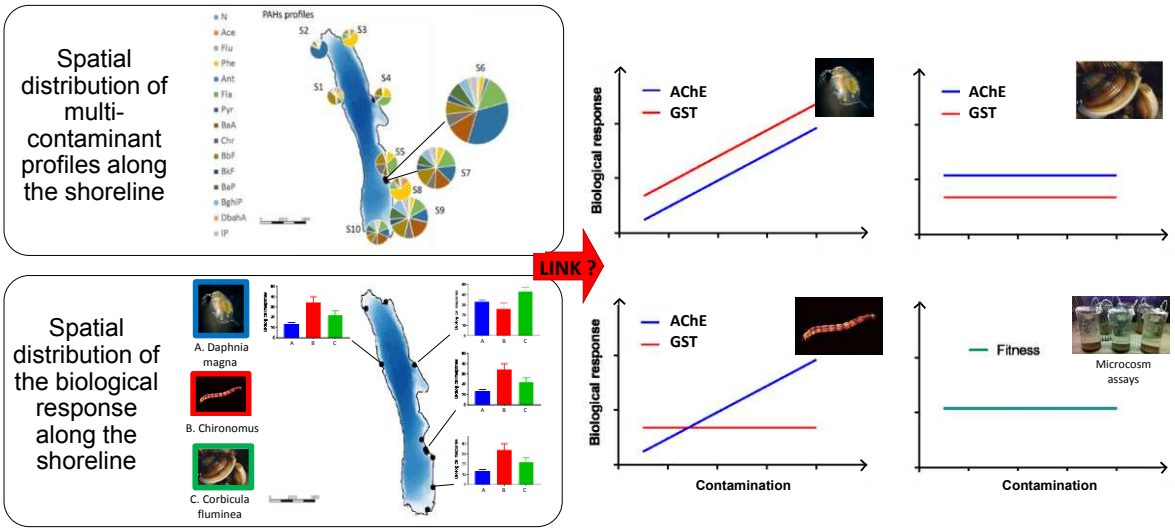
Highlights

- Contamination showed spatial heterogeneity in the littoral of a large French lake
- The laboratory and field biological responses spatially differed along the littoral
- Link between chemical and biological status depended on study endpoint and organism
- Littoral compartment should be considered when assessing lake ecological risk

Graphical Abstract



Abstract

The lake littoral sediment is exposed to a large array of contaminants that can exhibit significant spatial variability and challenge our ability to assess contamination at lake scale. In this study, littoral sediment contamination was characterized among ten different sites in a large peri-alpine lake (Lake Bourget) regarding three groups of contaminants: 6 heavy metals, 15 polycyclic aromatic hydrocarbons and 7 polychlorinated biphenyls. The contamination profiles significantly varied among sites and differed from those previously reported for the deepest zone of the lake. An integrative approach including chemical and biological analyses was conducted to relate site contamination to ecological risk. The chemical approach consisted in mean PEC quotient calculation (average of the ratios of the contaminants concentration to their corresponding Probable Effect Concentration values) and revealed a low and heterogeneous toxicity of the contaminant mixture along the littoral. Biological analysis including both laboratory (microcosm assays) and *in situ* (Acetylcholine Esterase (AChE) and Glutathione S-Transferase (GST) activity measurements) experiments highlighted significant differences among sites both in the field and in laboratory assays suggesting a spatial variation of the biota response to contamination. Linear regressions were performed between mean PEC quotients and biological results to assess whether littoral ecological risk was explained by the contamination profiles. The results highly depended on the study benthic or pelagic compartment. Regarding autochthonous *Corbicula fluminea*, no significant relationship between mean PEC quotients and biomarker activity was found while a significant increase in AChE was observed on autochtonous chironomids, suggesting different stress among benthic organisms. Both AChE and GST in caged pelagic *Daphnia magna* showed a significant positive relationship with mean PEC quotients. This study underlines the importance of accounting for spatial variations in lake littoral sediment contamination and the need for performing an integrative approach coupling chemical, field and laboratory analyses to assess the ecological risk.

Keywords

Pollutant mixture, microcosm assays, biomarker, trace metallic element, PAH, PCB.

Introduction

Chemical contamination is a major threat on ecosystems worldwide (Bernhardt et al., 2017). As receiving environments, freshwaters and especially lakes collect and accumulate a large array of contaminants that can significantly alter their health (Malaj et al., 2011). Chemical contamination has traditionally been assessed by considering deep sediment (Roussiez et al., 2006). Despite the fact that these deep sediments can efficiently show contamination and are suitable for determining the historical pollution of lakes (Fernández et al., 2000; Naffrechoux et al., 2015a), they may not be representative of the spatial heterogeneity of the contamination at the lake scale. Spatial variations of contaminant contents have been measured at the global scale (Marvin et al., 2004; Suresh et al., 2012). Such spatial variations are expected to occur in the littoral zone in particular because of its proximity to local sources of pollution inputs (Roussiez et al., 2006). Consequently, contamination in lake littoral sediments consists of a complex mixture of numerous chemicals reflecting the multiplicity of point sources and inducing differential ecological risks along the shoreline.

From this perspective, a widely used approach combining chemical screening, ecotoxicological tests and ecological surveys named the Triad approach, which was first proposed by (Long and Chapman, 1985), has been shown to provide robust assessments of ecological risk (Chapman et al., 2002; De Castro-Català et al., 2016; Marziali et al., 2017). Regarding the chemical approach, relevant tools can be used to compare the measured total content of individual chemicals in the sediment to ecotoxicological thresholds from the literature (e.g., the toxic unit approach, the comparison with consensus-based thresholds) (Höss et al., 2011; Long, 2006; MacDonald et al., 2011). However, since contaminants are present in various geochemical forms, bioassays are more appropriate to assess the bioavailable fraction of chemicals. Bioassays are usually conducted in a laboratory (e.g., microcosm assays) to study endpoints from the community to the sub-cellular level (Triffault-Bouchet et al., 2005). Additionally, *in situ* exposures can be performed to accurately observe the biological response in the conditions under which the fauna are exposed. Stress measurements can also be studied at a sub-cellular level using enzymatic biomarkers to provide information about the effects of contaminants (Capela et al., 2016). Among these, Acetylcholinesterase (AChE) is largely used as a biomarker of exposure to neurotoxic chemicals (Matozzo et al., 2005). It has been demonstrated that AChE activity in aquatic benthic invertebrates is mainly inhibited by carbamates (Alves et al., 2002) and organophosphorous compounds (Doran et al., 2001). However, as many other compounds affect the neurotoxicity of organisms, AChE activity can be impacted by other chemicals, such as heavy metals and persistent organic pollutants (Devi and Fingerman, 1995; Diamantino et al., 2000; Frasco et al., 2005; Guilhermino et al., 1998; Payne et al., 1996; Tilton et al., 2011). Another commonly studied biomarker is Glutathione S-transferase (GST), the activity of which is used for the detoxification of alkylating agents. An increase in this activity can thus be seen as a response to an oxidative stress following exposure to toxic compounds (Habig et al., 1974).

Lake Bourget is the largest natural lake in France. Its preservation is of great concern for economic reasons (tourism, drinking water resource), and the ecological status of the lake has thus been largely studied (Berdjeb et al., 2011; Jacquet et al., 2005). Past studies have observed the presence of several contaminant families, such as heavy metals and organic pollutants (PAHs, PCBs), in offshore sediments (Jung, 2009; Jung et al., 2008; Naffrechoux et al., 2015). In this study, we aimed to assess the spatial variability at the littoral scale of this contamination and the associated ecological risk by using an integrative chemical and biological approach, including laboratory microcosms and biomarker (AChE and GST) activity measurements. By comparing these results to historical data obtained from the deep zone, this work intends to provide the first contribution to comparing littoral versus offshore sediment analyses.

Materials and Methods

1. Study sites

Lake Bourget is located in Savoy, on the northwest edge of the French Alps (45°43'N, 5°52'E, Figure 1), and is the largest natural lake in France with a surface area of 42 km^2. The average and maximum depths are approximately 81 m and 145 m, respectively. Lake Bourget currently has an oligo to meso-trophic state. The 560 km^2 catchment area of Lake Bourget is covered by forests (45 %), agricultural areas (22 %), grazing fields (12 %), urban areas (13 %) and water bodies (8 %) (Lake Bourget excluded) (Cisalb, 2009). Over the 61 municipalities of this catchment area, Chambéry and Aix-les-Bains are the two largest cities, with a combined population of 90,000 inhabitants. The Leysse, Tillet and Sierroz Rivers are the main lake tributaries. They both flow through urban, industrialized and rural areas. Specifically, the Leysse River runs through Chambéry city, and both the Tillet and Sierroz Rivers flow through the Aix-les-Bains conurbation. The north and northwest areas of the lake are less urbanized than the south and south-eastern areas, where the two largest cities are located. Forestry is predominant in the north, and steep-slope areas in the west limit urban expansion. Lake Bourget is bordered by a railway and roads from south to north along the eastern shore, and the Chambéry airport is located on the southern side of the lake, which may contribute to the littoral contamination.

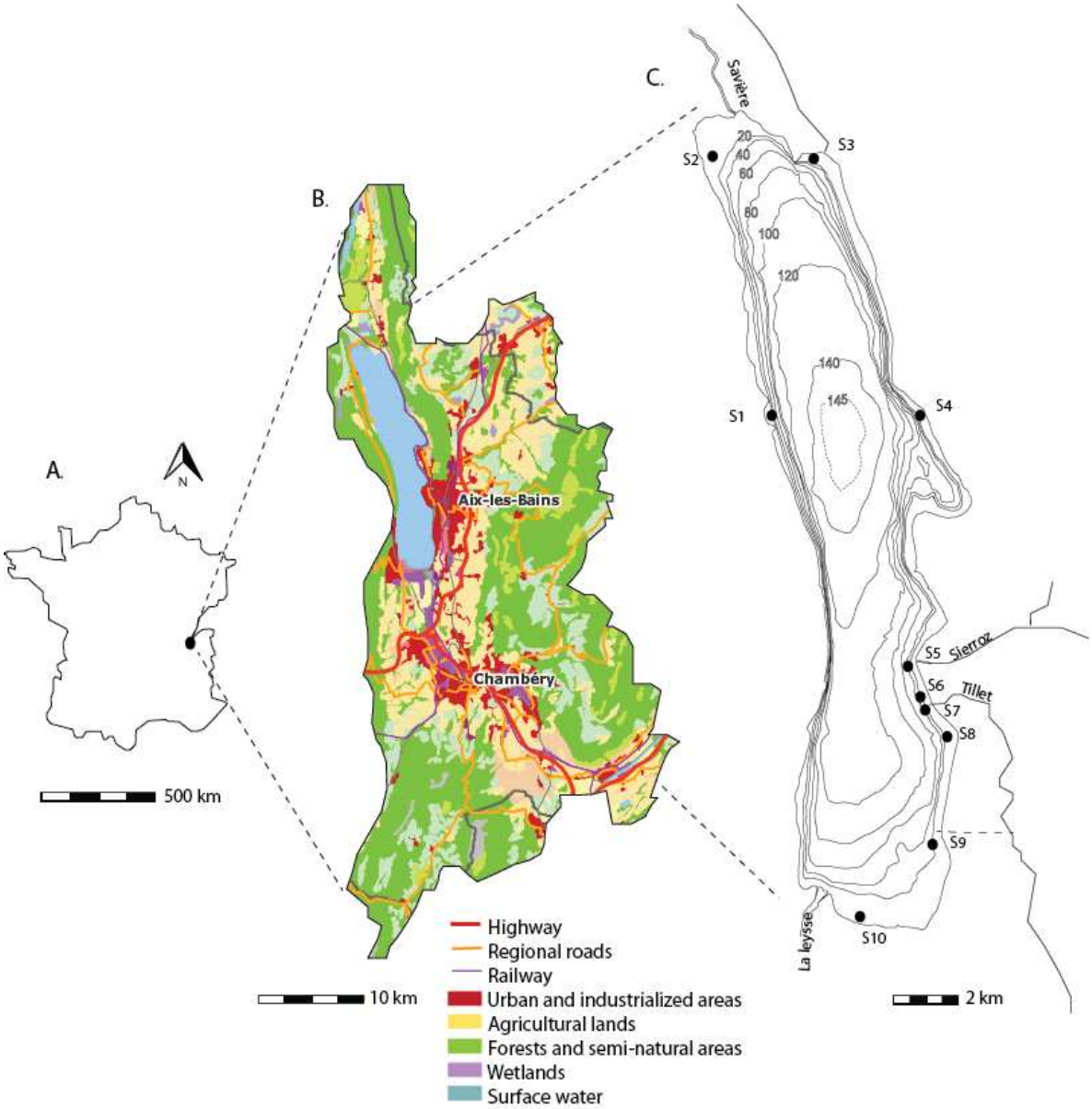


Figure 1. Lake Bourget, (a) localization, (b) land use of the catchment area (modified from ©CORINE Land Cover) and (c) localizations of the study sites. Blue triangles represent past study sampling sites (Chalhoub et al., 2013; Jung, 2009; Jung et al., 2008; Naffrechoux et al., 2015).

The sediment pollution in Lake Bourget was already investigated in terms of offshore sediments (Arnaud et al., 2006, 2004; Chalhoub et al., 2013; Herve, 1998; Jung et al., 2008, 2007; Naffrechoux et al., 2015) and those close to a tributary outlet (Chalhoub et al., 2013) (Table 1 and Figure 1-C).

Ten sites were selected along the littoral zone of the lake for sediment characterization (S1 to S10, Figure 1-C and Table S1). They were chosen according to the anthropogenic activities located on the shoreline or at the exit of the main tributaries. S1 was selected in a pristine area, where no point source was specifically identified, and S2, S3, S8 and S9 at nearby beaches. S5, S7, S9 and S10 are located close to a river outlet. S4 is adjacent to a railway and S6 to a car park. Six of these ten sites (S2, S3, S6, S8, S9 and S10) were selected for biomarker analysis on

autochthonous benthic macro-invertebrates and for exposure to caged laboratory *Daphnia magna*. These six sites were selected according to the large array of contamination intensity they exhibit and because they provided enough autochthonous macro-invertebrates for further analysis.

2. Sampling

At each site, surface (0-10 cm) sediment was collected at a water depth of 1.5 to 2.5 m using an Ekman grab. The sediment was then homogenized in a plastic tray and placed in pre-washed 2-L polyethylene bottles. The samples were transported to the laboratory in coolers and stored at -4 °C for 24 hours.
Benthic macro-invertebrates (*Corbicula fluminea* and chironomids) were also collected using an Eckman grab. The organisms were retrieved from the sediment using a sieving with a mesh-size of 500 µm and stored in 2-L polyethylene bottles at 4 °C prior to being frozen in liquid nitrogen and stored at -80 °C for subsequent analyses.

3. Sediment characterization

Sub-samples of each sediment were dried at 105 °C for 24 hours and sieved at 1600 µm, and the grain size measurement was performed by laser diffractometry (Malvern Mastersizer 2000G). The particle size distribution d50 (the grain size at which 50 % of the grains are coarser) and the distribution between clay, silt and sand fractions were obtained using the software package Gradistat V.8 (Blott and Pye, 2001). Each measurement was performed in triplicate.
Other sub-samples of sediment were dried at 105 °C overnight to determine the water content. The dried sample was then ignited at 550 °C for 4 hours to determine the loss on ignition (LOI) expressed as the weight percentage of the dry matter (Afnor, 2007).

4. Contaminants characterization

Sub-samples of the sediment were dried at 105 °C overnight and sieved at 2 mm. A total of 100 mg of the dried samples were then submitted to a mineralization step in a microwave oven (CEM/MARS Xpress, 2 mL ultra-pure HNO_3 + 6 mL ultra-pure HCl, 180 °C for 30 min, filtration with a 0.45-µm Whatman™ filter and dilution of the residue in 25 mL of ultra-pure water). Following acid digestion, the samples were analyzed for 6 heavy metals by atomic absorption spectrometry. Cd, Cr, Cu, Ni and Pb were analyzed in a graphite furnace at 1500 °C and Zn with an air-acetylene flame (Perkin Elmer, model PinAAcle 900T). The detection limits were Cd = 0.1 $\mu g.L^{-1}$, Cr = 0.040 $\mu g.L^{-1}$, Cu = 0.014 $\mu g.L^{-1}$, Ni = 0.07 $\mu g.L^{-1}$, Pb = 0.05 $\mu g.L^{-1}$, and Zn = 0.02 $\mu g.L^{-1}$.

Table 1. Past studies and present study results on Lake Bourget sediment contamination (in mg.kg^{-1} DM) and coefficient of variation when available in brackets (%). The CV in (Jung, 2009; Jung et al., 2008) was calculated between the G1, B2, L3, L4, L5 and L6 results for each contaminant.

				Content (mg.kg^{-1} DM)									
References	Sampling location	Sample name	Considered layer (cm)	Cd	Cr	Cu	Ni	Pb	Zn	sumPAHs	sumPCBs	TOC (%)	grain size (%)
Vernet and Favarger (1982)	-	6 m-long core	0-10	0.2	10	-	-	40	130	-	-	1.20	-
	-	L5-core	0-1.5	-	-	-	-	-	-	0.6	-	-	-
Arnaud (2003)	-	B16-core	0-0.6	-	-	-	-	33.2	-	-	-	-	-
			0.6-1.2	-	-	-	-	34.5	-	-	-	-	-
Naffrechoux et al. (2015a)	central deep point	core LDB09-P2-01	-	-	-	-	-	-	-	-	0.07	2.95	-
Chalhoub et al. (2013)	marina close to Tillet outlet	shovel sampling	bulk sediment	-	-	-	-	-	-	-	1.44	3	37.1 % silt
Jung (2009) Jung et al. (2008)	50 m-deep southeast	core LDB06-L5	0-1.0	-	-	-	-	-	-	0.56*	0.08		70.3% silt
		L3	0-1.0	-	-	-	-	-	-	0.3*	0.07	1.5	-
	central deep point	L4	0-1.0	0.4		16.4		12.1	64.8	0.69*	0.04	1.5	-
		core LDB06-L6	0-1.0	-	-	-	-	-	-	0.37*	0.08	1.5	-
		G1	0-1.0	0.35		18		7.5	53	0.46*	0.06	1.5	-
		B2 (central deep)	0-1.0	0.39		16		7	50	0.403*	0.05	1.5	-
	Central deep zone	Mean of G1, B2, L3, L4, L5 and L6 cores	0-1.0	0.38 (7 %)	-	16.8 (6 %)	-	8.87 (32 %)	55.93 (14 %)	0.46 (30 %)*	0.06 (26 %)	1.5 (0 %)	-
This study	littoral zone	Eckmann grab	0-10	0.09 (33 %)	37.6 (26 %)	3.86 (87 %)	8.21 (28 %)	4.47 (50 %)	42.89 (58 %)	0.488 (220 %)	0.018 (93 %)	LOI = 2.31 (41 %)	90.7 % sand

*sumPAHs corresponds, in this study, to the sum of Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenzo[ah]anthracene and Benzo[ghi]perylene.
"-" not available.

For organic pollutants, the sediment samples were dried with anhydrous sodium sulfate before extraction. Extraction was conducted by Accelerated Solvent Extraction (ASE200 - Dionex) using a mixture of acetone:dichloromethane (50:50) at 100 °C and 120 bar of pressure, for 3 cycles. Extracts of the sediment were concentrated to approximately 2 mL and evaporated under a gentle stream of nitrogen until almost a complete evaporation occurred. The extraction yield of the certified sediment BCR-536, which was extracted under the same conditions as the samples, indicated an extraction efficiency of 99 ± 13 % for the PCB-28.

The dry extracts were dissolved in heptane and passed through a silica gel chromatography column (2 g) for cleanup. PCBs and PAHs were eluted with 15 mL of a mixture of heptane:dichloromethane (98:2) followed by 10 mL of a mixture of heptane:dichloromethane (80:20). The samples were then treated with acid-activated copper granules to remove sulfur, filtered on 0.2 µm PTFE filters, and evaporated under a gentle stream of nitrogen. The dry extracts were dissolved in 200 µL of heptane before analysis. A total of 100 µL of each solutions was evaporated under a gentle stream of nitrogen and dissolved in 100 µL of methanol before the PAH analysis.

Seven PCB congeners (28, 52, 101, 118, 138, 153, 180) were analyzed on a Perkin Elmer gas-chromatography coupled with a Pulsed Discharge Ionization detector in the ECD mode. The gas chromatograph was equipped with a non-polar fused silica capillary column HP-5-MS (30 m, 0.25 mm i.d., 0.25 mm film thickness). Helium was used as the carrier gas (1.0 $mL.min^{-1}$). The oven temperature was set at 65 °C for 1 min, at 10 $°C.min^{-1}$ to 240 °C, at 5 $°C.min^{-1}$ to 320 °C and held at 320 °C for 5 min. The samples were injected in split/splitless mode at 300 °C. Individual congeners were identified by matching the retention times with the known PCB standard. The PCB fraction was spiked with PCB116-d5 as the internal standard. Calibration curves, using the internal standard, were realized to determine the PCB concentrations. The laboratory quality control consisted of period analysis of blanks and certified reference materials (BCR-536). The analytical results were blank-corrected. Briefly, the detection limits were on the order of 0.001 $µg.mL^{-1}$ for each of the PCB congeners. The method used for sediment analysis was validated by replicate (n = 14) analysis of reference sample BCR-536.

The 15 PAHs identified as priority pollutants by the US EPA (US EPA, 2011) were analyzed on a Perkin Elmer HPLC coupled with a fluorimetry detector and a C18 column (Optima5, 30m-MACHEREY NAGEL). Individual PAHs were identified by the retention times of matches with a known HAP standard. The calibration curve was realized for determining the PAH concentration.

5. Ecological risk assessment (ERA)

5.1. Chemical screening

The chemical approach of ERA, based on multi-contaminated sediments, was carried out by comparing the total element content with the corresponding sediment quality thresholds from the literature. In light of the multiplicity of sediment quality guidelines for freshwater ecosystems in the literature, we opted for the consensus-based probable effect concentrations (PECs) developed by (MacDonald et al., 2000a, 2000b). The PEC values correspond to the concentration above, in which harmful effects are expected to occur often. The mean PEC quotients, which consist of the arithmetic average of the ratios of the contaminants concentration to their corresponding PEC values, were calculated to assess the combined toxicity of the studied mixture of pollutants according to Long and MacDonald (1998) and MacDonald et al. (2000b). The mean PEC quotient for PCBs was calculated using the PEC value for the sum of the 209 congeners. Thus, the total concentration attributed to the 209 congeners in our study was calculated based on the sum of the 7 measured congeners multiplied by 4, which corresponds to the theoretical contribution of these congeners to Aroclor 1254 (Froescheis et al., 2000; Hoai et al., 2010). The PAHs were considered separately. Sediments were then predicted to not to be toxic for sediment dwelling organisms if the mean PEC quotients were below 0.1, potentially toxic if the mean PEC quotients fell into the range 0.1-0.5 and toxic if the mean PEC quotients exceeded 0.5 (MacDonald et al., 2000b).

5.2. Laboratory microcosm assays

D. magna was bred in a synthetic media (pH: 7.7, hardness: 60 mg $CaCO_3.L^{-1}$, alkalinity: 120 mg $CaCO_3.L^{-1}$, conductivity: 290 $\mu S.cm^{-1}$, phosphorous: 100 $\mu g.L^{-1}$, nitrogen: 1308 $\mu g.L^{-1}$, $FeEDTANa_2,6H_2O$: 109.4 $\mu g.L^{-1}$, oligo-elements and vitamins of M4 medium (Elendt and Bias, 1990)) at a density of 12-13 individuals.L^{-1}. Three days a week, neonates were removed from the beakers, and adults were fed with a suspension culture of *Pseudokirchneriella subcapitata*. Once a week, half of the media was renewed.

Sediment samples from S3, S6, S8 and S9 were selected for this test because of their wide pollution range. Wet sediment was sieved with a mesh-size of 2 mm, and 250 g of it was placed in an acid-rinsed beaker in triplicate for each site. The microcosms were then prepared as described in (Lamonica et al., 2016). Ten neonates of *D. magna* under the age of 24 hours were introduced for a 21-day exposure. Survival, reproduction, growth size and ingestion rates were chosen as the study endpoints. The body length of neonates and exposed adults from the same cohort were measured using a binocular magnifier. The growth rate was calculated using the Von Bertalanffy formula (Eq.1) (Piner et al., 2016; von Bertalanffy, 1938), and expressed as day^{-1}.

$$L(t) = L\infty - (L\infty - L0).e^{-kt}$$

Eq.1: Von Bertalanffy equation, where L(t) is the length (mm) of the daphnid at time t (days), L∞ is the theoretical maximum length estimated at 5 mm in this study, L0 is the initial length (mm) of the daphnia, and k is the growth rate (day^{-1}).

The ingestion rate (Eq.2, (Fernández-Casalderrey et al., 1993; Gauld, 1951)) was expressed in $cells.daphnid^{-1}.h^{-1}$.

$$I = \left(\frac{V}{n} \times \frac{(\ln Co - \ln Ct)}{t} - \frac{\ln Co - \ln C't}{t}\right) \times \sqrt{Co \times Ct}$$

Eq.2: Calculation of the ingestion rate I ($cells.daphnia^{-1}.h.^{-1}$), where Co is the initial algal density ($cells.mL^{-1}$), Ct is the final algal densities in the presence of daphnids, C't is the final algal density in the control (no daphnids), n is the number of daphnia in the volume V (mL) and t is the duration of the test (h). The reproduction rate was calculated for each day, dividing the total number of counted neonates by the total number of living adults.

5.3. Biomarker analyses

The method described by (Ellman et al., 1961; Fisher et al., 2000) based on microtiter plates was used to measure the AChE and GST activities. The same protocol was used for all organisms, and only the amount of available biomass introduced per sample varied: five fourth-instar larvae per Eppendorf tube for the *chironomids*, twenty adult females for the *D. magna* and the adductor muscle of one adult for the clams (Beltran and Pocsidio, 2010). The absorbance values were obtained at 405 nm by spectrophotometry. The AChE activity was expressed in $mol.L^{-1}.min^{-1}.g\ protein^{-1}$.

For GST, we followed the method employed by (Callaghan et al., 2001), which was an adaptation of the protocol suggested by (Habig et al., 1974) for use in microtiter plates. We introduced the same amount of biomass as for the AChE analysis, with the exception that we introduced approximately 5 mg of wet gills instead of the adductor muscles for the *C. fluminea,* as GST enzymes were mainly located in gills while AChE is in the adductor muscles (Beltran and Pocsidio, 2010).

5.4. Fitness tests on caged *D. magna*

For the *in situ* exposure, twenty *D. magna* neonates were introduced in cages that consisted of 500 mL cubic polyethylene bottles that opened on 2 opposite faces and on the top (diameter = 6 cm). All apertures were covered with a 150 µm mesh. In each study site, the 10 cages were deployed in an open plastic basket (60 x 40 x 13 cm) that was deposited on the sediment at 1 m deep and ballasted with weights. After exposure, the organisms were carefully collected and transferred into 20-mL plastic pill boxes filled with 20 mL of the same synthetic media used for the breeding of *D. magna*, stored at 4 °C prior to being frozen in liquid nitrogen and stored at -80 °C for biomarker analyses.

6. Statistical analysis

Differences in sediment contamination among sites were assessed using coefficients of variation (calculated as the quotient between the standard deviation and the mean of element content in percentage) calculated for each heavy metal, the sum of the 7 PCBs and the sum of the 15 PAHs between the 10 sites and the Chi-square test based on contaminant profiles. A principal component analysis (PCA) based on log10-transformed total contaminant content was conducted to segregate the sampling sites according to their contamination. The relationship between the chemical and biological status was assessed using linear models performed between mean PEC quotients and biomarker results and between mean PEC quotients and microcosm assays. Statistical analyses as well as graphical displays were carried out using R 3.4.0 (R Core Team Development 2016).

Results

1. Structural characteristics of sediments

The sediments exhibited similar structural characteristics, with low LOIs ranging from 1.3 % to 3.8 %, (Table 2) and were mainly sandy (74.62 - 96.64 %). Nonetheless, the sediment samples collected in S5 and S7 were categorized as slightly gravelly sand.

Table 2. Main structural characteristics of sampled sediments from the ten study sites. The results are shown as the mean ± standard deviation (n=3) except for LOI (n=1).

Site	Sediment type					
	Sand (%)	Silt (%)	Clay (%)	d50 (µm)	LOI (%)	Textural group
S1	94.50 ± 1.27	5.21 ± 1.03	0.29 ± 0.25	215.34 ± 3.00	1.5	Sand
S2	74.62 ± 4.04	23.89 ± 3.67	1.50 ± 0.37	227.09 ± 12.48	3.8	Muddy Sand
S3	86.25 ± 0.48	12.74 ± 0.43	1.01 ± 0.05	252.94 ± 4.39	1.7	Muddy Sand
S4	93.24 ± 1.93	6.23 ± 1.72	0.53 ± 0.21	404.67 ± 12.93	1.8	Sand
S5	96.64 ± 1.64	3.03 ± 1.34	0.31 ± 0.27	255.68 ± 4.71	1.3	Slightly Gravelly Sand
S6	89.47 ± 2.34	9.98 ± 2.14	0.55 ± 0.20	253.50 ± 8.22	2.8	Muddy Sand
S7	92.13 ± 1.72	7.31 ± 1.54	0.53 ± 0.18	354.35 ± 5.25	2.0	Slightly Gravelly Sand
S8	95.20 ± 2.41	4.37 ± 2.04	0.42 ± 0.37	266.33 ± 7.39	2.4	Sand
S9	91.80 ± 1.69	7.70 ± 1.54	0.50 ± 0.15	278.90 ± 8.69	4.0	Sand
S10	92.97 ± 1.89	6.25 ± 1.71	0.78 ± 0.18	210.19 ± 5.54	1.8	Sand

2. Spatial heterogeneity of heavy metal, PAH and PCB contents in the littoral zone

The contamination profiles for each group of contaminants significantly differed between sites (Figure 2 and 3, Table S2 and Chi-square tests, p-value < 0.01), and both sums of the 15 PAHs and the 7 PCBs exhibited important spatial variations between the 10 sites, as indicated by their coefficients of variation (CVs) higher than 90 % (Table 1).

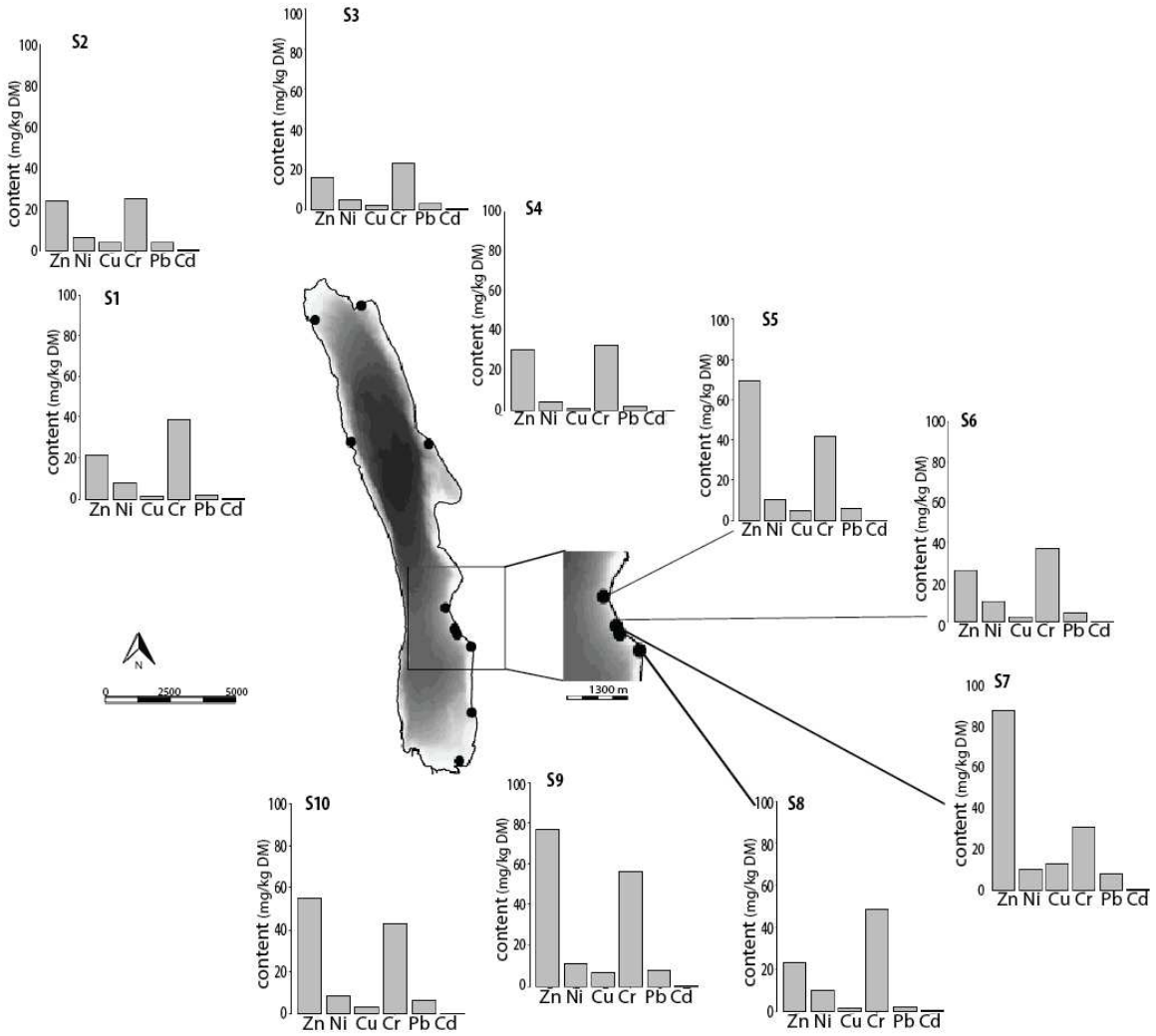


Figure 2. Mapping of heavy metal contents (mg.kg^{-1} DM) measured in the sediment of the 10 sites.

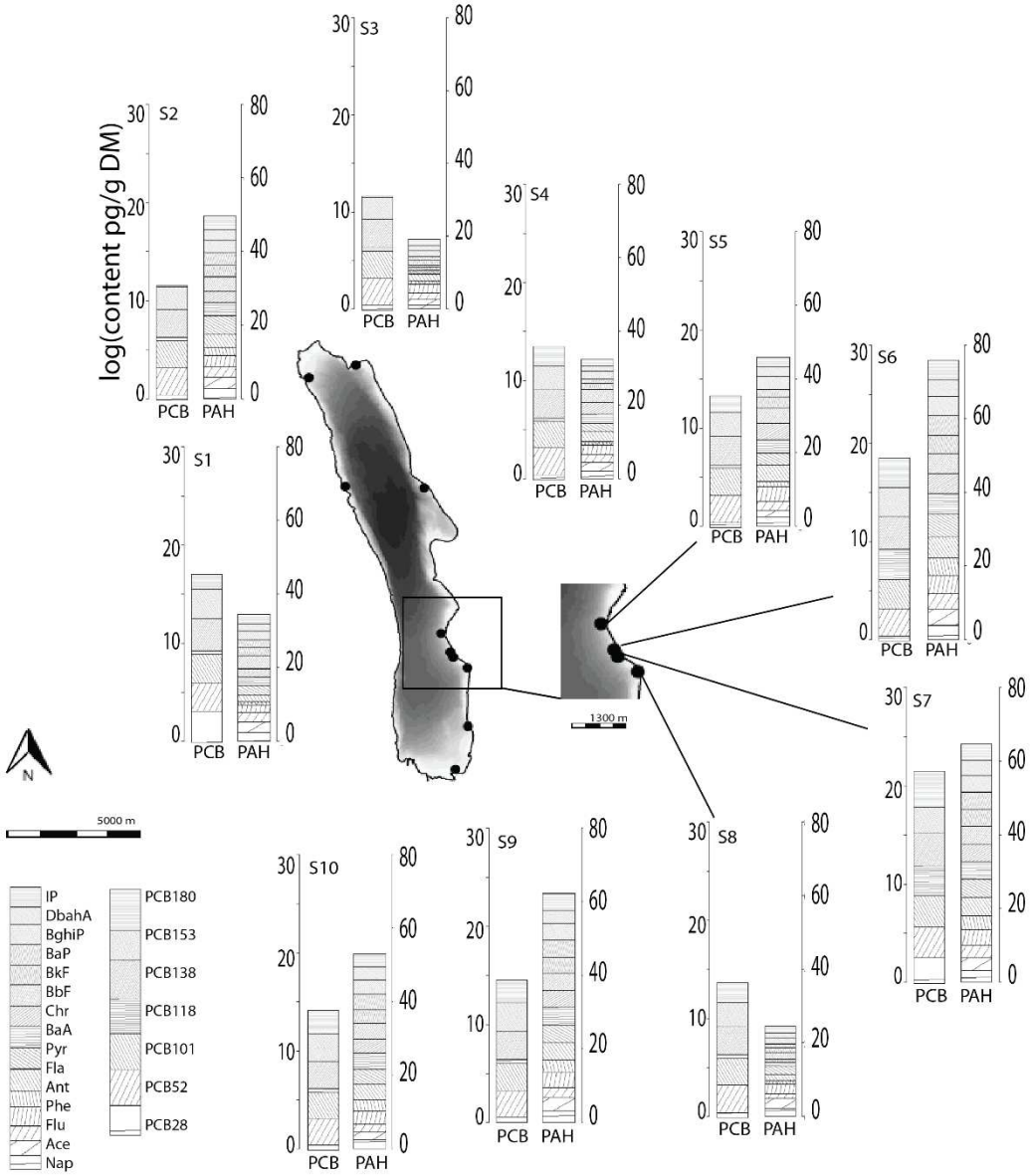


Figure 3. Mapping of organic pollutant contents measured in the sediment of the 10 sites. Left plots correspond to the sum of the 7 PCBs and the left Y-axis to the corresponding logarithm of the total contents (log_{10} pg.g^{-1} DM). Right plots correspond to the sum of the 15 PAHs and the right Y-axis to the corresponding logarithm of the total contents (log_{10} pg/g DM). Content, usually in μg.kg^{-1} DM in this article, was expressed in pg.g^{-1} to make this figure more readable.

The PCA conducted on the log10-transformed contents of the three contaminant families accounted for 80.5 % of the variation among sites (Figure 4). Most of the variation was supported by the PCA axis 1 (PC1), which accounted for 62.2 % of the total variation and highlighted a quantitative gradient from negative to positive PC1 scores. The contaminants associated with PC1 were mainly driven by PAHs, zinc, copper and lead (Table S3). In contrast, PC2 supported 13.1 % of the total variation and was mainly associated with variations in PCB concentrations, mostly congeners 28, 101, 138 and 52 (Table S3). The different sites were clearly scattered on

the PCA biplot, with S3, S8 and S4 exhibiting the most negative PC1 scores, which indicated that these sites were the less polluted regarding their multi-contamination profiles (Figures 2, 3 and 4). S5 and S10, and to a lesser extent S2, were characterized by an intermediate contamination in PAHs, as indicated by the PC1 scores close to 0 and a low contamination in PCBs. Nonetheless, the latter exhibited relatively high concentrations in Cr and Cd. The S9 contamination profile differed from the others by its particularly high contamination in cadmium and chromium. S6 was characterized by high positive PCA scores, indicating high concentrations of PAHs, which was confirmed by the profiles shown in Figure 3. S7 exhibited the highest concentrations of PCBs, and S1 had a particular PCB contamination, as it was the only site where PCB-28 was detected. The sediment in S10 was poorly contaminated by PCBs but had a particularly high content of chromium.

The linear regressions conducted between the PCA axis scores and both structural (i.e., grain size distribution and LOI) and spatial coordinates of the sites did not reveal any significant relationships.

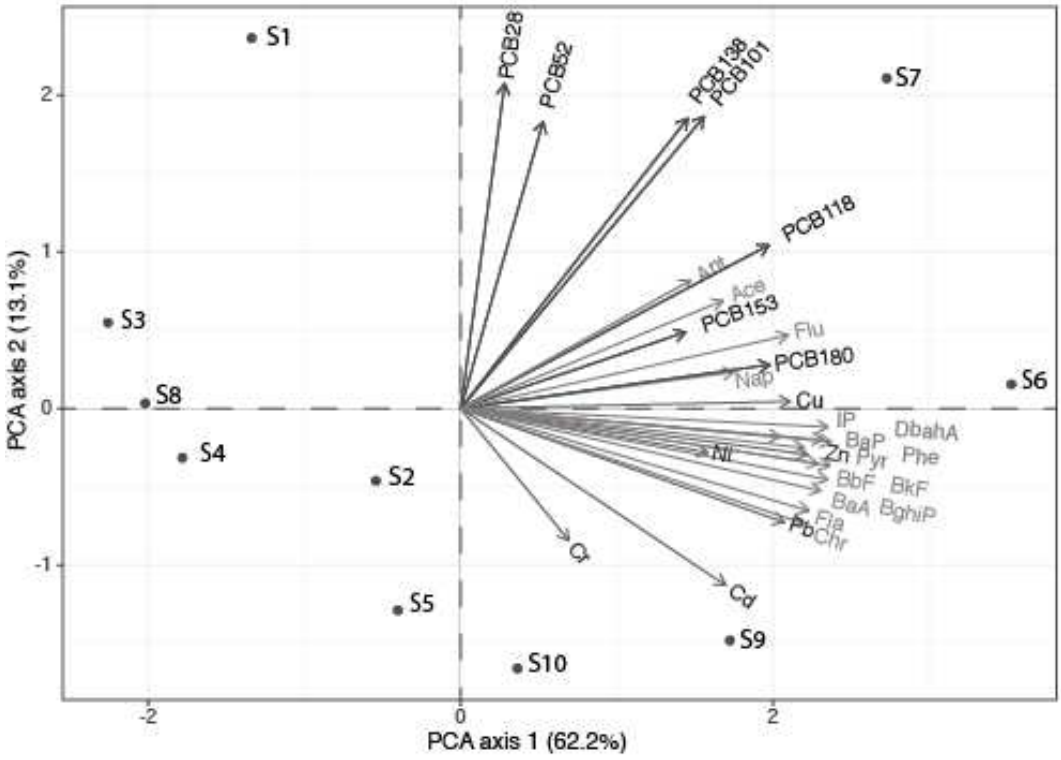


Figure 4. PCA biplot characterizing sites contamination. Studied parameters are mapped with arrows, while sampling sites are point-schematized. Black are PCBs, dark gray are heavy metals, and light gray are PAHs. Percentages in brackets refer to the proportion of variance supported by the different axes.

3. Spatial heterogeneity of ERA

3.1. Chemical screening

The mean PEC quotients decreased according the order of S7>S6>S9>S1>S10>S8>S5>S4>S2>S3 (Table 3). All mean PEC quotients were below 0.5. Nevertheless, the mean PEC quotient exceeded 0.1 in S6 and S7, which means that multi-contamination in this littoral sediment may be toxic for benthic macro-invertebrate fauna. The individual PEC quotients are also shown in Table 3. The chromium PEC quotients exceeded 0.1 in each site and were 0.5 in S9. The nickel PEC quotients also exceeded 0.1 in every site except in S4. The PCB PEC quotients exceeded 0.1 in S1, S6 and S7. Regarding PAHs, the element PEC quotients were all below 0.1, except in S6, where 8 out of 15 quotients exceeded 0.1 and one was 0.5.

Table 3. Individual PEC quotients calculated for each element in each sampling site and mean PEC quotient. Bold type indicates values between 0.1 and 0.5 and a probable toxic effect, bold type with a star indicates values over 0.5 and an identified toxic effect. The other values are under 100 and suggest an absence of toxic effect (Long and MacDonald, 1998; D. D. MacDonald et al., 2000a).

	Sites									
Contaminant	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Cd	0.008	0.014	0.010	0.024	0.020	0.028	0.024	0.014	0.024	0.022
Cr	**0.348**	**0.227**	**0.210**	**0.300**	**0.331**	**0.372**	**0.271**	**0.439**	**0.508***	**0.386**
Cu	0.009	0.027	0.011	0.008	0.017	0.031	0.085	0.010	0.042	0.019
Ni	**0.150**	**0.129**	**0.104**	0.085	**0.213**	**0.209**	**0.206**	**0.197**	**0.225**	**0.170**
Pb	0.015	0.032	0.021	0.014	0.036	0.045	0.062	0.016	0.058	0.051
Zn	0.047	0.053	0.034	0.067	0.057	**0.151**	**0.188**	0.050	**0.168**	**0.120**
sumPCBs	**0.160**	0.044	0.050	0.049	0.051	**0.179**	**0.343**	0.053	0.066	0.054
Nap	0.001	0.001	0.000	0.000	0.001	0.014	0.003	0.000	0.003	0.001
Ace	0.005	0.013	0.003	0.002	0.000	**0.173**	0.020	0.005	0.028	0.001
Flu	0.001	0.001	0.000	0.000	0.001	0.031	0.004	0.000	0.001	0.000
Phe	0.002	0.002	0.004	0.006	0.022	**0.175**	0.060	0.006	0.026	0.007
Ant	0.000	0.000	0.000	0.000	0.000	0.086	0.006	0.000	0.003	0.001
Fla	0.000	0.002	0.000	0.003	0.014	**0.228**	0.040	0.000	0.023	0.008
Pyr	0.000	0.067	0.000	0.000	0.001	**0.784***	0.053	0.000	0.032	0.009
BaA	0.000	0.003	0.000	0.000	0.006	**0.414**	0.079	0.000	0.071	0.022
Chr	0.000	0.001	0.000	0.001	0.013	**0.163**	0.033	0.000	0.026	0.007
BbF	0.000	0.001	0.000	0.000	0.001	0.016	0.006	0.000	0.005	0.001
BkF	0.000	0.000	0.000	0.000	0.000	0.008	0.002	0.000	0.002	0.000
BaP	0.000	0.002	0.000	0.000	0.000	**0.178**	0.033	0.000	0.030	0.008
BghiP	0.000	0.001	0.000	0.000	0.001	0.054	0.013	0.000	0.013	0.003
DbahA	0.001	0.005	0.000	0.000	0.003	**0.319**	0.076	0.000	0.027	0.018
IP	0.000	0.001	0.000	0.000	0.000	0.041	0.010	0.000	0.008	0.001
Mean PEC quotients	0.085	0.044	0.038	0.044	0.056	**0.166**	**0.171**	0.058	0.085	0.063

3.2. Biological laboratory screening

In the laboratory bioassays, a significantly lower survival rate was observed in S9 (Figure 5-A), and a significantly lower reproduction rate in S8 (mean reproduction rate = 1.42 ± 0.29 neonates.mother^{-1}.day^{-1}) and S9 (1.28 ± 1.24 neonates.mother^{-1}.day^{-1}) microcosms was observed compared to the control (3.52 ± 0.11 neonates.mother^{-1}.day^{-1}) (Figure 5-C, ANOVA, p-value < 0.05). The growth rate was only available for one replicate in the S9 beakers due to the high mortality, but this value was inferior to the other sediments and the control (0.0095 day^{-1} in S9 compared to 0.0279 day^{-1} in the control, Figure 5-B). No significant difference was observed when the ingestion rate endpoint was considered (Figure 5- D, ANOVA, p-value > 0.05).

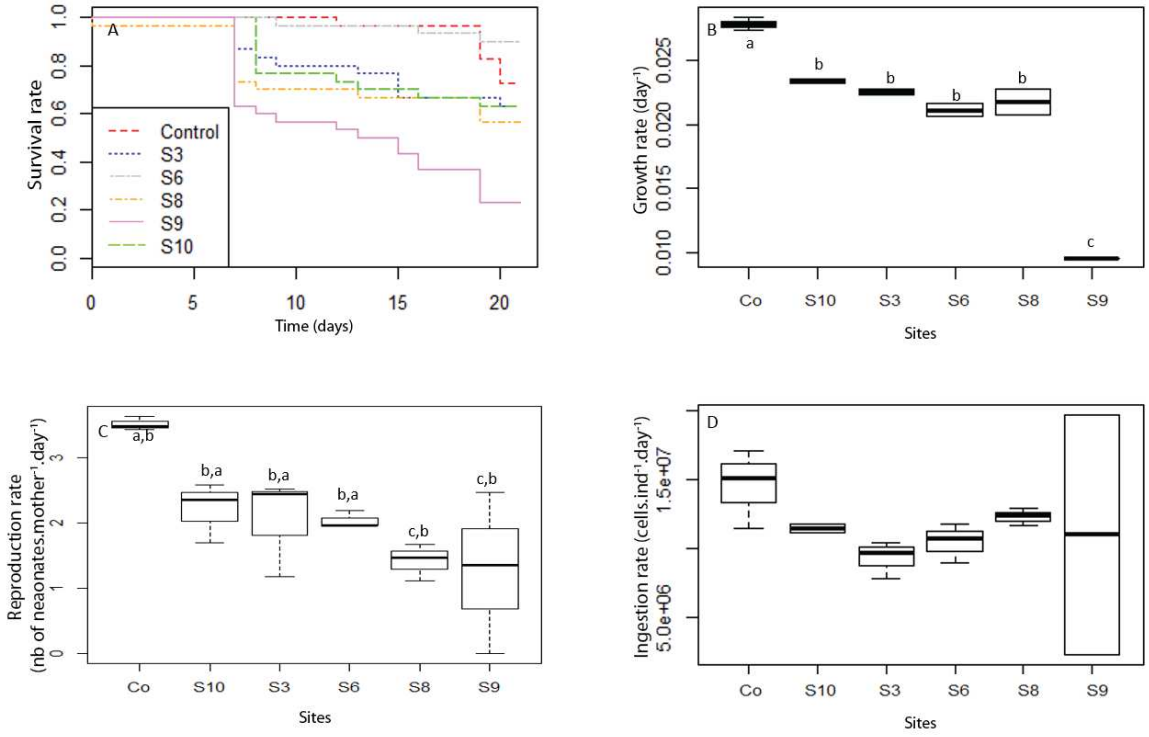


Figure 5. Bioassays results for cladocerans exposed to the different sediment samples, with (A) survival curves of cladocerans exposed to the different treatments, (B) growth rates (day^{-1}) according to the Von Bertalanffy formula, (C) Reproduction rates (total numbers of neonates per mother per day) and (D) mean ingestion rates (cells/ind/day) of daphnids of the 3 tests. Co means Control. Box-plots illustrate the median, 25 % and 75 % percentiles, minimum and maximum, and letters denote the significance between results.

3.3. Biological *in situ* screening

For *in situ* tests, the AChE activity was significantly higher (Figure 6-A, ANOVA, p-value < 0.05) in chironomids from S9 (15.21 ± 3.11 µmol.min^{-1}.g protein^{-1}) compared to S3 (6.28 ± 4.23 µmol.min^{-1}.g protein^{-1}) and S8 (4.45 ± 1.78 µmol.min^{-1}.g protein^{-1}), indicating that those two sites may exert more stressful conditions for benthic fauna. In contrast, there was no significant difference between sites in the GST concentrations and no significant correlation between AChE and GST values in chironomids (Figure 6-B, Pearson, p-value > 0.05). The results obtained from *C. fluminea* showed no significant difference between sites regarding the studied enzymatic activities (Figure 6-C and D). The AChE activity in the caged *D. magna* was significantly lower (Figure 6-E, ANOVA, p-value < 0.05) in S2 (mean AChE activity of 2.27 ± 0.20 µmol.min^{-1}.g protein^{-1}) and S3 (2.93 ± 0.78 µmol.min^{-1}.g protein^{-1}) compared to S6 (5.09 ± 0.40 µmol.min^{-1}.g protein^{-1}) and S9 (5.32 ± 1.00 µmol.min^{-1}.g protein^{-1}). Similarly, the GST activity was significantly lower in the *D. magna* (Figure 6-F, ANOVA, p-value < 0.05) in S2 (3.07 ± 0.17 µmol.min^{-1}.g protein^{-1}) and S3 (2.85 ± 0.26 µmol.min^{-1}.g protein^{-1}) compared to S6 (3.98 ± 0.25 µmol.min^{-1}.g protein^{-1}) and S9 (4.25 ± 1.32 µmol.min^{-1}.g protein^{-1}).

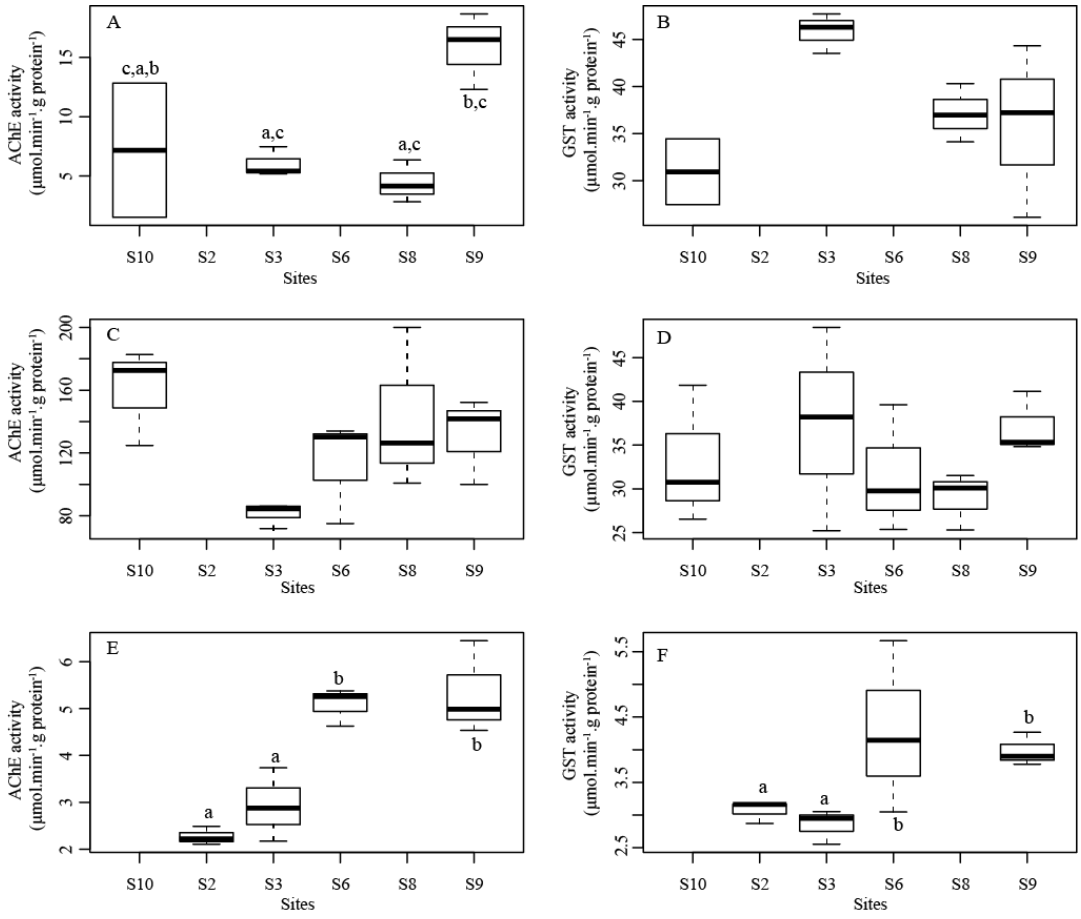


Figure 6. AChE and GST activities (µmol.min^{-1}.g protein^{-1}) measured in autochthonous chironomids and C.fluminea, A) AChE in chironomids, B) GST in chironomids, C) AChE in C.fluminea, D) GST in C.fluminea, E) AChE in D. magna and F) GST in D. magna. Box-plots illustrate the median, 25 % and 75 % percentiles, minimum and maximum, and letters denote the significance between results.

4. Relationship between chemical and biological results

Linear regressions between the mean PEC quotients and AChE activity measured in chironomids showed a significantly positive relationship (Figure 7-A). However, this was not the case for GST activity (Figure 7-B). For C. *fluminea*, no significant relationship was found between the biomarker responses and site mean PEC quotients (Figure 7-C and D). The AChE and GST activities measured in the caged *D. magna* were positively dependent on the mean PEC quotients (Figure 7-E and F). However, in the laboratory bioassays, no study endpoint of exposed *D. magna* was significantly linked to site mean PEC quotients (linear regression test, p-value >0.05).

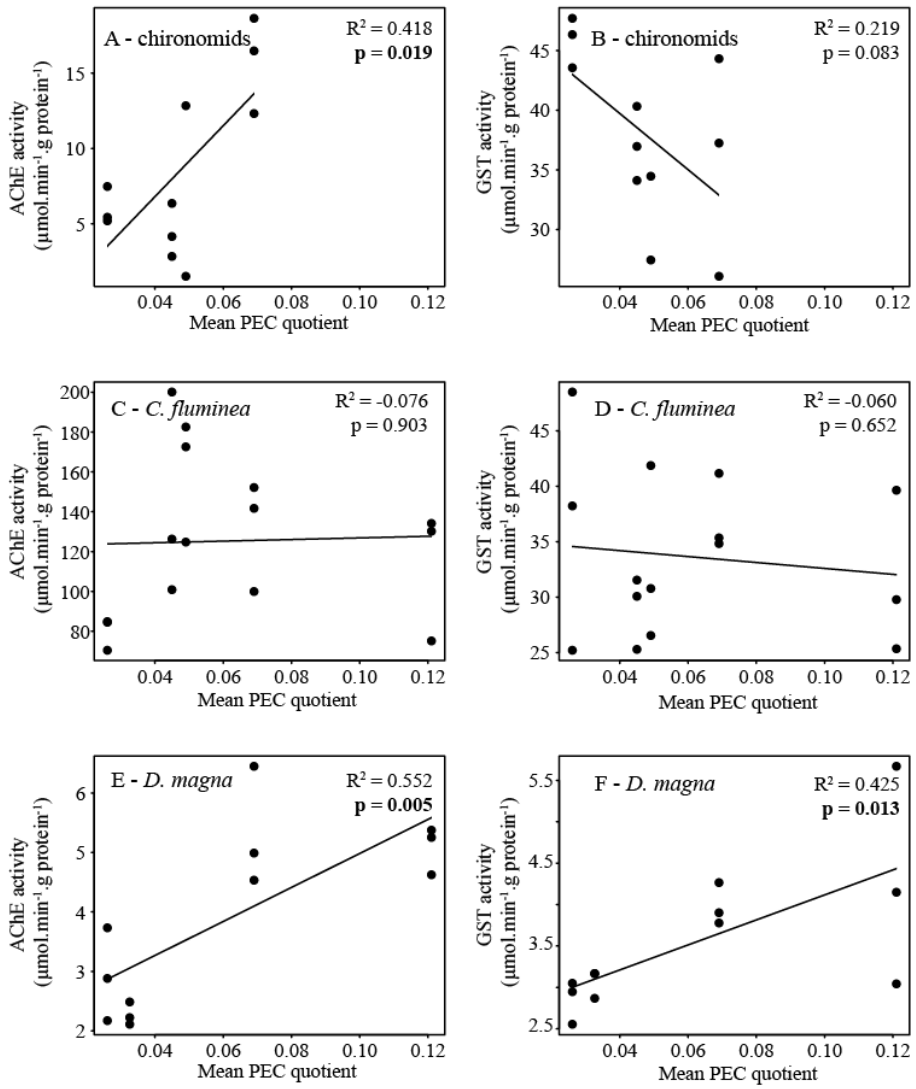


Figure 7. Linear regression plots of biomarkers activity (µmol.min^{-1}.g protein^{-1}) measured on the suited autochthonous and exposed organisms against the site mean PEC quotients. A) AChE in chironomids, B) GST in chironomids, C) AChE in C. fluminea, D) GST in C. fluminea, E) AChE in D. magna and F) GST in D. magna. R^2 corresponds to the adjusted R^2 and p to the p-value obtained following the linear regression statistical test. Numbers in bold highlight significant relationships.

Discussion

1. Spatial heterogeneity of littoral contamination

The sediment structure, such as particle size and organic matter, can modify heavy metal and persistent organic pollutant bioavailability (Eggleton and Thomas, 2004; Reid et al., 2000; Zhang et al., 2014). In the present study, these potential confounding factors regarding pollutant bioavailability did not significantly differ along the littoral and would thus not be expected to explain differences in the contaminations measured along the littoral zone of the lake. Regarding this contamination, a wide diversity of profiles was observed. The heterogeneity between littoral sediments was more than twice that between the offshore sediment samplings from past studies (Table 1). The coefficients of variation calculated between central deep cores sampled by Jung (2009) and Jung et al. (2008) in Lake Bourget for heavy metals ranged from 6 and 32 %, while littoral sediments exhibit CVs between 26 and 87 % (Table 1). This difference was even greater when focusing on the sum of the 7 PCBs (CVs equals to 26 among offshore versus 93 % among littoral sediments) and the sum of the 15 PAHs (from 30 % among offshore to 220 % among littoral sediments). These differences may be explained by the presence of point sources on the watershed that may locally influence the sediment quality along lake littoral more than in central deep sediments (Roussiez et al., 2006). The northern part of the lake (sites 1 to 5) was less contaminated than the southern part (sites 6 to 10) where the two largest urban areas are located (i.e., Aix-les-Bains and Chambéry, of respectively 30,291 and 59,490 inhabitants (Insee, 2014)). As the outlets of the main lake tributaries are located in this same area, they may have acted as contamination pathways from potential pollution sources receiving urban storm water discharge (Cisalb, 2012). Naffrechoux et al. (2015) found a similar PCB profile in surficial lake sediments and in the Tillet River, which was contaminated by a former industrial site located 700 meters from the shoreline and producing electric capacitors with pyralene between 1945 and 1985. The high content of PCBs measured in S7 at the outlet of the river may be explained by the influence of this potential point source. Similarly, a former 43.208 m^2 industrial zone in Chambéry that closed in 2003 is still likely to contaminate groundwater connected to the Leysse, notably in terms of Cr, Cu, Pb, PCB and hydrocarbons (Basol, French Ministry of Ecology). Finally, denser road networks and traffic (CG 73, 2017) associated with the presence of the Chambery airport are potential local sources that can contribute to the contamination intensity measured in the southern part of the lake. Based on the available data, the comparison between littoral and offshore sediment contaminations showed higher contents in deep central than in littoral sediments. This result appears paradoxical as point sources have been shown to be strongly involved in the contamination of this lake (Jung et al., 2008; Naffrechoux et al., 2015a). Therefore, a higher contamination would be expected in the littoral. A possible explanation may lie in the difference in sediment characteristics (sandy littoral and silty deep sediments) mainly due to differences in hydrodynamic processes partitioning sediment grain size and deposition (Cyr, 1998; Håkanson, 2011; Schall et al., 2017). Because contamination preferentially adsorbs on fine sediment fractions (Ghosh et al., 2003; Suresh et al., 2012), this may induce a higher

accumulation of contaminants in deep sediments compared to those in the littoral. However, despite a lesser accumulation of contamination in the littoral zone, contaminant pulses and flows through this zone may lead to a gap between the measured contamination and the effects on the biota. Therefore, biological tests can provide complementary information for a comprehensive assessment of the ecological risk of littoral contamination.

2. Ecological risk assessment

ERA becomes challenging when focusing on a mixture of pollutants in a complex zone such as the lake littoral. Mean PEC quotients were calculated to assess the toxicity of the mixture of pollutants as a whole. Littoral sediments were not predicted to be toxic except in S6 and S7, where the particularly high contamination in PAHs and PCBs, respectively, were susceptible to negatively impact the exposed biota. Concomitantly, the GST activities measured in *D. magna* exposed in S6 and S8 were significantly higher than the activities measured in S2 and S3, suggesting that stressful conditions may have induced these sub-lethal responses. Linear regression between GST activity and mean PEC quotient values was in accordance with this result since the activity increased with the mean PEC value. Chemicals may be the main stressors leading to the induction of the enzymatic defense mechanism. Unlike in the laboratory exposed *D. magna*, the GST activity measured in autochthonous benthic macro-invertebrates did not vary between sites, nor according mean PEC quotients. Considering the coarse grain size observed in the littoral zone, surficial sediment might be less toxic for sediment dwelling organisms compared to pelagic fauna, mainly exposed to fine particles and dissolved fractions of chemicals in the water column. Thus, the feeding strategy but also the metabolism rate from the molecule uptake to its excretion are factors inherent to species that can modify pollutant bioavailability (Eggleton and Thomas, 2004, Labrot et al., 1999). Additionally, considering the lipophilic properties of organic pollutants, lipid content in organisms is a key factor in contaminant bioconcentration and bioaccumulation and can vary among species and development stages (Geyer et al., 2000). The exposure history was also effectively proven to influence bioavailability (Wang and Rainbow, 2005). A short exposure of organisms bred in standardized laboratory conditions may be more stressful than a continuous exposure for autochthonous organisms that have always been in contact with the littoral contamination. Some species are also able to adapt or acclimate and protect against environmental constraints and potentially against pollution stressors. *C. fluminea,* for example, is able to close its valves to reduce exposure or supplement its filter-feeding intake by deposit-feeding (Naimo, 1995; Way et al., 1990). This might explain why no change in AChE activity between littoral sites nor mean PEC quotients was observed for *C. fluminea* in addition to the GST results, as well as a lower sensitivity to toxic exposure (Labrot et al., 1999; Tišler and Zagorc-Končan, 2002). However, unexpected AChE activities were measured in chironomids and *D. magna*. While a toxic exposure to toxic compounds is supposed to induce an inhibition of AChE activity (O'Brien, 1976), AChE activities increased with mean PEC quotients. This result suggests that stressful conditions, such as the presence of

other non-measured contaminants (Sarkar et al., 2006; Sturm et al., 2000; Wogram et al., 2001), affected the AChE activity in chironomids and *D. magna* in sites where the mean PEC quotients were therefore low. It is also important to emphasize that contaminants are equally involved in the calculation of mean PEC quotient calculation. In other words, mean PEC quotients do not consider synergic or antagonistic contaminant behavior (Long, 2006). As an arithmetic mean, this calculation can thus minimize the toxic effect of a single chemical in a mixture with other low concentrated chemicals. Chromium, for example, exhibited high content all along the littoral in our study. In sampling sites where the great majority of study contaminants showed low contents, the mean PEC quotient was below 0.1, while the chromium PEC quotient was higher than 0.1 or 0.5 (Table 3) and *de facto* susceptible to exert a toxic impact. This underlines the importance of pairing biological assays with chemical screening in ERA. Laboratory microcosms, for instance, did not show a significant effect on *D. magna* fitness when exposed to S6 sediment, which was supposed to be toxic according to the mean PEC calculation. In contrast, the S8 and S9 sediments appeared to exert a negative impact on *D. magna*. In addition, no significant relation was obtained between microcosms results and mean PEC quotients. In the S8 and S9 sediments, chromium PEC quotients were equal to 0.4 and 0.5, respectively (Table 3), suggesting that chromium could have caused the observed biological response. Additionally, the environmental inference that can occur in field experiments may have induced a stress in the *D. magna* that it did not experience in laboratory assays under controlled parameters. Another hypothesis considers the study endpoints in this type of study. In a context of low multi-contamination, looking at the sub-cellular level with biomarkers may have enabled us to see a biological response to contamination that we did not manage to observe at higher levels, such as biological traits in laboratory microcosms

Conclusion

The contamination of surficial sediments highly differed along the Lake Bourget littoral zone. This spatial heterogeneity, which is greater than that in offshore sediments from previous studies, may be the result of watershed point sources that locally impact the sediment quality. Based on this observation, contamination contents were expected to be higher in shoreline than in offshore sediments. However, a coarser sediment texture and potential hydrodynamic processes led to an opposite result.

Ecological risk assessment was conducted, integrating littoral multi-contamination and biological responses measured in two compartments (i.e., benthic and pelagic) and at different levels of biological complexity (i.e., sub-cellular and individual) to have a fine and complementary vision at the littoral scale. Even if mean PEC quotients were low except in two sites, the biological response varied along the lake littoral, both in the field and laboratory assays. Pelagic *D. magna* seemed to be directly impacted by the mixture toxicity. The comparison between laboratory bioassays and biomarker measurements suggested that sub-cellular endpoints such as enzymatic activities are better indicators of a toxic stress than higher physiological levels in the context of

low multi-contamination. A direct link between the measured contamination and the biological response among autochthonous benthic invertebrates was less clear. The results suggested that the benthic compartment was less impacted by a toxic effect of littoral contaminants, due to physico-chemical processes (e.g., pollutant migration to offshore sediments with fine particles movements) or potential native acclimation to pollution.

Regarding the results of the present work and considering the great ecological and economical importance of the littoral zone, which is known to be the most productive part of the lake ecosystem (Décamps and Naiman, 1990; Raspopov et al., 1996), particular attention should be paid to the littoral zone when assessing lake pollution and the associated ecological risks.

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Supplementary data

Table S1: GPS coordinates of the ten study sites and principal land use and occupation.

Site name	Site code	GPS coordinates	Land use	Watershed occupation
Hautecombe	S1	45°45'20.16''N, 5°50'17.987''E	Monastery	Rural
Conjux	S2	45°47'42.936 ''N, 5°49'21.575''E	Beach and WWTP*	Rural
Châtillon	S3	45°47'57.228"N, 5°50'44.412"E	Beach	Rural, forestry
Railway	S4	45°45'14.832''N, 5°52'35.724''E	Railway	Rural
Sierroz	S5	45°42'5.184''N, 5°52'55.56''E	River outlet	Urban
Esplanade	S6	45°41'40.452''N, 5°53'10.715''E	car park	Urban
Tillet	S7	45°41'33.828''N, 5°53'15.107''E	Harbour, river outlet	Urban and industrial
Rowing	S8	45°41'19.032''N, 5°53'39.3''E	Beach, road	Urban
Lido	S9	45°40'3.288''N, 5°53'36.276''E	Beach, river outlet	Urban and industrial
South reed bed	S10	45°39'7.92''N, 5°53'11.184''E	Reed bed, river outlet	Urban and industrial

*Waste Water Treatment Plant

Table S2: Heavy metals (mg.kg^{-1} DM DM), PCBs and PAHs contents (µg.kg^{-1} DM), mean contents, corresponding PEC values in the littoral zone.

		Sites										
	Sites	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	PEC[a]
Hevay metals (mg.kg^{-1}DM)	Cd	0.04	0.07	0.05	0.12	0.10	0.14	0.12	0.07	0.12	0.11	4.98
	Cr	38.58	25.16	23.34	32.81	36.70	41.31	30.10	48.74	56.39	42.84	111
	Cu	1.31	4.01	1.67	1.18	2.49	4.69	12.69	1.42	6.29	2.88	149
	Ni	7.29	6.29	5.07	4.11	10.35	10.17	10.00	9.58	10.95	8.25	48.6
	Pb	1.90	4.05	2.67	1.83	4.59	5.81	7.92	2.01	7.4	6.47	128
	Zn	21.6	24.36	15.64	30.58	26.05	69.49	86.10	22.96	77.14	54.97	459
PCBs (µg.kg^{-1} DM)	PCB-28	7.88	ND	ND	ND	ND	ND	1.60	ND	ND	ND	-
	PCB-52	2.67	2.15	2.52	2.09	2.26	2.07	5.96	2.6	1.88	1.81	-
	PCB-101	4.04	2.22	2.10	1.95	2.01	4.40	6.63	1.88	2.26	1.8	-
	PCB-118	ND	ND	ND	ND	ND	5.67	4.94	0.09	ND	ND	-
	PCB-138	7.50	2.52	3.19	3.27	3.38	9.66	12.94	3.34	3.31	2.36	-
	PCB-153	4.84	0.64	0.56	0.64	0.78	4.02	1.46	0.75	3	2.29	-
	PCB-180	0.06	ND	ND	0.27	0.12	4.35	24.49	0.28	0.66	0.87	-
	sumPCBs	26.99	7.52	8.37	8.22	8.55	30.18	58.02	8.93	11.11	9.14	676[b]
PAHs (µg.kg^{-1} DM)	N	0.29	0.62	0.00	0.11	0.34	7.84	1.65	0.17	1.58	0.34	561
	Ace	0.62	1.62	0.43	0.31	0.06	22.20	2.62	0.58	3.64	0.14	128
	Flu	0.42	0.77	0.06	0.12	0.31	16.86	1.91	0.02	0.6	0.13	536
	Phe	0.88	0.88	2.24	3.34	12.54	98.44	33.79	3.19	14.46	3.74	561-1170
	Ant	0.00	0.17	0.00	0.00	0.02	72.65	4.90	0	2.27	0.92	845
	Fla	0.42	3.54	0.49	5.67	31.32	509.19	90.32	0.52	51.56	17.34	2230
	Pyr	0.56	101.49	0.16	0.16	1.42	1191.5	80.65	0.16	48.05	13.73	1520

Table S2: continued.

		Sites										
	Sites	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	PEC[a]
PAHs (µg.kg^{-1} DM)	BaA	0.22	3.17	0.00	0.33	6.77	434.57	83.47	0.11	74.96	22.58	1050
	Chr	0.18	1.42	0.00	1.57	16.69	209.63	42.84	0	33.65	9.60	1290
	BbF	2.80	9.53	0.26	3.18	20.07	221.06	85.26	0.45	62.77	14.52	13400
	BkF	0.14	1.23	0.02	0.04	1.08	108.6	26.90	0.02	21.59	5.75	13400
	BaP	0.16	2.28	0.01	0.02	0.11	257.88	48.44	0.01	43.01	11.6	1450
	BghiP	0.27	2.97	0.05	0.15	3.18	172.39	40.97	0.05	40.06	9.83	3200
	DbahA	0.10	0.66	0.02	0.02	0.39	43.00	10.21	0.02	3.69	2.45	135
	IP	0.35	3.83	0.07	0.07	0.38	131.19	30.91	0.07	25.8	4.03	3200
	ΣPAHs	7.39	134.19	3.79	15.08	94.68	3497.01	584.83	5.36	427.7	116.7	22800

[a] Consensus-based PEC (Probable Effect Concentration) (D. D. MacDonald et al., 2000b)

[b] Value accounting for the 209 PCB congeners

Table S3: Loadings of variables (elements) on the first two principal components measured on the 10 sediment samples. The eigenvalue and variance of each principal component are also given. The values in bold mean that these loadings are significant.

Variable	PC1	PC2
Zn	**0.910**	-0.120
Ni	0.648	-0.115
Cu	**0.864**	0.018
Cr	0.284	-0.345
Pb	**0.848**	-0.298
Cd	0.695	-0.462
PCB28	0.116	**0.849**
PCB52	0.216	**0.749**
PCB101	0.638	**0.763**
PCB118	**0.808**	0.427
PCB138	0.595	**0.758**
PCB153	0.590	0.200
PCB180	**0.716**	0.095
Nap	**0.810**	0.114
Ace	0.688	0.281
Flu	**0.859**	0.191
Phe	**0.838**	-0.074
Ant	0.603	0.335
Fla	**0.913**	-0.268
Pyr	**0.902**	-0.103
BaA	**0.944**	-0.216
Chr	**0.897**	-0.300
BbF	**0.937**	-0.144
BkF	**0.969**	-0.149
BaP	**0.950**	-0.082
BghiP	**0.963**	-0.186
DbahA	**0.971**	-0.087
IP	**0.963**	-0.049
Eigenvalue	17.40	3.68
Variance (%)	62.16	13.14

3. Synthèse

Cette étude met en évidence la difficulté d'évaluer l'écotoxicité d'un mélange de polluants d'une matrice naturellement contaminée, d'autant plus dans une région du lac où les interactions biotiques (Crane et al., 2002; Ippolito et al., 2017) et abiotiques (Finlay et al., 2001) sont susceptibles d'influencer à la fois l'exposition, la biodisponibilité et la sensibilité des organismes. De manière générale, la réponse des biomarqueurs dans cette étude est similaire à celles de la littérature en conditions non stressantes (Tableau 2), à l'exception de l'activité AChE des chironomes qui semble inhibée dans notre étude, pouvant indiquer un stress de ces organismes en zone littorale. L'activité GST des Daphnies présente des valeurs anormalement basses par rapport à la littérature, mais du même ordre de grandeur que celles mesurées en laboratoire sur des Daphnies de contrôle (1,2 ± 0.3 µmol min^{-1} g $protéine^{-1}$). Il est possible que des divergences entre protocoles expérimentaux aient créé cet écart entre notre étude et la littérature.

Tableau 2. Comparaison des résultats d'activités moyennes de biomarqueurs (µmol min^{-1} g $protéine^{-1}$) de l'Article 1 avec ceux de la littérature.

Activité (µmol min^{-1} g $protéine^{-1}$)		Notre étude	Littérature	Référence
Chironomes	AChE	8,5 ± 5,7 (n=4)	31,3 ± 18,0 (n=5)	Berra et al. (2004) (3 mois différents sur 1 site)
	GST	38,0 ± 7,2 (n=4)	30,0 ± 7,04 (n=4)	Crane et al. (2002) (témoins de laboratoire)
C. fluminea	AChE	125,3 ± 39,9 (n=5)	154,7 ± 0,20 (n=6)	Beltran and Pocsidio (2010) (6 témoins de laboratoire)
	GST	33,6 ± 7,1 (n=5)	16,5 ± 6,2 (n=4)	Oliveira et al. (2015) (4 mois différents sur 1 site peu contaminé)
D. magna	AChE	3,9 ± 1,5 (n=4)	3,2 ± 0,2 (n=4)	Barata et al. (2005) (essais témoins en laboratoire)
	GST	3,5 ± 0,9 (n=4)	321,5 ± 14,3 (n=4)	Barata et al. (2005) (essais témoins en laboratoire)

La discussion autour de l'influence de sources ponctuelles sur l'hétérogénéité spatiale de la multi-contamination littorale a été évoquée dans ce Chapitre. Le Chapitre 2 vise à approfondir cette question. En effet, comprendre l'influence des sources de pollution de la zone littorale s'avère pertinent dans l'évaluation de l'écotoxicité de son sédiment et dans une perspective de préservation / restauration de l'écologie de cette zone.

Chapitre 2

Influence des sources locales sur l'hétérogénéité spatiale de la contamination littorale lacustre

1. Démarche générale

La diversité d'occupation des sols à l'échelle des bassins-versants des grands lacs peut être à l'origine d'une pollution hétérogène des lacs, tant en intensité qu'en profil de contamination. Evaluer l'influence de ces sources de pollution sur la contamination lacustre ainsi que leurs voies d'entrée majoritaires (e.g. atmosphérique, *via* les tributaires) est une étape importante pour le maintien du bon état écologique des lacs. Ce constat amène à la question suivante : **la contamination sédimentaire littorale, par son hétérogénéité de profils de contamination, peut-elle nous renseigner sur l'influence des sources de pollution locales ?**

L'intensité de la multi-contamination dans le lac du Bourget (c.f. Article 1) semble suivre un gradient du sud au nord allant dans le même sens que la densité urbaine du bassin-versant. En effet, les agglomérations d'Aix-les-Bains et de Chambéry qui concentrent une plus forte densité de population, d'activités urbaines et industrielles, de trafic routier et aérien que dans le reste du bassin versant, sont probablement à l'origine d'une pollution à la fois locale (i.e. à l'échelle du bassin-versant) et diffuse (i.e. multiplicité des sources et des modes de rejets).
Les polluants organiques sont susceptibles de se propager davantage que les ETM dans l'atmosphère et au sein du lac depuis une source locale. Au sein même de ces familles, les différences structurales conditionnent la distance de transport et l'affinité au sédiment (Bidleman, 1988; Chen et al., 2002; Choi et al., 2008; Klecka et al., 2000).
Les tentatives de remonter depuis un profil de contaminants sédimentaires aux sources d'émissions sont nombreuses dans la littérature (Akyüz and Çabuk, 2010; Qiao et al., 2006; Ravindra et al., 2008; Tobiszewski and Namieśnik, 2012; Zhang et al., 2008). Elles se basent en majorité sur un principe de similarité entre les profils d'étude de contamination et celui de sources « types ». Par exemple, un ratio (Ant/(Ant+Phe)) < 0.1 peut indiquer une origine pétrogénique. A l'inverse, le même ratio > 1 indiquerait une source pyrogénique de la contamination (Pies et al., 2008). De la même façon, pour le ratio (Ip/(Ip+BghiP)), un résultat < 0.2 indiquerait une provenance pétrogénique, entre 0.2 et 0.5 une origine liée à la combustion de pétrole et > 0.5 une combustion de charbon, bois et herbes (Yunker et al., 2002).
Néanmoins, ces rapprochements, en ne tenant compte que de certains HAP, sont quelquefois biaisés compte tenu des modifications qu'un profil de polluants organiques peut subir lors du transport (Galarneau, 2008).

L'Article 2 vise à expliquer la variabilité des profils de contamination en polluants organiques le long du littoral par l'influence des émissions diffuses depuis le tissu urbain dense au sud du lac. Pour cela, un profil sédimentaire de contamination en HAP et PCB au cœur de ce tissu urbain, dit « profil de référence », a été utilisé pour la comparaison avec les profils littoraux des sites d'étude.

Deux approches ont été employées dans cet objectif :

1. L'étude des similarités entre le profil de référence par rapport aux profils littoraux, via le calcul d'un indice de similarité. Plus le profil d'étude ressemble à celui de la source de référence, plus la probabilité que ce site ait été impacté par cette source est forte.
2. L'étude de l'abondance de contaminants aux propriétés physico-chimiques proches permettant d'accéder à des informations relatives à la distance à la source. Plus la contribution des éléments dits lourds (i.e K_{ow} et K_{oa} élevés) dans le profil est forte, plus la probabilité que cette contamination soit le résultat d'une source proche est forte (Naffrechoux et al., 2015a).

2. Article 2 - Dissecting organic pollutants (OPs) signatures in littoral sediments to assess the influence of a local urban source at the whole lake scale

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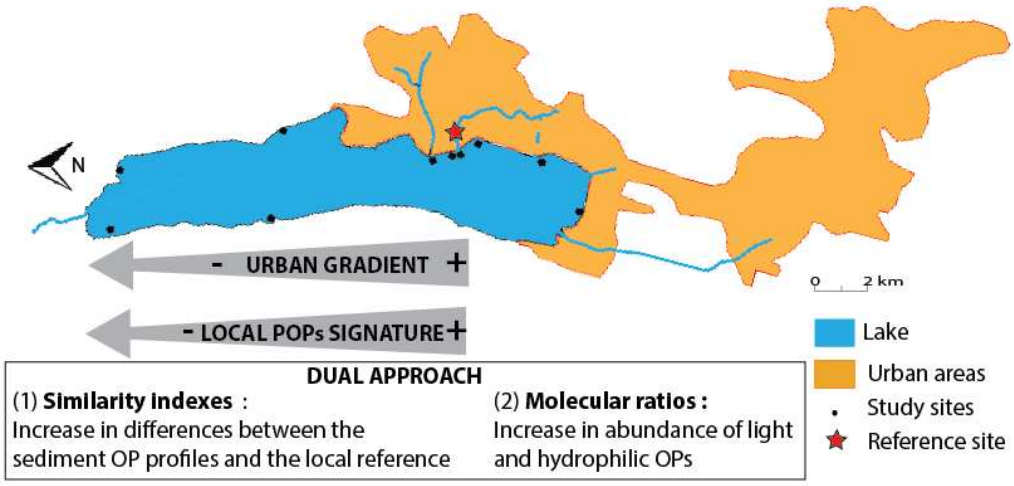
Highlights

- North-South changes in littoral sediment OP profiles of Lake Bourget reflected the land-use of the lake watershed.
- Similarity between OP profiles of littoral sediments and a local reference sediment led to confirm this North-South gradient of contamination and profiles.
- Another method based on molecular ratios showed less contaminated sediments with a higher proportion of light molecular weight OPs in the North
- Lake tributaries appeared as important contamination pathways to lake littoral sediments.

Graphical abstract



Abstract

Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are organic pollutants (OPs) that can originate from both the watershed (i.e. local sources) and long range emissions. Even when local sources are identified, the propagation of OPs in aquatic systems remain poorly known. The southern part of Lake Bourget (France) is known to be impacted by PAHs and PCBs from local urban sources and surficial sediments exhibit OP concentrations higher than in the North. However, little is known about the propagation of this pollution within the lake. We propose a dual approach to assess the propagation of 13 PAHs and 7 PCBs in ten littoral sites. The first method quantifies the similarities between the OP profiles of the sites and that of a local urban signature used as a reference of the southern watershed, the second method is based on concentration ratios. The two independent methods provided convergent results and supported a south-north gradient of the OPs propagation. Southern sediments exhibited the highest OP contents, similarities in profiles with the local signatures and abundance of heavy molecular weight congeners. PAH contents and profiles seemed to be more variable than for the PCBs. Changes in the littoral OP profiles with tributary distance illustrated the spread from tributary outlets that may act as contamination pathways. Two littoral sites did not match this north-south gradient for PAH contamination, indicating another potential point sources. These results furthermore underline the relevance of focusing on the littoral zone in the prospect of assessing propagation of pollution within a lake.

Keywords

Polychlorinated biphenyl, polycyclic aromatic hydrocarbon, lacustrine sediment, pollution source, fate

Introduction

Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) have received increasing attention in the last decades as potential carcinogens and mutagens (Breivik et al., 2004; French Ministry of Ecology, n.d.; Oger-Jeanneret and Abarnou, 2008; UNEP, 2001; Vestreng, 2002).

Inland water bodies with anthropized watersheds are natural recipients for these organic pollutants (OPs). Lakes are especially vulnerable to OPs because of their persistent properties combined with their long residence times compared to running waters (Varekamp, 2003). OP accumulation preferentially occurs in sediments due to the hydrophobic and lipophilic properties of these substances (UNEP, 2003). As a consequence, sediment acts as a valuable integrator of these contaminants (Payne et al., 1996; Sutherland, 2000) and the identification of their origin and propagation appears as a prerequisite for managers to the design effective pollution remediation programs (Poté et al., 2008).

PAH and PCB concentrations from sediment cores sampled in the deep sediments of Lake Bourget (France) raised a higher pollution in the southern part of the lake than in the north in line with the lake watershed that exhibits a south-north urban gradient (Jung, 2009). In addition, surficial sediments sampled along the lake littoral exhibited an overall similar trend but the contents were much more variable between sites (Lécrivain et al., 2018). This study aims at assessing the propagation of OPs within the lake by studying 13 PAH and 7 PCB profiles from these littoral sediments. Surface sediments, compared to deep sediments are more likely to reflect the current impacts of pollution sources and the respective propagation of OPs within the lake.

The approach implemented a dual analysis of the contamination of the littoral sediments using two independent tools. The first tool consisted in measuring the deviation of the study profiles to reference PAH and PCB profiles reflecting the local sediment OP signature. This profile was obtained from the sediment of a lake tributary that flows through urban and industrial areas representative of the main contamination sources of the lake watershed (Jung, 2009; Naffrechoux et al., 2017, 2015). The second tool was based on the inter-site comparison of the molecular concentration ratios of the PAHs and PCBs with the lightest molecular weights, octanol/water and octanol/air partitioning coefficients (K_{ow} and K_{oa}, respectively) over the total. These ratios allow for the comparison of the abundances of PAHs and PCBs that are preferentially mobilized and/or transported far from local sources with that of the more lipophilic and less-volatile ones accumulated in the sediment adjacent to local sources (Choi et al., 2008; Harner et al., 2004; Naffrechoux et al., 2015). Consequently, the propagation of OPs from the identified main local sources within the lake was expected to follow a south-northern gradient exhibiting simultaneously (1) an increasing dissimilarity with the reference profile and (2) a change in proportions from the less to the more volatile and hydrophilic OPs in the sediment.

In addition, lake tributaries can act as a preferential vector for OP contamination from the watershed (Melymuk et al., 2014). To test this assumption in Lake Bourget, changes in the

littoral OP profiles with the distance to tributary outlets were studied with the assumption that it would illustrate the spread of OP contamination from the tributaries.

Materials and methods

1. Study sites and data selection

Lake Bourget is the largest natural lake in France with a surface area of 42 km2, a volume of 3.6 km3 and a maximal depth of 145 m. It is located on the northwest edge of the French Alps (45°43'N, 5°52'E, Figure 1-A). Lake Bourget is currently meso- to oligotrophic (Jacquet et al., 2017), with water residence times between 7 and 10 years. The precipitations (annual mean precipitations = 1200 mm) are regularly associated with northerly winds.

The 560 km2-catchment area of the lake is covered by forests (45 %), agricultural areas (22 %), grazing fields (12 %), urban areas (13 %) and water bodies (8 %) (CISALB, 2009). The anthropogenic development along the littoral zone of the lake is highly contrasted. The south and southeastern areas of the lake watershed are densely urbanized due to urban expansion around two largest cities of the watershed (i.e., Chambéry and Aix-les-Bains with a combined population of 90,000 inhabitants (Insee, 2018)) (Figure 1-B). The road networks and traffic are consequently the densest of the lake watershed (CG 73, 2017) and the Chambéry airport, with an annual capacity of 1 million passengers, is located on the southern side of the lake. The north and northwest areas of the lake are less urbanized. Forests are predominant in the north, and steep-slope areas in the west limit urban expansion.

Lake Bourget has three main tributaries (Figure 1-B). The Leysse River (T1) is the main tributary with a mean annual flow of 6.1 $m^3.s^{-1}$ (CISALB, 2013). It runs through Chambéry city and close to a 43.208 m^2 former industrial area that closed in 2003 but is still likely to contaminate groundwater connected to the Leysse (BASOL, 2013). In addition, (Jung et al., 2008) assessed horizontal PAHs and PCBs contamination to the lake from the T1 along a transect of deep sediment coring covering its plume. The Tillet River crosses Aix-les-Bains city and divides into 2 arms (T2 and T3) before flowing into the lake. T2 has a mean annual flow equal to 0.4 $m^3.s^{-1}$ and 0.2 $m^3.s^{-1}$ for T3. T3 was contaminated by a former industrial site that has produced electric capacitors with pyralene between 1945 and 1985. This tributary consequently acts as a PCB contamination pathway to the lake (Naffrechoux et al., 2017, 2015). The Sierroz River (T4) has a mean annual flow of 2.3 $m^3.s^{-1}$ and crosses agriculture and urban areas since it flows through the northern area of Aix-les-Bains agglomeration. Together, T1 and T4 drain more than 70 % of the lake watershed and they both receive urban storm-water discharge (CISALB, 2012). The Savières Channel at the North constitutes the lake outlet.

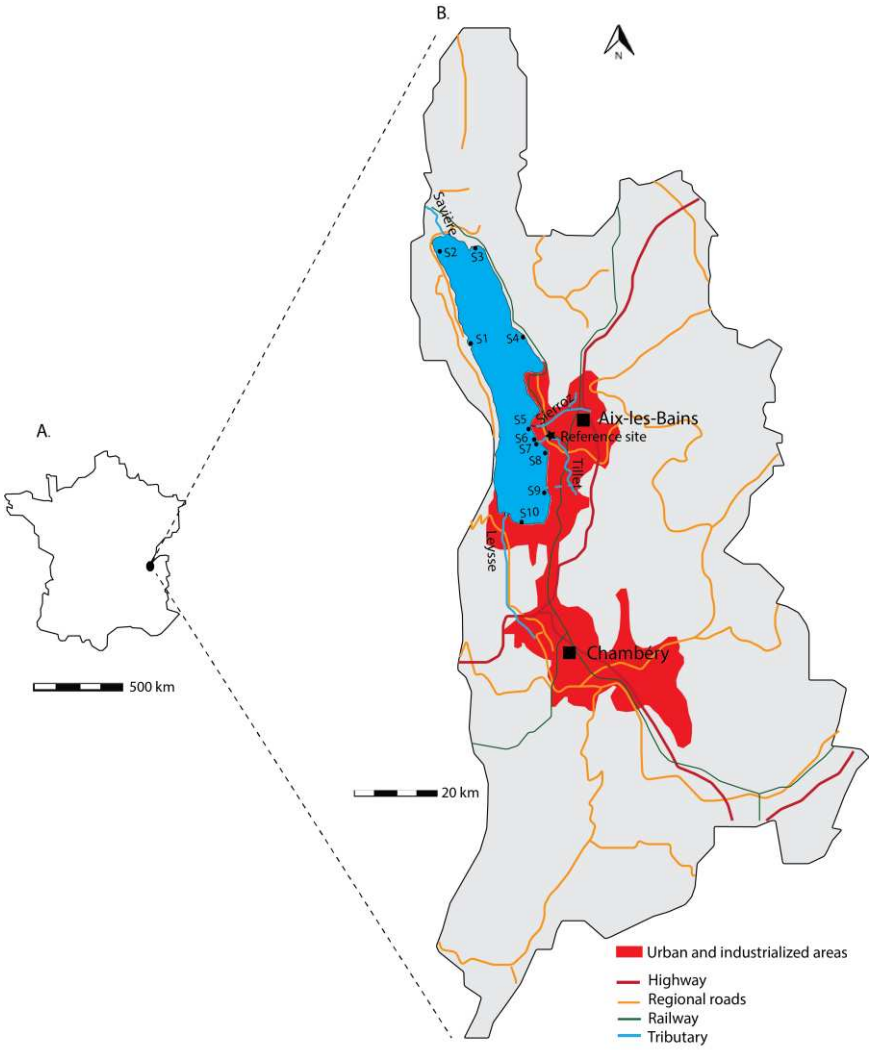


Figure 1. Location of Lake Bourget (A) in France and (B) in the catchment area, locations of the study sites (S1 to S10) and lake tributaries: the Leysse River (T1), the small arm of the Tillet River (T2), the Tillet River (T3), the Sierroz River (T4) and the Savière channel (Lake exutory) (modified from ©CORINE Land Cover).

Ten study sites were selected along the littoral zone of the lake (S1 to S10, Figure 1-B, see Table S1 for the supporting information), from which surface sediments (0-10 cm) were collected at a water depth of 1.5 to 2.5 m using an Ekman grab from a boat in June 2016. The sampled sediments had a similar sandy grain size distribution, measured by laser diffractometry (Malvern Mastersizer 2000G), so that grain size would not exert a bias in the inter-site comparisons of the OP contamination (Ghosh et al., 2003).

Thirteen PAHs of the 16 PAHs listed as priority pollutants by the United States Environmental Protection Agency (USEPA) were selected: fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[ah]anthracene (DbahA), benzo[g,h,i]perylene (BghiP) and indeno[1,2,3-c,d]pyrene (IP).

The lightest molecular weight PAHs (naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace))) were excluded to limit analytical bias linked to their high volatility. The 7 indicator PCBs were analyzed: congeners 28, 52, 101, 118, 138, 153 and 180. Among the 209 congeners, these seven PCBs are referenced by the European Community Bureau of Reference (Dargnat and Fisson, 2010) and commonly studied because of their occurrence in the environment (Keith, 2015; Pozo et al., 2006). Details regarding the sampling sites, sediment characterization and OP measurements are described in (Lécrivain et al., 2018). Briefly, a subsample of each sediment was used for water content determination and ignited at 550 °C for 4 hours to determine LOI (Afnor, 2007) and another subsample for the measurement of OP contents. Extraction was conducted by accelerated solvent extraction (ASE200 - Dionex) using a mixture of acetone:dichloromethane (50:50). PCBs were analyzed on a Perkin Elmer gas-chromatography coupled with a pulsed discharge ionization detector. PAHs were analyzed on a Perkin Elmer HPLC equipped with a C18 column (Optima5, 30 m-MACHEREY NAGEL) and coupled with a fluorimetric detector. Detailed analytical procedure including clean-up is described in (Lécrivain et al., 2018).

2. First approach: the similarity index calculation

The similarity index allows for the comparison of the OP profiles in the sediment of the study sites with a OP profile used as a reference. PAH and PCB profiles consisted in the percentages of each chemical to the total PAH or PCB contents for each study and reference sediments. A similarity index, i.e. the Bray-Curtis similarity index (1), ranging between 0 and 1, was attributed to each study site according to the resemblance of its OP profile to that of the reference. A similarity index close to 1 between a study profile and the reference profile reflects a high resemblance between the two profiles.

$$s_j = \frac{2\sum_i^p \min(a_{ij}, a_{ir})}{\sum_i^p (a_{ij} + a_{ir})} \quad (1)$$

Where a_{ij} and a_{ir} correspond to the proportion of the contaminant i in the study profile j and the reference profile r respectively, and p is the total number of contaminants.

There was an attempt to select a reference that consisted in a large-scale OP sediment signature from a remote area. A similarity index close to 0 would consequently suggest that the OP signature in the study site would have been highly impacted by the local sources. For this aim, a literature overview was performed to collect PAH and PCB profiles from remote lacustrine sediments. A detailed analysis provided in the Method section of the Supplementary Information revealed a large heterogeneity between these large-scale profiles. In consequence, no large-scale signature suited for this study.

The selected reference profiles for this study were local (i.e. watershed) PAHs and PCBs signatures from surficial sediments sampled in the watershed. These local samples tend to minimize the potential bias linked to the OP reactivity during their atmospheric transport from the source to the sediment (Fu et al., 2012; Moza et al., 1999). PAH and PCB profiles came from surficial sediments sampled in the Tillet River (T3), 300 m upstream from its outlet into the lake (Figure 1-B, and Supplementary Information Table S1). Located in Aix-les-Bains, the second largest city of the lake watershed, this sampling site is known to be impacted both by PCBs and PAHs from urban and industrial sources (BASOL, 2013; Jung et al., 2008; Naffrechoux et al., 2015). The PCB profile at this site matched the profiles from other sediments impacted by local PCB sources in France (Supplementary Information, Figure S1, Rhône and Huveaune Rivers and Berre lagoon in France). This river site is also located downstream sites of PAH contamination from urban storm-water. The PAH profile of the Tillet surficial sediment effectively matched those measured in suspended particles in storm-water runoffs and rain water particles from urban sites (Supplementary Information, Figure S2-A and C).

3. Second approach: the molecular concentration ratios

The behavior of OP compounds in the environment is mainly controlled by their physicochemical properties, which are driven by their molecular structure (Choi et al. 2008; Bidleman 1988; Klecka et al. 2000; Chen et al. 2002). PAHs and PCBs with low octanol-water and octanol-air partitioning coefficients (K_{ow} and K_{oa}, respectively) are preferentially mobilized and/or transported far from their emission sources (Harner et al., 2004; Mackay and Wania, 1995; Naffrechoux et al., 2015; Shoeib and Harner, 2002). In the present study, the ratios of PCBs and PAHs were constructed as the sum of the contents of the PCBs and PAHs with the lowest K_{oa} and K_{ow} values over the sum of 5 PCBs and 13 PAHs, respectively. PCB 101 and 118 were deliberately removed from the $ratio_{PCB}$ because of their intermediate properties (log K_{ow} = 6.2 and 6.3, log K_{oa} = 9.4 and 10.1 for respectively PCB 101 and PCB 118 (Yuan et al., 2016)). Summing OP contents with similar physicochemical properties was further assumed to limit the influence of nonsignificant analytic fluctuations of individual molecule concentrations that can occur between samples.

$$ratio_{PCB} = \frac{[PCB28]+[PCB52]}{[PCB28]+[PCB52]+[PCB138]+[PCB153]+[PCB180]} \quad (2)$$

$$ratio_{PAH} = \frac{[Flu]+[Ant]+[Phe]+[Fla]}{[\Sigma PAHs]} \quad (3)$$

Thus, $ratio_{PCB}$ (2) and $ratio_{PAH}$ (3) were selected to reflect the extent of the contributions of the main local source to the study site contamination. Consequently, the higher these ratios, the less importantly the main local source would contribute to the OP signatures.

By quantifying the abundance of easily transportable OPs in the sediment samples, the selected ratios aimed to assess the propagation of OPs from a major lake OP source of contamination instead of a specific source apportionment. The use of molecular diagnostic ratios (MDRs) which are the concentration ratios of selected pairs of individual compounds (Katsoyiannis et al., 2011, 2007) as source markers assumes that OP source profiles are unique by source type, which is still discussed in the literature (Galarneau, 2008), undermines the weathering of the profiles during the transport of OPs and may deliver contradictory results (Moeckel et al., 2013).

4. Lake tributaries as a possible contamination pathway

To assess whether lake tributaries may be involved in the transfer of local contamination, the relationships of the distances between each site to the 4 outlets of the lake tributaries with the $ratio_{PCB}$ and $ratio_{PAH}$ were assessed using linear models. A significant positive linear regression implies decreases in the ratios (i.e., an increase in less-volatile, less-hydrophilic and more-lipophilic PCB and PAH contents) with a decrease in the distance to the tributary outlet and consequently suggests its role as a contamination pathway.

5. Data and statistical analysis

The contamination contents were corrected by the loss on ignition (LOI) (%) for each sediment sample prior to analyses as a proxy of the organic matter content to avoid organic matter content as a potential confounding factor when comparing OP concentrations between study sites (Allen-King et al., 2002; Burgess et al., 2001; Tsapakis et al., 2003). The organic matter abundance (%) and total contents of PCBs and PAHs ($\mu g.kg^{-1}$ OM) are provided in the Supplementary Information (Table S2) and the similarity indexes and ratios in Table S3. Throughout the manuscript, values following "±" correspond to the standard deviation of the data.
All statistical analyses, as well as graphical displays, were carried out using R (Team, 2017). The similarity index was calculated using the Bray-Curtis similarity index with the vegan package (Oksanen et al., 2013). The spatial distances between the study sites and each lake tributary were calculated using the spaa package (Zhang, 2016) and simple linear regressions between those distances with the ratios were performed using the lm function from the stats package (R Core Team, 2015).

Results and discussion

1. Changes in littoral OP profiles

Northern littoral sediments (from S1 to S4) exhibited a lower OP contamination than in the southern littoral (from S5 to S10), except for S1 regarding PCBs and S2 regarding PAHs, with a mean of ΣPCBs equal to 832 $\mu g.kg^{-1}$ OM compared to 968 $\mu g.kg^{-1}$ OM in the South and a mean of ΣPAHs equal to 1230 $\mu g.kg^{-1}$ OM compared to 29552 $\mu g.kg^{-1}$ OM (Figure 2-A and D). The

North-South differences in sediment OP contamination may suggest that local sources in the South may mostly affect southern sediments rather than the northern ones.

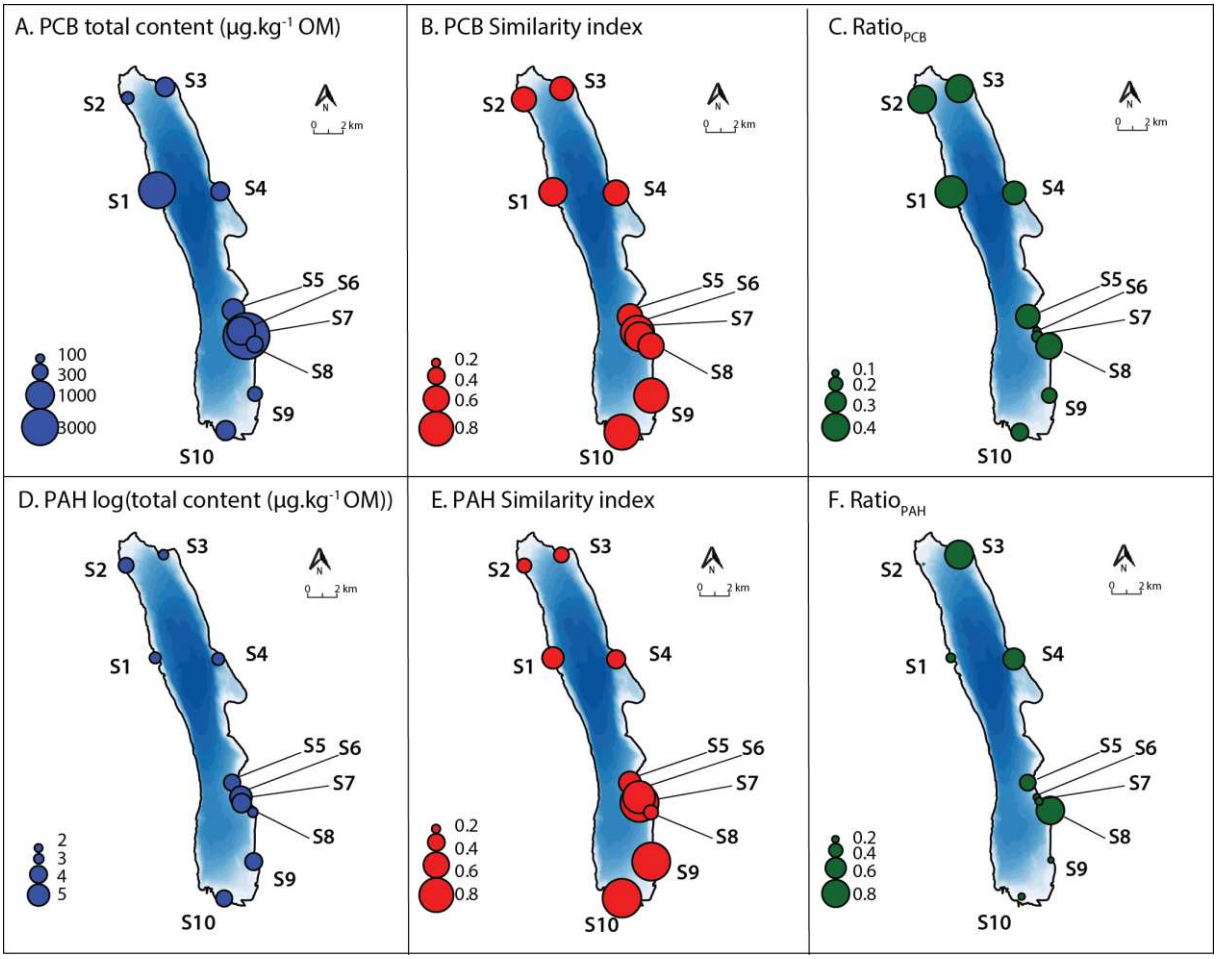


Figure 2. Mapping of (A) total contents of PCBs (µg.kg^{-1} OM), (B) PCB similarity indexes to the reference profile and (C) ratios$_{PCB}$, (D) total contents of PAHs (log(µg.kg^{-1} OM), (E) PAH similarity indexes to the reference profile, (F) ratio$_{PAH}$.

The highest similarity indexes with the reference were obtained in the southern sites, from S6 to S10 for PCBs (Figure 2-B), and in S1, S5, S6, S7, S9 and S10 for PAHs (Figure 2-E), where local OP sources are consequently assumed to prevail in the sites contaminations. Similarly to PCB and PAH sediment total contents, PCB similarity indexes, which ranged from 0.55 in the North to 0.82 in the South, exhibited lower differences between the north and southern parts of the lake compared to the PAH similarity indexes that ranged from 0.33 in the North to 0.90 in the South. Likewise, (Jung, 2009) found similar PCB pattern along time in northern and southern sediment cores (G1 and L cores), while PAH profiles were much variable between the same cores. Changes in ratios between North and South were consistent with variations of the similarity indexes as there was a significant negative linear regression between the site similarity indexes and the ratios (Figure 3, p-value < 0.05). Indeed, the lowest ratios were found in the South, in S6, S7, S9 and S10 for PCBs (from 0.11 to 0.25, Figure 2-C) and S1, S5, S6, S7, S9 and S10 for

PAHs (from 0.16 to 0.23, Figure 2-F), suggesting a high predominance of heavy molecular weight OPs in the South, while in the North the higher ratios would explain the abundance of lighter OPs that could have been transported from the South. Once again, the differences between south and northern ratios were greater according to the PAH than the PCB contamination, which consequently supports the assumption of a more conservative propagation of PCBs compared to PAHs within the lake.

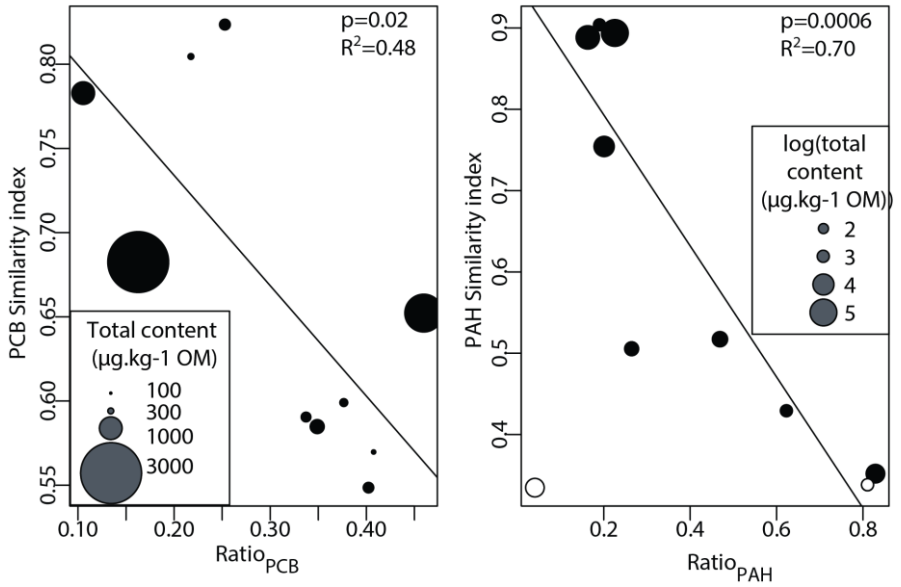


Figure 3. Linear regression plots of the ratios against the similarity indexes for the studied sites. PCB on the left, PAH on the right. p corresponds to the p-value obtained following the linear regression statistical test and R^2 corresponds to the adjusted R^2. The size of the points illustrates the total content of the contamination (in µg.kg^{-1} OM for PCBs and log(total content in µg.kg^{-1} OM) for PAHs). Empty circles represent the S2 and S8 results, which were not considered in the linear regression statistics.

Therefore, the results from the dual approach suggest a decrease in the influence of the local source signatures from the southern urbanized part of the lake to the northern more rural part (Figure 1). Urban-rural gradients in OP profiles were also studied in the literature on air (Gingrich et al., 2001; Harner et al., 2004; Pozo et al., 2012), soil (Peng et al., 2016; Vane et al., 2014; Wong et al., 2004; Xie et al., 2012), sediment (Hong et al., 2012) and water (Ruge et al., 2015), underlining the propensity of urban and industrial activities to exert a local impact on environmental media. Complementarily to these studies, the present study performed in a littoral lake zone focuses on the influence of urban OP sources at a finer scale (i.e., kilometric scale) since the two furthest littoral sampling points are less than 20 km apart. OP fluctuations at this kilometric scale were also studied by (Poté et al., 2008) and (Totten et al., 2006) who highlighted the propensity of OP contents and profiles to rapidly change at a small scale. In the present study, PCB and PAH contamination transformations along this urban-rural transect seem yet to be different; PCB contents and profiles looking more stable than for the PAHs. These results suggest that the PCBs propagation within the lacustrine ecosystem might be more conservative

than for the PAHs, probably linked to the high adsorption capacity of PCBs to the suspended particles in the water column that may increase their transport within the lake (Dean et al., 1993; Fitzgerald and Steuer, 2006). Another assumption would involve the higher mobility of PAHs between the hydrosphere and atmosphere leading to higher transformations in PAHs patterns within the lake (Dimashki et al., 2001; Fu et al., 2012; Melymuk et al., 2014; Schneider et al., 2002).

In addition to their higher mobility, PAHs differ from PCBs according to their greater multiplicity of emission sources. Even if the dual approach raised a global urban-rural gradient in PAHs profiles from South to North, some littoral sites exhibited PAHs content and profiles that did not match this gradient. Site S2 located in the northwestern part of the lake was heavily contaminated by pyrene, inducing a low $ratio_{PAH}$ at this site compared to the adjacent sampling sites (Figure 2-F). This particular profile may be partly influenced by wastewater treatment effluents located a few meters from the sampling point, since pyrene was proven to be an abundant PAH congener in raw and treated wastewater (Poté et al., 2008), sewage and stabilized sludges (Busetti et al., 2006; Pham and Proulx, 1997; Villar et al., 2006). This potential local source is coherent with the higher total PAH content (3472 $\mu g.kg^{-1}$ OM) at S2 compared to the adjacent sampling sites S1 and S3 (433 and 198 $\mu g.kg^{-1}$ OM, respectively). Inversely, the southern site S8 exhibited low contamination (192 $\mu g.kg^{-1}$ OM) and a predominance of low molecular weight PAHs compared to the adjacent sites S7 and S9 among the more heavily contaminated sites (Figure 2-F). Considering the littoral morphology at this site (Figure 1), it was assumed that the sediment sampled from S8, situated south of reed beds, may have been protected from the T3 plume (Hudon and Carignan, 2008; Naffrechoux et al., 2000). This assumption would explain why sediment PAH contamination at S8 exhibited a large-scale signature even though it was located in the southeastern urbanized littoral zone.

In addition to establish a OP gradient of the local sources from the closest to the furthest receiving littoral sediments, this approach highlights exceptions that will help to direct the focus on specific sites where local shoreline sources may specifically impact the littoral sediment.

2. Implication of the tributaries as potential contamination pathways

All lake tributaries flow through urbanized areas, which leads to question their implication in OP contamination to the lake. Increasing attention is paid worldwide on tributaries contamination as major pollutant pathways to the lakes (Baldwin et al., 2016; Benoit et al., 2016; Elliott et al., 2017; Van Metre and Mahler, 2004). The contribution of T3 in PCB lake Bourget contamination, for example, was previously investigated (Naffrechoux et al., 2017, 2015). Linear regressions performed between the $ratio_{PCB}$ values and the distance to lake tributaries indicated significant positive relationships between the increase in distance from the T1, T2 and T3 outlets and the abundance of light congeners (Figure 4, p-value < 0.05). These results suggest that these tributaries may act as PCB contamination pathways to the adjacent littoral sites as the PCB contaminations at the study sites shift from the less to the more easily mobilized PCBs when the

distance to these outlets increases. In contrast, this tendency was not observed for T4 (p-value = 0.053), which does not cross any industrial site or landfill site that could have acted as potential PCB point sources.

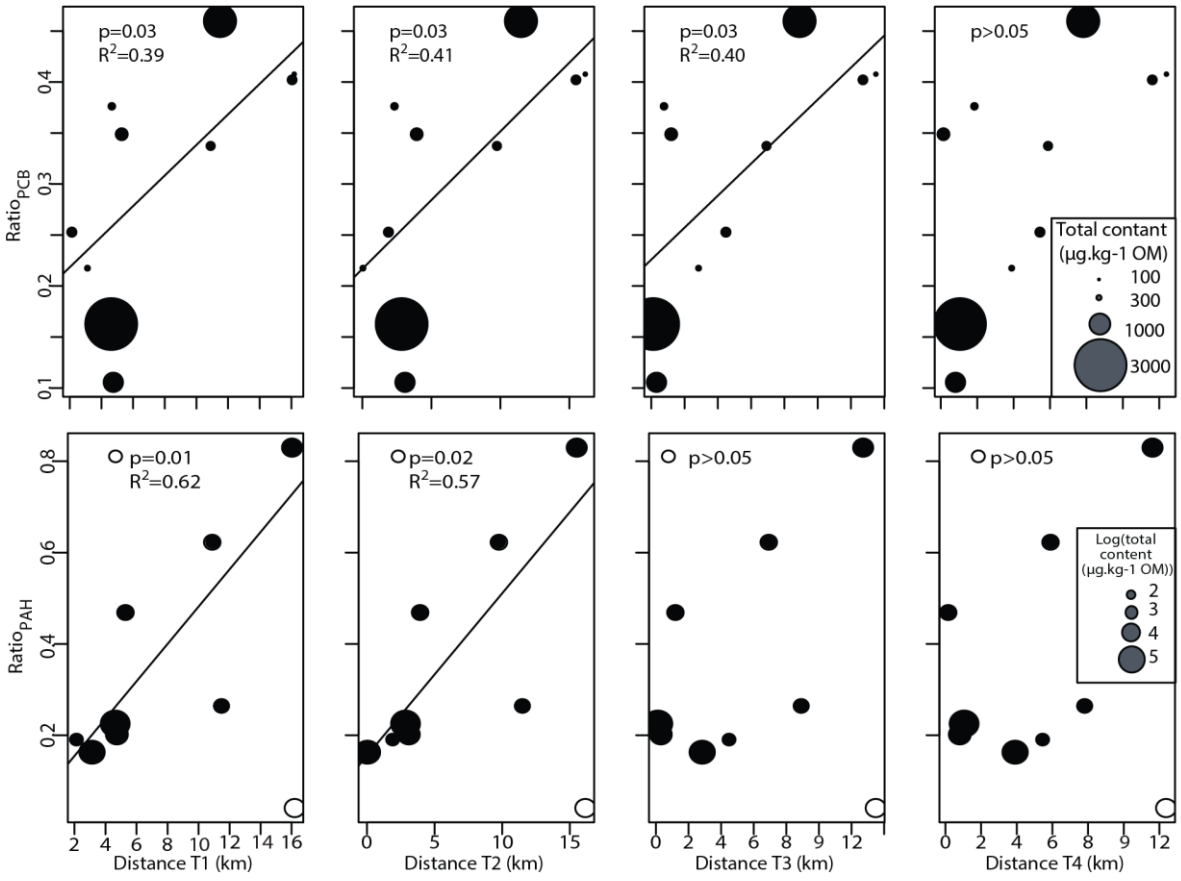


Figure 4. Linear regression plots of the ratios in sites against the distances of the sites to tributaries (from tributary 1, T1, to tributary 4, T4). PCB plots are above, and PAH plots are below. p corresponds to the p-value obtained following linear regression statistical test and R^2 corresponds to the adjusted R^2. The sizes of the points illustrate the total content of the contamination (in µg.kg^{-1} OM). Empty circles represent the S2 and S8 results, which were not considered in the linear regression statistics.

The PAH ratios significantly increased with the distance from the T1 and T2 (Figure 4, p-value <0.05), suggesting that these southern tributaries may also contribute to the local contamination of the closest study sites by the less easily mobilized PAHs. T3 and T4 did not seem to significantly support PAH local pollution to the lake (p-value > 0.05).

Surprisingly, the relationships between OP ratios and the corresponding distances of the sites from the T4 outlet were not significant while this tributary is one of the biggest, in drainage network and flow, of the watershed. One should question this result since the strength of current flow, fetch distances could be confounding factors affecting the detection of the tributary influences.

Overall, the tributaries are likely to act as OP contamination to the lake and this is consistent with the available data from the monitoring of water quality that considers PAH concentrations

in T1, T3 and T4 (T2 non available) too high to reach the good chemical quality class (Eaufrance, French Ministry of Ecology, 2018).

Conclusion

OP total contents in surficial sediment of the Lake Bourget littoral exhibited spatial fluctuations with higher levels in the Southern part of the lake. This was consistent with the land-use of the lake watershed that exhibits a greater urbanization in the South compared to the North. To improve knowledge in this local propagation within the lake, this study attempted to relate changes in OP profiles from these littoral sediments to the distance to the local sources in the South through a dual approach. Similarity indexes and molecular ratios gave consistent results in the sense that the northern sediments were the less contaminated, the most different from the local source reference and exert an abundance of light molecular weight OPs, while the opposite was observed in the South. The sites that did not match this north-south gradient were found to be locally impacted or protected by this OPs contamination. In addition, tributaries are likely to play a major role in OPs contamination pathway to the lake, which may give additional keys for lake managers to design local pollution control strategies.

Supporting Information

With the additional data on study sites location and contamination, the Supplementary Information details the procedure, results and discussions about the search for remote pristine OP signatures as references for the similarity index.

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Supplementary Information

Table S1. GPS coordinates of the ten study sites (S1-S10), the reference site and the tributaries (T1-T4) outlets.

Site code	GPS coordinates
S1	45°45'20.16''N. 5°50'17.987''E
S2	45°47'42.936 ''N. 5°49'21.575''E
S3	45°47'57.228"N. 5°50'44.412"E
S4	45°45'14.832''N. 5°52'35.724''E
S5	45°42'5.184''N. 5°52'55.56''E
S6	45°41'40.452''N. 5°53'10.715''E
S7	45°41'33.828''N. 5°53'15.107''E
S8	45°41'19.032''N. 5°53'39.3''E
S9	45°40'3.288''N. 5°53'36.276''E
S10	45°39'7.92''N. 5°53'11.184''E
Reference site	45°41'38.8''N. 5°53'34.1''E
T1	45°39'21.9''N. 5°52'3.2''E
T2	45°40'3.9''N. 5°53'36.9''E
T3	45°41'33.9''N. 5°53'18.9''E
T4	45°42'4.9''N. 5°53'0.7''E

Table S2. Organic matter (OM) abundance (%), PCB and PAH contents (µg.kg^{-1} OM) in the sediments of the ten littoral sites.

Site		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
OM (%)		1.5	3.8	1.7	1.8	1.3	2.8	2	2.4	4	1.8
PCB (µg.kg^{-1} OM)	PCB-28	525.33	ND	ND	ND	ND	ND	80.00	ND	ND	ND
	PCB-52	178.00	56.58	148.24	116.11	173.85	73.93	298.00	108.33	47.00	100.56
	PCB-101	269.33	58.42	123.53	108.33	154.62	157.14	331.50	78.33	56.50	100.00
	PCB-118	ND	ND	ND	ND	ND	202.50	247.00	3.75	ND	ND
	PCB-138	500.00	66.32	187.65	181.67	260.00	345.00	647.00	139.17	82.75	131.11
	PCB-153	322.67	16.84	32.94	35.56	60.00	143.57	73.00	31.25	75.00	127.22
	PCB-180	4.00	ND	ND	15.00	9.23	155.36	1224.50	11.67	16.50	48.33
PAH (µg.kg^{-1} OM)	Flu	28.00	20.26	3.53	6.67	23.85	602.14	95.50	0.83	15.00	7.22
	Phe	58.67	23.16	131.76	185.56	964.62	3515.71	1689.50	132.92	361.50	207.78
	Ant	0.00	4.47	0.00	0.00	1.54	2594.64	245.00	0.00	56.75	51.11
	Fla	28.00	93.16	28.82	315.00	2409.23	18185.36	4516.00	21.67	1289.00	963.33
	Pyr	37.33	2670.79	9.41	8.89	109.23	42553.57	4032.50	6.67	1201.25	762.78
	BaA	14.67	83.42	0.00	18.33	520.77	15520.36	4173.50	4.58	1874.00	1254.44
	Chr	12.00	37.37	0.00	87.22	1283.85	7486.79	2142.00	0.00	841.25	533.33
	BbF	186.67	250.79	15.29	176.67	1543.85	7895.00	4263.00	18.75	1569.25	806.67
	BkF	9.33	32.37	1.18	2.22	83.08	3878.57	1345.00	0.83	539.75	319.44
	BaP	10.67	60.00	0.59	1.11	8.46	9210.00	2422.00	0.42	1075.25	644.44
	BghiP	18.00	78.16	2.94	8.33	244.62	6156.79	2048.50	2.08	1001.50	546.11
	DbahA	6.67	17.37	1.18	1.11	30.00	1535.71	510.50	0.83	92.25	136.11
	IP	23.33	100.79	4.12	3.89	29.23	4685.36	1545.50	2.92	645.00	223.89

ND = "Non Detected"

Table S3. Total contents (µg.kg^{-1} OM), similarity indexes and ratios based on PCB and PAH profiles in the 10 study sites in Lake Bourget and in reference site.

	Total content (µg.kg^{-1} OM)		Similarity indexes		Ratio values	
Site	PCB	PAH	PCB	PAH	$ratio_{PCB}$	$ratio_{PAH}$
S1	1799	433	0.65	0.51	0.46	0.26
S2	198	3472	0.57	0.33	0.41	0.04
S3	492	198	0.55	0.35	0.40	0.83
S4	457	815	0.59	0.43	0.34	0.62
S5	658	7253	0.58	0.52	0.35	0.47
S6	1078	123820	0.78	0.75	0.11	0.20
S7	2901	29028	0.68	0.89	0.16	0.23
S8	372	192	0.60	0.34	0.38	0.81
S9	278	10562	0.80	0.89	0.22	0.16
S10	508	6457	0.82	0.90	0.25	0.19
Mean ±SD	874 ± 855	18223 ± 38111	0.66 ± 0.10	0.59 ± 0.24	0.31 ± 0.12	0.38 ± 0.28
Reference site	1250*	152710**	1	1	0.11	0.28

* total content given in µg.kg^{-1} DM (dry matter) (from BIOSED program, non publisehed data)

** from BIOSED program

SD: standard deviation

Method S1. Dissecting OP profiles of remote lakes.

In the present study, there was an attempt to select a second reference that consisted in a large-scale OP signature from a remote area. For this aim, a literature overview was performed to collect PAH and PCB profiles from lacustrine media such as surficial sediments, water, air, snow and ice. Within each medium, available profiles were classified into categories according to their location (European, Arctic or Canadian) and their anthropization level (urban or remote). Remote European lakes were selected in alpine or rural sites at the same latitudinal range as Lake Bourget. Profiles in different seasons and years were added when available to prevent potential bias. Moreover, the distinction between the contamination in the gaseous/dissolved and particulate phases of air and water was brought when available; otherwise, they were considered as bulk media. The results from this literature overview are listed in Table S4 and S5.

For the PCBs, seven categories were specified from the literature; remote European sediment, remote Canadian sediment, Arctic sediment, urban European sediment, air, water and snow (Figure S1-A). For the PAHs, twelve categories were gathered from the literature, allowing the distinction between the gaseous/dissolved and particulate phases of the remote European air and urban European water (Figure S2-A).

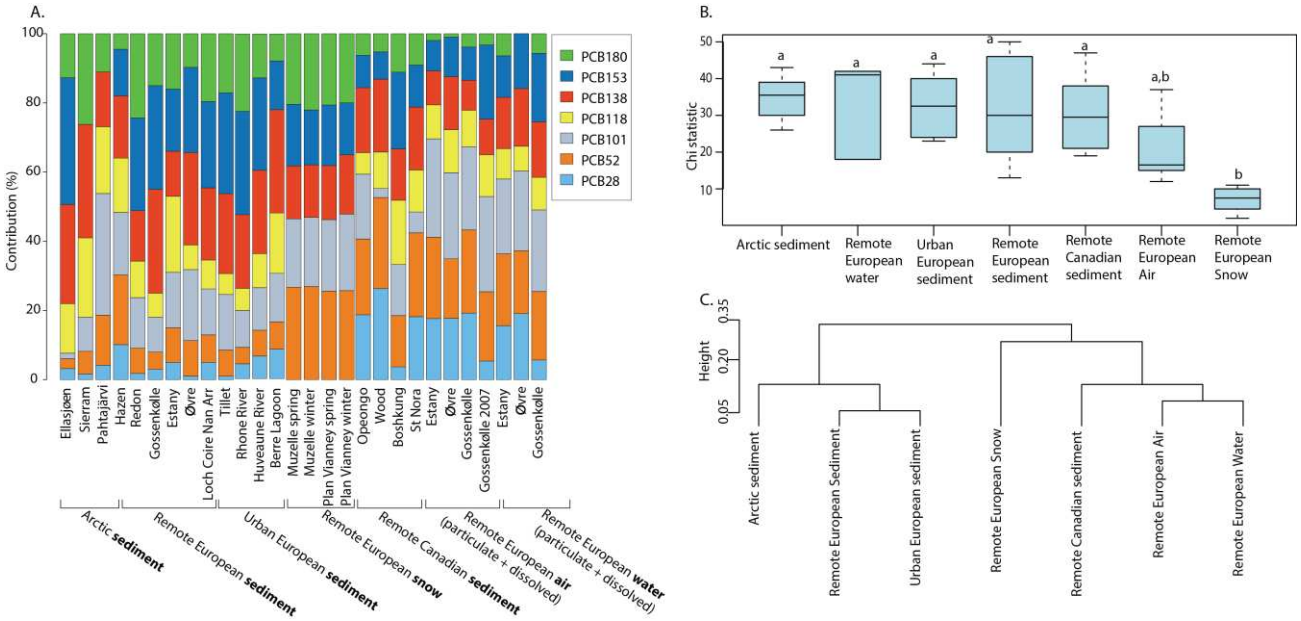

Figure S1. Results of the literature search for large-scale PCB profiles including (A) PCB profiles given in abundance (%) of each congener over the sum of the 7 PCBs, (B) Chi² statistical boxplots of the different compartments based on the individual profiles and (C) dendrogram of the different categories based on Bray-Curtis dissimilarity methods. Different letters in (B) indicate significant differences between the Chi² results (Kruskal-Wallis tests).

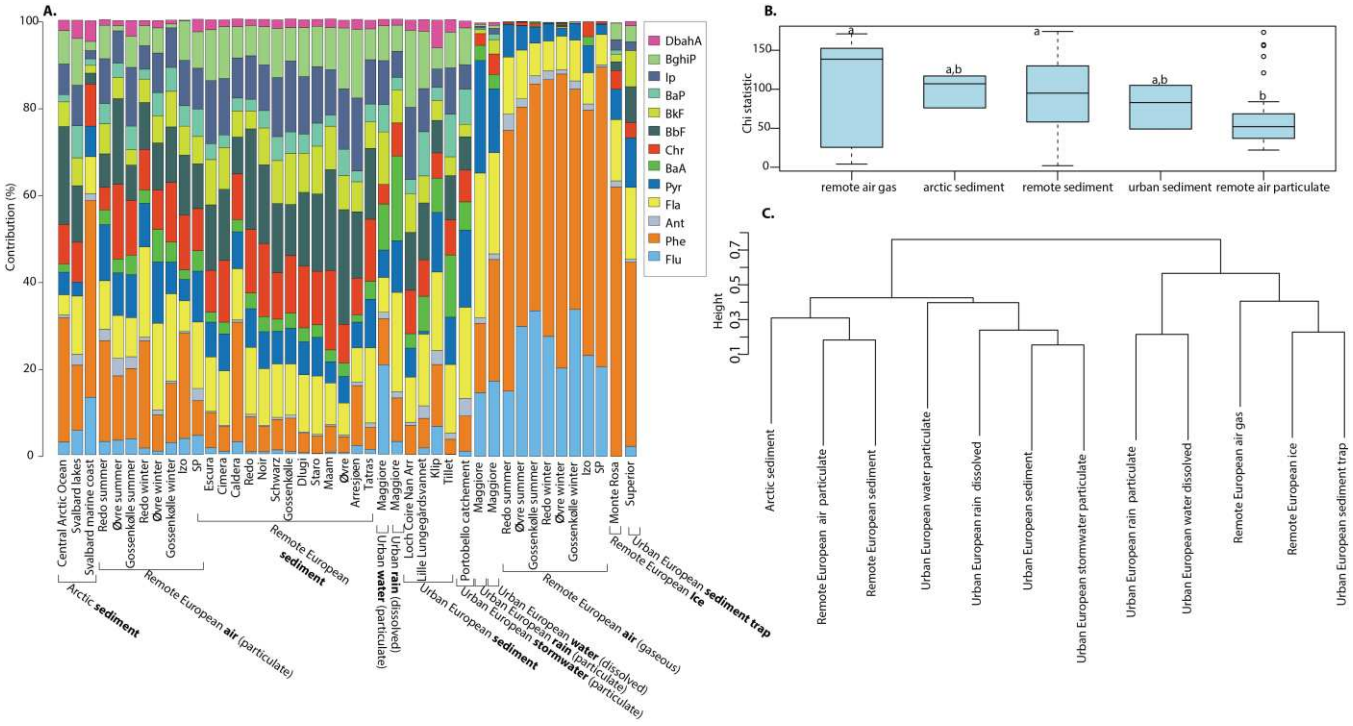

Figure S2. Results of the literature search for large-scale PAH profiles including (A) PAH profiles given in abundance (%) of each PAH over the sum of the 13 PAHs, (B) Chi² statistical boxplots of the different compartments based on these individual profiles and (C) dendrogram of the different compartments based on Bray-Curtis dissimilarity methods. Different letters in (B) indicate significant differences between the Chi² results (Kruskal-Wallis tests).

For the large-scale reference, PCB and PAH profiles that were searched for remote European lake sediments needed to fulfill the following eligibility criteria; (1) the sediment belonged to a stable category, and (2) it appropriately reflects the large-scale OP signature. To test the validity of the first criterion, the variations between profiles within the different categories were assessed and compared using Chi² and Kruskal-Wallis tests with the *pgirmess* package (Giraudoux and Giraudoux, 2018). The validity of the second criterion was tested by comparing the mean profiles in each category to determine whether the profiles in remote European sediments were similar to those in remote European air and water and different from those in urban European sediments. The remote sediment and water categories had more heterogeneous OP profiles than the air and snow categories (Figure S1-B and 3-B. Chi² and Kruskal-Wallis tests. p-value<0.05). Water and sediment can receive OPs from several more pathways other than wet and dry atmospheric deposition, such as lake tributaries or direct runoff, and ice and snow melting that could contribute to the different fractionation of the large-scale OP profile according to the watershed morphologies (i.e.. drainage area to lake surface ratio) of the remote lakes (Van Metre and Mahler, 2004; Yang et al., 2002), even without local source influences. Internal lake processes are also susceptible to the control of OP exchanges between water and sediment (Nellier et al., 2015). Lake biota, for example, is assumed to play an important role in water-to-sediment transports of PCBs through the differences in OP assimilations according to species, such as in settling particle fluxes and bioturbation activities (Berglund et al., 2001; Goutte et al., 2013; Nizzetto et al., 2012;

Reynoldson, 1987). In addition, sediment grain size distribution, organic matter quality and quantity can interfere in the partitioning of OPs between the sediment and the water column, depending on the K_{ow} of the considered OPs (Allen-King et al., 2002; Burgess et al., 2001; Tsapakis et al., 2003). Altogether, these processes may explain why the mean PCB profile of remote European sediment was more similar to the urban European sediment profile than those of remote European lake water and air (Figure S1-C). The two latter media exhibited higher abundances of more volatile congeners (PCB 28 and 52) than the sediments, suggesting these low K_{ow} congeners may be less efficiently trapped by the sediment than the less-volatile and hydrophobic ones. For PAHs, remote European sediment profiles were similar to those from the particulate phases of air and water (Figure S2-C), which exhibited a predominance of the heavy molecular weight (HMW) PAHs in contrast with the low molecular weight (LMW) enriched profiles from gaseous and dissolved phases. Similar to PCBs, remote lake sediments may act as a more efficient sink for particulate-bound HMW PAHs than dissolved LMW PAHs exhibiting low K_{ow} values (Arzayus et al., 2001; Augusto et al., 2010; Wong et al., 2004). Consequently, the more volatile PAHs and PCBs tend to be transported larger distances until their condensation at cold, high-latitude sites (Blais et al., 1998; Scheringer et al., 2000; Wania and Mackay, 1993). This phenomenon would explain why both remote and urban European sediments exhibit similar OP profiles dominated by heavy PCBs and PAHs, while remote Canadian and Arctic sediments at higher latitudes exhibit the reverse profiles and are dominated by light chemicals.

Finally, considering the variability of OP profiles within the remote categories and the resemblance with the urban profiles, the PCB and PAH profiles in remote European sediments did not meet the criteria to appropriately reflect the large-scale signature. This is the reason why sedimentary OP profiles from the urbanized part of the lake Bourget watershed were selected for the rest of this study.

Table S4. PAH profiles (%) from the literature overview for the selection of the large-scale reference and the respective literature references

Site	Category	Flu	Phe	Ant	Fla	Pyr	BaA	Chr	BbF	BkF	BaP	Ip	BghiP	DbahA	Reference
Escura	remote European sediment	1.4	8.1	0.3	12.5	8.0	2.3	9.6	15.1	10.4	3.7	14.5	11.7	2.3	Fernández et al. (1999)
Cimera	remote European sediment	0.6	5.7	0.3	12.5	8.5	2.7	14.2	16.4	9.6	2.9	13.0	11.9	1.6	
Caldera	remote European sediment	2.8	27.5	0.5	11.8	8.5	2.8	10.5	8.5	6.0	3.0	9.2	7.2	1.8	
Redo	remote European sediment	0.5	8.0	0.6	15.4	8.9	3.6	14.6	23.2	4.1	2.7	10.0	7.0	1.4	
Noir	remote European sediment	0.5	5.8	0.3	13.0	8.5	3.5	16.8	18.1	8.5	4.0	10.5	8.8	1.7	
Schwarz	remote European sediment	0.9	7.0	0.5	12.3	7.5	2.8	10.7	15.9	9.9	5.5	13.6	11.3	2.0	
Gossenkølle	remote European sediment	0.5	7.7	0.7	11.8	8.2	3.5	13.2	11.8	11.7	5.0	16.3	7.7	2.0	
Dlugi	remote European sediment	0.3	4.4	0.3	13.2	7.6	3.2	14.2	17.0	9.0	4.4	13.2	11.3	1.8	
Staro	remote European sediment	0.1	4.0	0.4	13.4	8.9	2.9	12.3	17.8	11.0	5.3	13.0	9.3	1.6	
Maam	remote European sediment	0.4	6.0	0.4	9.5	4.9	2.7	18.3	23.2	10.0	2.6	10.4	9.7	2.0	
øvre	remote European sediment	0.3	3.6	0.4	7.4	6.1	3.1	8.9	26.4	7.8	6.1	13.9	14.0	1.8	
Arresjøen	remote European sediment	1.9	13.8	0.8	7.9	5.9	1.7	8.4	15.3	6.9	2.5	16.8	15.8	2.3	
Tatras	remote European sediment	1.0	5.1	1.0	17.3	11.2	4.1	14.3	16.3	6.1	4.1	10.2	7.1	2.0	Fernández et al. (2000)
Loch Coire Nan Arr	remote European sediment	NA	6.7	0.7	10.4	6.7	3.3	10.0	13.3	8.9	3.3	16.6	17.7	2.4	Rose et al. (2005)
Lille Lungegårdsvannet	urban European sediment	1.5	6.8	2.9	16.5	0.6	8.1	8.4	13.1	6.2	10.2	9.9	13.2	2.7	Andersson et al. (2014)
Klip	urban European sediment	6.5	14.2	3.2	18.1	13.7	7.9	5.8	7.5	4.6	3.0	4.2	4.9	6.4	Pheiffer et al. (2018)
Tillet	urban European sediment	0.1	3.4	1.4	15.8	10.9	14.3	8.1	10.2	4.3	9.8	10.7	8.2	2.9	BIOSED program
Central arctic ocean	arctic sediment	2.9	28.6	0.6	4.7	5.2	1.9	9.1	22.5	5.7	1.7	7.0	7.7	2.4	Ma et al. (2017)
Svalbard lakes	arctic sediment	5.6	15.0	2.5	13.4	3.2	NA	9.2	13.0	6.4	7.4	9.3	10.8	4.2	Jiao et al. (2009)
Svalbard marine coast	arctic sediment	13.2	45.3	1.6	8.5	7.0	NA	9.7	2.5	1.8	1.5	1.9	2.1	4.8	
Redo summer	remote European air (particulate)	3.0	23.2	2.6	11.2	12.9	3.4	5.2	7.7	6.9	4.7	10.3	7.7	1.3	Fernández et al. (2000)
Ovre summer	remote European air (particulate)	3.3	14.8	4.1	9.8	9.8	3.2	17.2	19.7	4.9	3.3	7.4	1.2	1.2	

Table S4. Continued

Site	Category	Flu	Phe	Ant	Fla	Pyr	BaA	Chr	BbF	BkF	BaP	Ip	BghiP	DbahA	Reference
Gossenkolle summer	remote European air (particulate)	3.6	16.2	2.7	9.0	9.9	4.5	12.6	8.1	3.6	5.4	13.5	7.2	3.6	
Redo winter	remote European air (particulate)	1.5	24.7	0.8	20.8	10.0	3.1	9.3	10.8	5.4	2.3	5.4	4.6	1.2	
Ovre winter	remote European air (particulate)	0.8	8.3	1.2	19.9	14.1	7.5	9.1	10.8	6.2	5.4	9.1	5.8	1.7	
Gossenkølle winter	remote European air (particulate)	2.7	13.7	0.5	20.1	7.3	4.6	13.7	12.8	8.2	5.5	9.1	0.9	0.9	Drooge et al. (2010)
Izo	remote European air (particulate)	3.7	24.2	0.4	7.1	4.9	2.2	12.6	13.8	6.7	4.7	10.4	9.1	0.2	Fernández et al. (2002)
SP	remote European air (particulate)	4.4	8.0	2.8	15.3	11.7	4.7	9.7	10.3	6.3	6.3	9.4	8.4	2.9	
Redo summer	remote European air (gaseous)	15.0	60.0	3.8	13.1	7.5	0.1	0.4	0.1	ND	0.0	0.0	0.0	0.0	
Ovre summer	remote European air (gaseous)	29.9	50.5	1.9	11.2	5.6	0.1	0.7	0.1	0.1	0.0	0.0	0.0	0.0	
Gossenkølle summer	remote European air (gaseous)	33.5	52.2	1.9	7.5	3.7	0.2	0.6	0.2	0.0	0.2	0.0	0.0	0.0	
Redo winter	remote European air (gaseous)	27.6	59.1	2.0	6.9	3.9	0.1	0.3	0.0	0.0	0.0	0.0	0.0	0.0	
Ovre winter	remote European air (gaseous)	20.3	67.7	1.0	7.7	1.9	0.3	0.3	0.2	0.2	0.1	0.1	0.1	0.0	
Gossenkølle winter	remote European air (gaseous)	33.8	50.7	1.9	9.4	3.8	0.1	0.3	0.0	0.0	0.0	0.0	0.0	0.0	
Izo	remote European air (gaseous)	23.2	56.5	1.4	7.2	6.2	2.1	3.4	0.0	0.0	0.0	0.0	0.0	0.0	Drooge et al. (2010)
SP	remote European air (gaseous)	20.6	69.0	0.5	7.0	2.3	0.2	0.5	0.0	0.0	0.0	0.0	0.0	0.0	
Monte Rosa	remote European ice	NA	62.0	1.4	14.1	7.0	NA	4.3	2.0	1.7	1.0	2.4	3.8	0.1	Gabrieli et al. (2010)
Maggiore	urban European water (dissolved)	17.3	28.0	1.3	23.3	14.7	3.3	4.7	NA	3.3	1.3	1.3	0.7	0.7	Olivella (2006)
Maggiore	urban European water (particulate)	20.6	10.6	1.5	8.0	6.3	10.6	4.5	NA	12.1	6.3	10.1	8.0	1.5	
Maggiore	urban European rain (particulate)	14.6	16.0	1.3	33.3	25.9	3.5	2.7	NA	0.9	0.4	0.4	0.4	0.4	
Maggiore	urban European rain (dissolved)	2.9	10.0	1.4	22.9	11.9	19.5	7.6	NA	7.6	2.9	6.0	6.0	1.4	
Superior	urban European sediment trap	2.3	42.4	0.7	16.5	11.4	NA	3.5	8.3	8.3	NA	2.0	3.7	1.0	Jeremiason et al. (1998)

ND = “Non Detected”

NA = “Non Available”

Table S5. PCB profiles (%) from the literature overview for the selection of the large-scale reference and the respective literature references

Site	Category	PCB28	PCB52	PCB101	PCB118	PCB138	PCB153	PCB180	Reference
Redon	remote European sediment	1.8	7.3	14.6	10.6	14.6	26.8	24.4	Grimalt et al. (2004)
Gossenkølle	remote European sediment	3.0	5.0	10.0	7.0	30.0	30.0	15.0	
Estany	remote European sediment	5.0	10.0	16.0	22.0	13.0	18.0	16.0	Carrera et al.
Ovre	remote European sediment	1.0	10.3	20.5	7.2	26.7	24.6	9.7	(2002)
Loch Coire nan Arr	remote European sediment	5.0	7.9	13.3	8.3	20.8	25.0	19.6	Rose and Rippey (2002)
Opeongo	remote Canadian sediment	18.8	21.9	18.8	6.3	18.8	9.4	6.3	
Wood	remote Canadian sediment	26.3	26.3	2.6	10.5	21.1	7.9	5.3	
Boshkung	remote Canadian sediment	3.7	14.8	14.8	18.5	14.8	22.2	11.1	Macdonald and
St Nora	remote Canadian sediment	18.2	24.2	6.1	12.1	18.2	12.1	9.1	Metcalfe (1991)
Tillet	urban European sediment	1.0	7.5	16.1	6.0	23.1	29.1	17.1	BIOSED program
Rhône	urban European sediment	4.3	4.8	10.7	6.4	21.4	29.9	22.5	Desmet et al. (2012)
Huveaune	urban European sediment	6.6	7.5	12.3	9.9	24.2	26.8	12.8	Kanzari et al.
Berre Lagoon	urban European sediment	8.5	7.9	14.1	17.5	30.0	14.2	7.8	(2014)
Ellasjøen	arctic sediment	3.2	2.9	1.6	14.3	28.7	36.6	12.7	Evenset et al. (2007)
Sierram	arctic sediment	1.6	6.6	9.8	23.0	32.8	NA	26.2	Vartiainen et al.
Pahtajärvi	arctic sediment	4.1	14.5	35.2	19.3	15.9	NA	11.0	(1997)
Hazen	arctic sediment	10.1	20.2	18.0	15.7	18.0	13.5	4.5	Muir et al. (1996)
Estany	remote European air (gaseous + particulate)	17.6	23.5	28.4	9.8	9.8	8.8	2.0	Carrera et al. (2002)

Table S5. Continued

Site	Category	PCB28	PCB52	PCB101	PCB118	PCB138	PCB153	PCB180	Reference
Ovre	remote European air (gaseous + particulate)	17.7	17.2	24.9	12.4	15.3	11.5	1.0	
Gossenkølle	remote European air (gaseous + particulate)	19.2	24.0	24.0	10.6	8.7	9.6	3.8	
Gossenkølle 2007	remote European air (gaseous + particulate)	5.4	20.0	27.5	12.1	10.3	21.4	3.3	Arellano et al. (2015)
Muzelle summer	remote European snow	NA	26.8	19.7	NA	15.3	17.8	20.4	
Muzelle winter	remote European snow	NA	26.9	20.0	NA	15.2	15.9	22.1	
Plan Vianney summer	remote European snow	NA	25.6	20.6	NA	15.6	17.5	20.6	Nellier et al.
Plan Vianney winter	remote European snow	NA	25.7	22.1	NA	17.1	15.0	20.0	(2015)
Estany	remote European water (dissolved + particulate)	15.6	20.8	21.6	8.8	14.8	12.0	6.4	
Ovre	remote European water (dissolved + particulate)	19.0	18.3	23.0	7.1	16.7	15.9	0.0	
Gossenkølle	remote European water (dissolved + particulate)	5.7	19.8	23.6	9.4	16.0	19.8	5.7	Carrera et al. (2002)

ND = “Non Detected”
NA = “Non Available

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3. Synthèse

Dans ce chapitre, des outils permettant de comprendre l'influence des sources locales et lointaines sur la contamination sédimentaire littorale ont été recherchés. Il était question d'étudier les similarités de profils à la fois avec des références locales (i.e. référence utilisée dans l'Article) et lointaines (i.e. avec des profils de lacs de montagne éloignés des sources locales). L'étude en Supplementary data a montré que ces profils de lacs de montagne ne divergeaient pas significativement de ceux impactés par des sources urbaines locales et souligne ainsi la complexité des mécanismes régissant le transport atmosphérique de longue distance des polluants organiques et leur transfert au compartiment sédimentaire.

A l'échelle locale, l'intensité et les profils de contamination sédimentaire en zone littorale du lac du Bourget montrent une transformation depuis la distance au principal noyau urbain au sud du bassin-versant. Cette transformation met en lumière à la fois l'influence des principales sources urbaines à l'échelle du bassin-versant, mais également celles de sources ponctuelles en bordure de lac. Nous pouvons alors nous questionner sur le rôle de ces sources ponctuelles dans la contamination du biote littoral.
En effet, l'Article 1 a mis en évidence des liens complexes entre contamination du sédiment et effets sur le biote, à la fois en laboratoire et *in situ*. Il serait alors possible que la biodisponibilité de la contamination sédimentaire ne soit pas directement reflétée par sa contamination totale et/ou que les concentrations internalisées de polluants ne soient pas toujours suffisantes pour déclencher des effets chez les organismes observés. Les concentrations internes du biote littoral pourraient alors davantage nous renseigner sur l'influence exercée par les sources locales sur la contamination du biote. Les relations entre contaminations sédimentaire et du biote benthique pourraient également nous éclairer sur la biodisponibilité de la contamination du compartiment sédimentaire.

Chapitre 3

Identification des sources locales de la contamination du littoral et évaluation du transfert au biote benthique

1. Démarche générale

La mesure des concentrations internes en polluants sur organismes exposés (i.e. biosurveillance active) ou prélevés (i.e. biosurveillance passive) sur le terrain est un outil fréquemment utilisé dans l'évaluation de la qualité écologique des écosystèmes côtiers marins (Fialkowski and Rainbow, 2017) ou des cours d'eau (Bonnail et al., 2019; Wong et al., 2017). Cependant, peu d'études s'attachent à appliquer cette biosurveillance à l'échelle littorale des lacs (Besse et al., 2012).

L'article suivant propose d'analyser la contamination en 6 ETM et 14 HAP dans les sédiments et les *Corbicula fluminea* autochtones au niveau de 20 sites littoraux du lac d'Annecy. Au moyen de régressions linéaires multiples, nous avons cherché à expliquer les fluctuations de contamination de ces bivalves à l'échelle littorale avec des variables caractérisant des sources locales de pollution internes au lac (e.g. puissance motrice des bateaux des ports) et provenant du bassin-versant (e.g. surface drainée par les eaux pluviales). Le sédiment littoral est également considéré comme source interne de contamination au lac dans cette analyse et la notion de transfert de contamination depuis le sédiment est elle aussi abordée par le calcul de facteur de bioconcentration.

2. Article 3 - Tracking sources and transfer of contamination according to pollutants variety at the sediment-biota interface using a clam as bioindicator in peri-alpine lakes

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Abstract

The pollution of lakes may vary greatly along the littoral zone as a function of the influence of potential point sources possibly leading to local ecological risks. The concomitant chemical analysis of littoral-benthic autochthonous organisms and sediment can provide insights into the bioavailability and thus the ecological risk of contaminants. In this study, the autochthonous clam *Corbicula fluminea* was used to assess the possible sources and transfer of six trace metals (TMs) and fourteen polycyclic aromatic hydrocarbons (PAHs) to the littoral-benthic biota of a large peri-Alpine lake. The contaminant concentrations spatially varied with a value scale from 1 to 280 000 times along the lake littoral in both the sediment and *C. fluminea*. Multiple linear regressions were performed to explain the spatial variability of *C. fluminea* contamination by considering both watershed and in-lake sources. The internal concentration of the sum of PAHs in clams was significantly correlated with sediment contamination, suggesting that the main PAHs contamination of the benthic biota occurred from the sediment. However, most of the internal TM concentrations of *C. fluminea* were significantly correlated with stormwater drainage areas in the lake watershed, highlighting the importance of stormwater runoffs in the lake littoral biota, compared to potential in-lake sources such as the engines of boats in harbors. For As, Cu, Pb and the sum of PAHs, concentrations in *C. fluminea* were also positively correlated with environmental variables such as wave energy and slope. The transfer of TM and PAH contaminants was assessed through the bioconcentration factor (BCF) defined as the ratio of internal and sediment concentrations. As, Cd, Cu, Zn and light molecular weight PAHs were more bioconcentrated in *C. fluminea* compared to Pb, Sn and heavy molecular weight PAHs, suggesting differences in the bioavailability of these contaminants. Considering these differences in contaminant bioavailability, this study underlines the relevance of using autochthonous organisms as bioindicators of lake littoral biota contamination concomitantly with sediment matrices, and illustrates the challenge of tracking pollution sources in lakes.

Keywords

Trace metal, polycyclic aromatic hydrocarbon, bioindicator, bioconcentration, *Corbicula fluminea*.

Introduction

The sediment compartment is of great importance when assessing the ecological risk of contaminants for biological organisms (Atkinson et al., 2007; Bryan and Langston, 1992; Burton, 2018). Chemical analyses of sediments can be compared to ecotoxicological thresholds from the literature (e.g. Threshold Effect Concentration (MacDonald et al., 2000)). Sediment can also be used in bioassays as a contaminated matrix to which study laboratory organisms are exposed to assess their response (Triffault-Bouchet et al., 2005). In the literature, the sediment is considered as a more stable and integrative compartment compared to water (Payne et al., 1996; Sutherland, 2000) and can exhibit significantly higher contaminant concentrations leading to a higher ecological risk (Atkinson et al., 2007; Bryan and Langston, 1992). However, the binding capacity of pollutants to the sediment greatly varies according to their molecular structure. As an example, PAHs with low octanol / water partitioning coefficient (K_{ow}) tend to bind to the sediment organic matter in a lesser extent than those with higher K_{ow} (Harner et al., 2004; Naffrechoux et al., 2015; Shoeib and Harner, 2002). Secondly, many abiotic (e.g. temperature, dissolved oxygen, hydrodynamic regime) and biotic (e.g. trophic interactions, bioturbation) factors can influence the bioavailability of sediment-borne contaminants (Eggleton and Thomas, 2004). It is therefore essential to perform concomitant measurements in biological matrices, in addition to sediment, to provide a better insights regarding the bioavailability of sediment-borne contaminants (Guo and Feng, 2018) and their transfer throughout lake food webs.

The Asian clam *Corbicula fluminea* is a benthic filter-feeder (Cataldo et al., 2001) commonly used as a bioindicator of the ecological status of stream and coastal environments over large time (Riva et al., 2010) and spatial (Goldberg, 1986) scales. *C. fluminea* is a widespread bivalve mollusk leaving in upper part of sediment and filtering water at the sediment surface. These characteristics make of *C. fluminea* a great biological model to test for the bioavailability of contamination at the sediment-water interface.

Lake Annecy is a large French peri-alpine lake with an anthropized watershed. Although the physico-chemical and biological parameters of the water column have been monitored for several decades (Frossard et al., 2018), only a few studies have focused on anthropogenic contamination (GREBE, 2008; Lallée, 2009; Naffrechoux et al., 2015) and mostly concern contamination in the deepest part of the lake.

Using Lake Annecy as case study, we so aim at assessing whether the contamination of *C. fluminea* provides insights (1) into the transfer and bioavailability of sediment-borne pollutants to benthic organisms in the lake littoral zone, and (2) into the identification of sites and point sources that may exert ecological risks. In particular, this study attempts to assess the contribution of potential in-lake versus watershed sources in the contamination of the littoral biota by studying *C. fluminea* multi-contamination.

Two contaminant families are studied; Trace Metals and Metalloids (TMs) and Polycyclic Aromatic Hydrocarbons (PAHs). These families are widespread in the lacustrine environment and differ by way of their mobility, persistence, bioavailability and toxicity (Naimo, 1995; UNEP,

2003), thereby justifying a large-scale assessment of *C. fluminea's* capacity to reflect biota contamination in the littoral zone. Another objective is to identify a large array of potential pollution sources.

We first expected that *C. fluminea* contamination will exhibit significant spatial variability in the littoral zone due to the influence of local point sources of pollution. In particular, harbors are expected to exert significant in-lake influence on littoral biota contamination, with a greater concentration of TMs in organism (Guevara-Riba et al., 2004). On the contrary, external sources, such as surface and stormwater runoffs, are expected to play a role in the contamination by PAHs of the littoral biota (Brown and Peake, 2006). In addition, two buffer zones around the study sites of respectively 200 and 600 m were assessed in order to account for small and medium-scale sources that may influence *C. fluminea* contamination. We therefore expect that point sources included in the small buffer zone (i.e. 200 m) will more precisely explain the clams contamination than higher scales. The last assumption is that *C. fluminea* contamination will differ from sediment contamination according to the bioavailability of the contaminants. Particularly, differences in PAH contaminations in the sediment and biological matrices should be greater (i.e. by bioconcentration effect) than for TMs due to their greater reactivity (i.e. lipophilicity, molecular degradation through biological, chemical and physical processes; Moza et al., 1999). However, some differences are expected according to light and heavy molecular weight PAHs that exhibit different molecular properties (e.g. water / octanol partitioning coefficient K_{ow}).

Materials and Methods

1. The study lake

Lake Annecy is a large monomictic and oligotrophic lake located in Savoie (France), on the northwest edge of the French Alps (45°51'N, 6°10'E, Figure 1A). It has a surface area of 27 km^2 and mean and maximum depths of 41 and 65 m, respectively. The 250 km^2-catchment area of Lake Annecy is covered by forests (56 %), agricultural areas (20 %), urban areas (17 %) and water bodies (6 %) (Corinne Land Cover, 2000). Its watershed has been subject to rapid anthropization over recent decades (Rulliere et al., 1972). The total population in the watershed, about 125 000 inhabitants, doubles in summer during the tourist season.

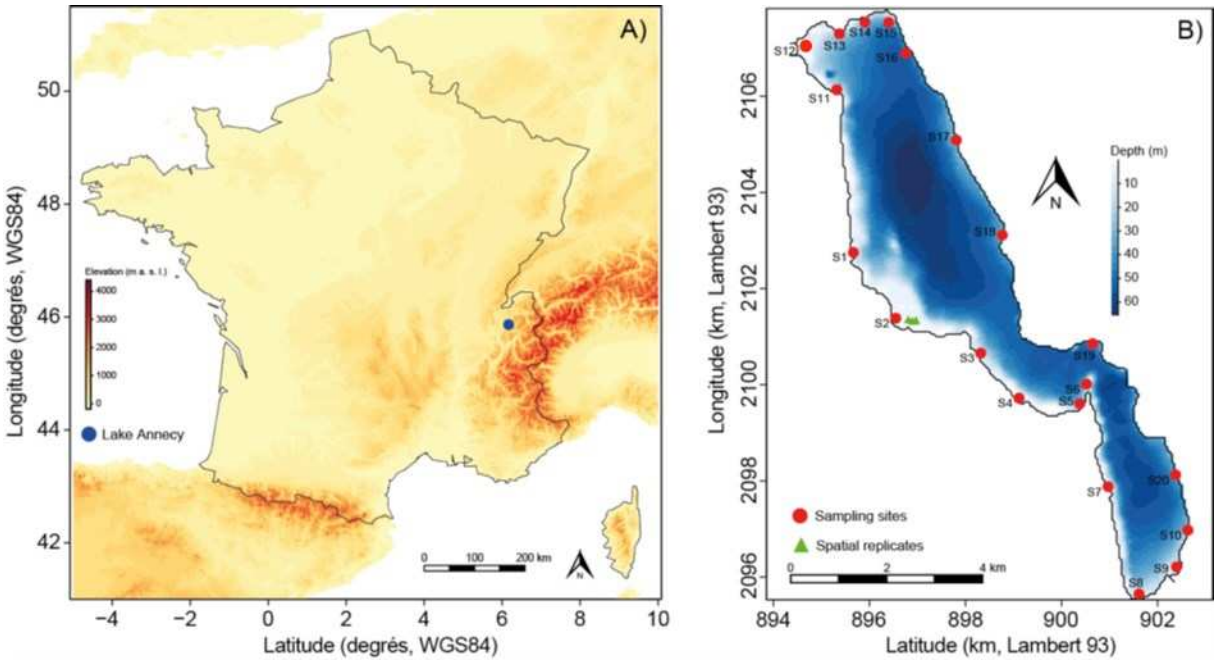

Figure 1. Map of Lake Annecy in the east of France (A) and the locations of the sampling sites (B). Red circles indicate main sampling sites and green triangles replicates for assessment of local contamination variability.

2. Sampling sites

Twenty littoral sites were selected to cover the overall lake littoral and included different land-use contexts (i.e. beaches, reed beds, roadsides, harbors) (Figure 1-B). At all sites, surface sediments (i.e. the first 5-cm sediments) and *C. fluminea* were sampled using an Ekman grab at a water depth of 1.5 to 2.5 m, depending on the topographic constraints. Sediment samples were homogenized, sieved through a 2-mm mesh to remove debris and stored at 4°C

The sampled *C. fluminea* were selected according to similar ranges of shell size (i.e. between 1.5 and 2.5 cm) to limit possible ontogenic differences in contamination. We checked for the representativeness of each sample by sampling 3 replicates close from each other (<12m) in the site S2 (Fig. 1). No significant differences in *C. fluminea* contamination for PAHs and TMs (see details in appendix A1).

3. Contamination quantification

As and Sn were measured in the sediment and *C. fluminea* by inductively coupled plasma mass spectrometry (ICP-MS) while Cd, Cu, Pb and Zn were quantified by inductively coupled plasma atomic emission spectroscopy (ICP-AES). PAHs were measured in the sediments and *C. fluminea* using high performance liquid chromatography (HPLC) with fluorescence detection. Among the 16 PAHs prioritized by the US Environmental Protection Agency (US-EPA), 14 were quantified; acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[ah]anthracene (DbahA),

benzo[g,h,i]perylene (BghiP) and indeno[1,2,3-c,d]pyrene (IP). Light molecular weight PAHs, also called light PAHs are Ace, Flu, Phe, Ant and Pyr, while the others are considered as the heavy PAHs.

To limit biases in the analysis of contamination data related to physicochemical properties, PAH concentrations in sediments and *C. fluminea* were normalized to organic matter (OM) concentration and lipid content, respectively. The average percentage of lipids for all the *C. fluminea* sampled was estimated at 12.9% based on C:N ratios (Figure S2). The organic matter content of the sediments was estimated by measuring loss on ignition according to Heiri et al. (2001) (Fig. A3). The sum of the 14 PAHs was thus expressed in μg kg^{-1} OM for the sediments and in μg kg^{-1} lipids for *C. fluminea*. Grain size distribution of sediment was measured by laser diffractometry (Malvern Mastersizer 2000G) and presented a homogeneous sandy size group (Fig. A3). The grain size distribution of sampled sediment could not consequently exert a major bias in the contaminant bioavailability (Eggleton and Thomas, 2004; Reid et al., 2000; Zhang et al., 2014). Concentrations below the detection limits were estimated at a value equal to the detection limit divided by √2 according to Croghan and Egeghy (2003). The raw data of sediment and *C. fluminea* contaminant concentrations are presented in Table S1.

4. Bioconcentration factor (BCF)

The transfer from sediment borne contaminants to the clams was assessed through the ratio of the non- normalized contaminant concentrations between *C. fluminea* and the sediments designated as the bioconcentration factor (BCF) (Jia et al., 2018; Mendoza-Carranza et al., 2016; Mountouris et al., 2002). A contaminant was considered as bioconcentrated when the BCF was equal to or greater than 1. The relationship between the BCFs and the sediment contamination was studied to assess whether potential biological regulation mechanisms may occur in the organisms exposed to an increasing sediment contamination (McGeer et al., 2003).

5. Explanatory variables of *C. fluminea* contamination

We defined explanatory variables which represented of in-lake and external contamination sources to identify which one contributed to contaminant concentration in clams. First, potential in-lake sources of pollution were considered using the total engine power of boats (hp) in the harbors, to provide a realistic pollution capacity of the boats (Figure S4). A total of 1635 boats were counted throughout the lake littoral, moored at private pontoons and in large public harbors. The individual power of each engine was read directly on the engine for 70% of the boats and estimated for the remaining 30%. Second potential watershed sources consisted of the number of stormwater outlets and their associated drainage areas (Figure S4). To test the influence of the spatial scale in *C. fluminea* contamination by these candidate variables, two buffer sizes around the sampling sites were considered, i.e. 200 and 600 m (Figure S5). The mean wave energy and slope and the sediment organic content of the sampling sites were also

considered to influence the contamination of *C. fluminea*. The mean wave energy was calculated as a proxy of the hydrodynamic regime within a 200 m diameter circle around each site, based on the hydrodynamic models described in Rohweder et al. (2008) and Marchand and Gill (2017), by coupling bathymetric data from the BRGM / SILA lake (Bisson et al., 2006) and the direction and wind speed from the Météo-France Meythet station (i.e. hourly data over 4 annual cycles). The average wave energy within a 200 m diameter circle around the site was calculated over the entire meteorological time range (Fig. S6). The mean slope (%) within a 50 m radius around the site was calculated from BRGM / SILA (1990) bathymetric lake data. The sediment contamination was also considered to explain the contamination of *C. fluminea*.

6. Data analysis

We assess contamination in *C. fluminea* performing multiple linear regressions with backward selection, using *C. fluminea* contamination (for each TMs separately and for the sum of the PAHs) as response variable against the potential explanatory variables (i.e. section 2.5). Site S11 was removed prior to modeling for the PAHs because of its concentration several orders of magnitude higher than the other sites that can be explain by the vicinity of a main road with huge daily traffic. For the TMs, sites S7, S8, S10, S13, S16, S17, S18, S20 could not be considered since the biological masses sampled were not sufficient to carry out the analyses. All the statistical analyses and models as well as the graphical displays were carried out using R (Team, 2017).

Results

1. Sediment and *C. fluminea* contaminations

The TMs contamination of the sediment exhibited a high spatial heterogeneity along lake littoral with a value scale from 1 to 8 (As), 9 (Pb), 12 (Cu), 31 (Zn) and 42 (Sn) times (Figure 2). Similarly, internal concentrations in clams were also highly variable with a value scale from 1 to 2 (As, Cd), 3 (Sn) and 4 (Cu, Pb) times (Figure 3). However, the pattern of TMs contamination was significantly different between the sediment and the organisms along the lake littoral (Chi^2 tests, p-value < 0.05).

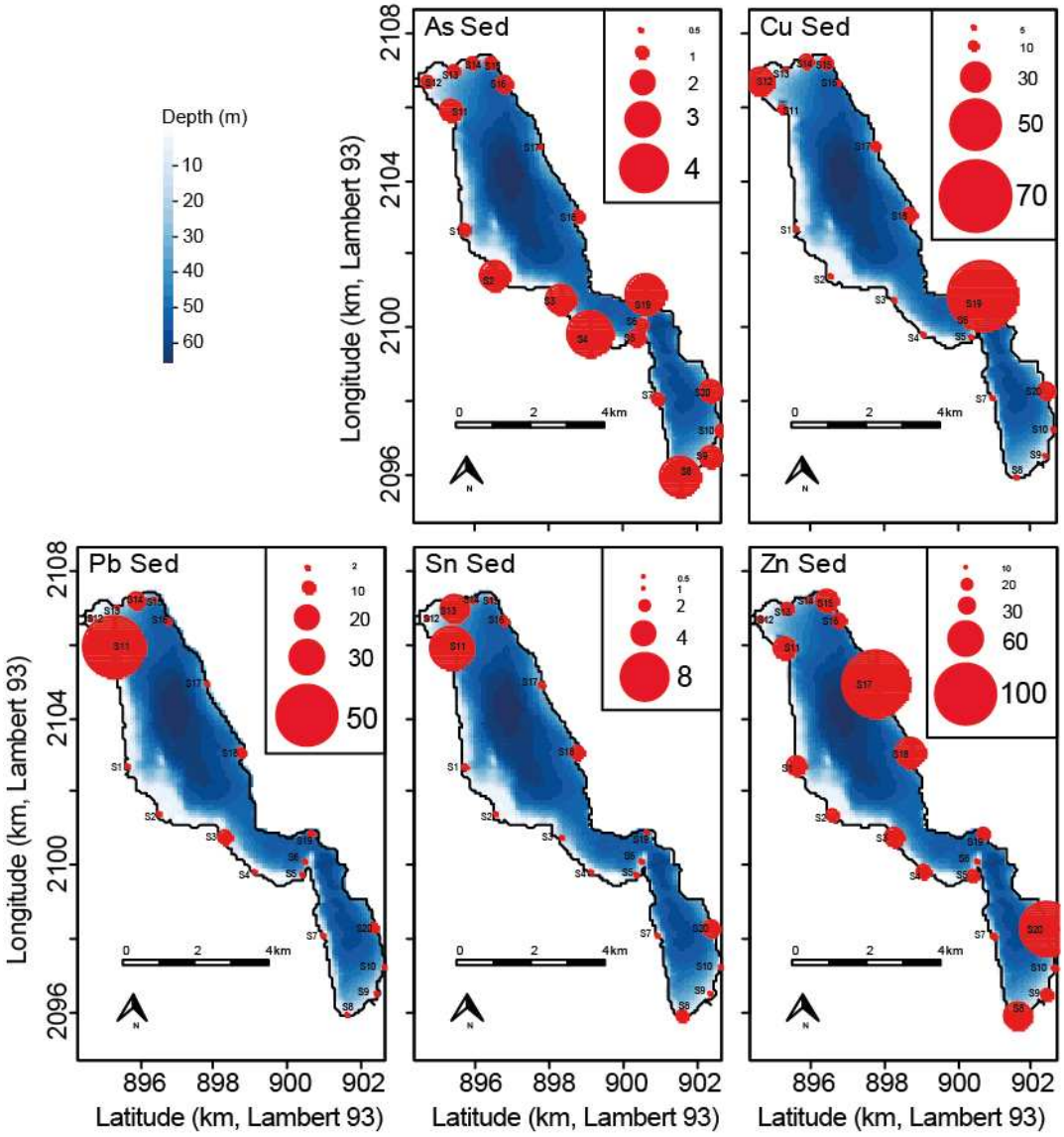

Figure 2. Mapping the TMs sediment contamination (mg kg^{-1} DM) along Lake Annecy littoral.

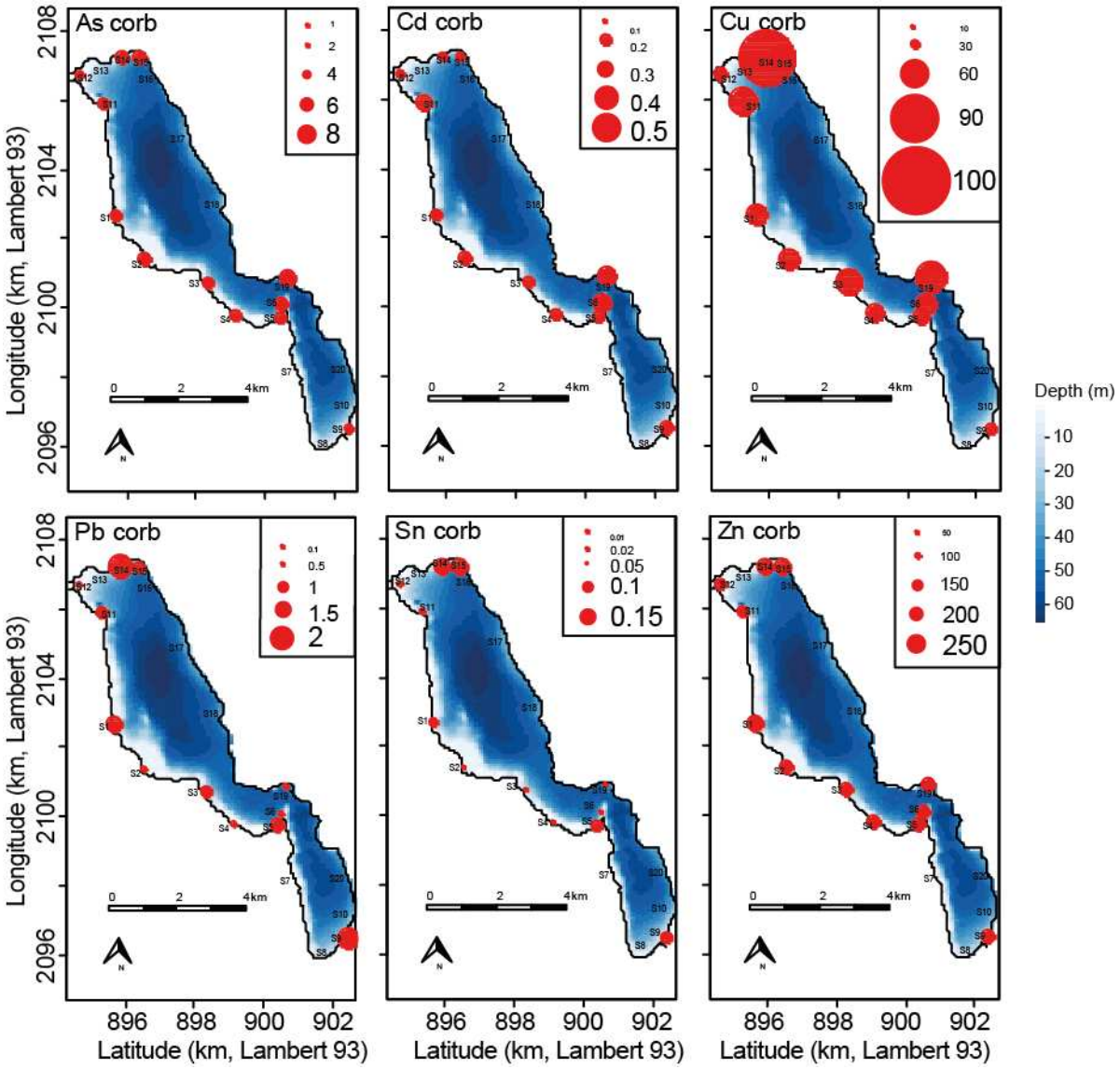

Figure 3. Mapping the TMs C. fluminea *contamination (mg kg^{-1} DM) along Lake Annecy littoral.*

The average sum of PAHs in the lake littoral was equal to $1.10^5 \pm 4.10^5$ µg kg^{-1} OM in the sediment and 165.6 ± 150.2 µg kg^{-1} lipids in *C. fluminea* and also varied considerably according to the location considered in the littoral in both matrices (i.e. sediments and *C. fluminea*; Figure 4).

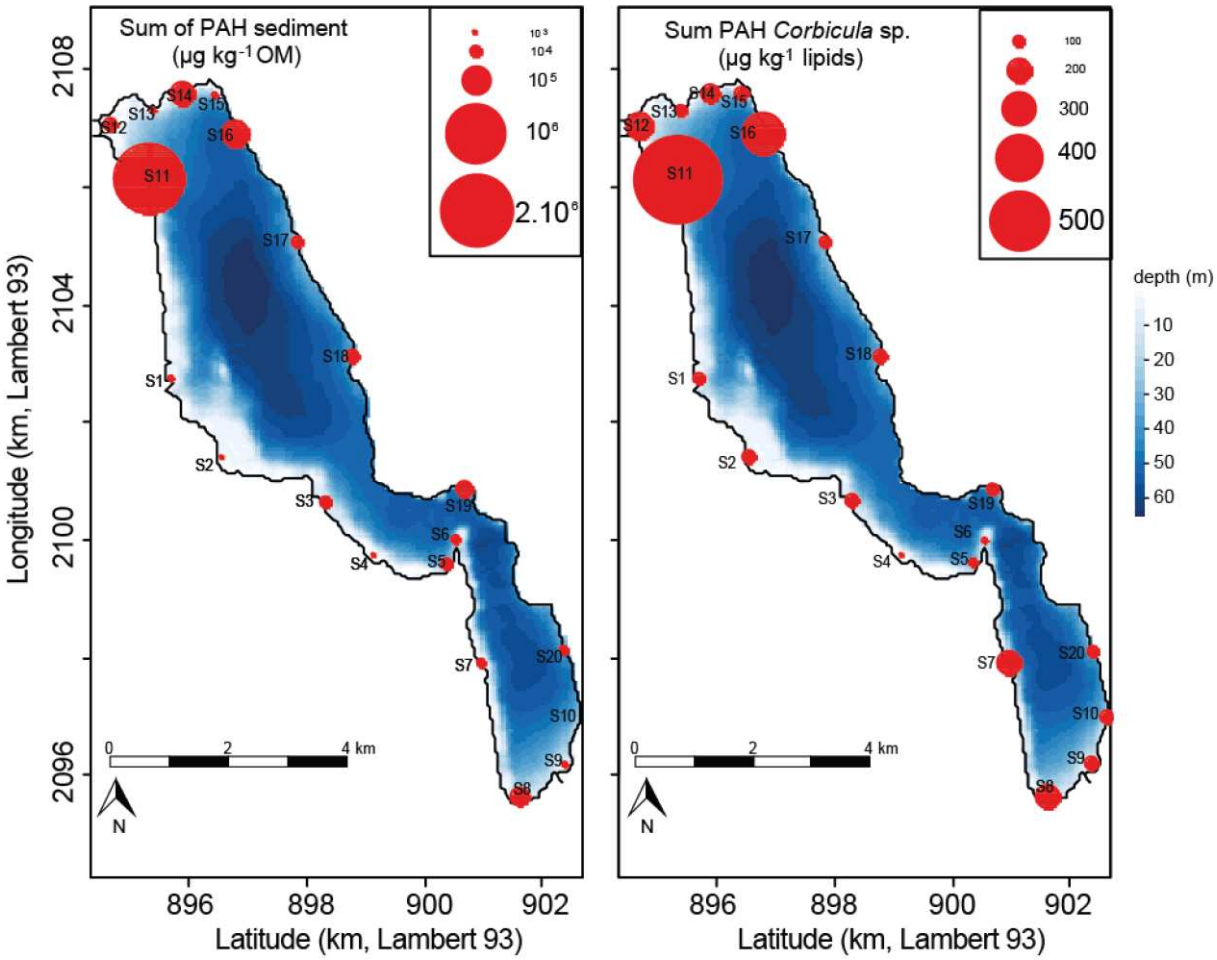

Figure 4. Map of the sum of PAHs in the sediment (µg kg^{-1} OM) on the left side and in C. fluminea *(µg kg^{-1} lipids) on the right side.*

S11 exhibited the highest contamination with concentrations of 1.7 10^6 µg kg^{-1} OM in the sediment and 734.1 µg kg^{-1} lipids in *C. fluminea*. In addition, *C. fluminea* exhibited lower proportions of heavy PAHs (23 ± 10 %) than in the sediment (62 ± 10 %) (Figure 5).

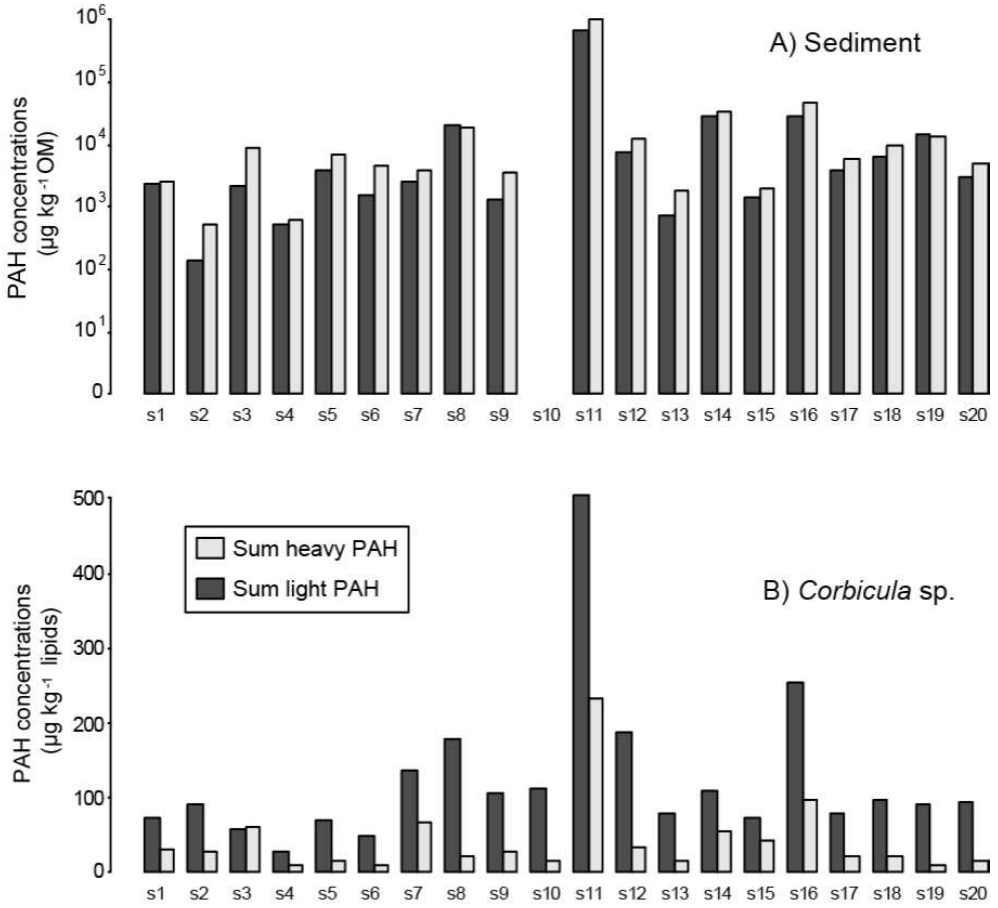

Figure 5. Barplots representing the composition in light and heavy PAHs in A) the sediments (µg kg^{-1} OM) and B) C. fluminea *(µg kg^{-1} lipids).*

2. Contamination transfer

BCFs differed significantly among contaminants for both PAHs and TMs and among sites for PAHs (ANOVA, p-value < 0.01; Fig. 6). For TMs, the BCFs for As, Cu and Zn were > 1 while they were < 1 for Pb and Sn (Figure 6A). The BCF for Cd could not be calculated as it was not detected in the sediment.

BCFs were higher for light PAHs compared to heavy ones, especially Flu for which values exceeded 400 (Figure 6B). Regarding the spatial distribution of BCFs along the lake littoral, S2 and S3 had the highest BCFs (Table S2).

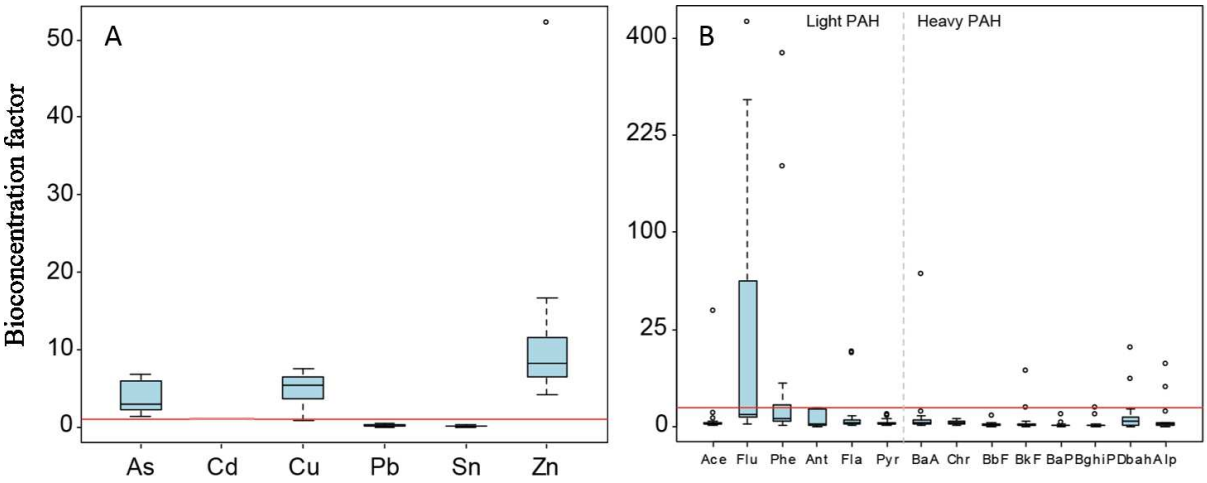

Figure 6. Boxplots of the bioconcentration factors (BCF) for A) TMs and B) PAHs. The horizontal line represents a BCF equal to 1.

3. Contamination sources

All the candidate variables were significantly related to *C. fluminea* contamination for at least one contaminant for a given buffer radius, and the R-squared were relatively high and varied from 0.49 to 0.9 (except 0.28 for Pb at 200m radius, Table 1).

For the TMs, the sediment contamination was not correlated with that of *C. fluminea* meaning that the concentrations in the clams were likely not directly impacted by the sediment contamination. All other variables were at least significant for one TM and, most of them were positively correlated with *C. fluminea* contamination, suggesting that these variables may favor their contamination. However, some significant negative relationships indicate that the influence of the explanatory variables may differ from one TM to another. For example, the number of stormwater outlets exerted a significant positive influence on the contamination for As and Cd but a negative one for Cu, Pb and Sn.

We also noted that many more variable were detected to have an effect on clams contamination in TMs at the larger scale (600 m radius) than at the local scale (200 m radius), except for the proportion of organic matter in sediment (Table 1). R-square were also similar or higher for the 600m radius confirming the better prediction power at this scale.

Considering the sum of PAHs, the main explanatory variable was the sediment contamination while the slope of the site had a marginally negative influence on internal PAH concentrations in *C. fluminea* whatever the scale of the study (Table 1).

Table 1. Results from the multiple linear regressions relating C. fluminea *contamination to candidate variables. "+" and "-" symbolize a positive and negative relationship with* C. fluminea *contamination respectively. The significance rate was symbolized as following: "." for 0.1 > p-value > 0.05; "*" for 0.05 > p-value > 0.01; "**" for 0.01 > p-value > 0.001 and "***" for p-value < 0.001. The adjusted R-squared (Adjusted-R²) indicates the proportion of variations in* C. fluminea *contamination explained in the final models.*

Contaminants		As		Cd		Cu		Pb		Sn		Zn		Sum of PAHs	
	Radius	200 m	600 m	200 m	600 m	200 m	600 m	200 m	600 m	200 m	600 m	200 m	600 m	200 m	600 m
Candidate variables	Sediment contamination (µg kg^{-1} DM / mg kg^{-1} DM)													*** +	*** +
	Sediment organic matter (%)						**-			*+		** +			
	Number of outlets	.+	.+		**-		.-		**-		.-				
	Drained watershed area (ha)					*** +	** +	*+	** +	.+	** +		*+		
	Mean wave energy (W m-1)		.+				** +								
	Slope (%)	** +	** +			*+	** +		*-					.-	.-
	Engine power (hp)								*+			** +	.+		
Adjusted-R²		0.54	0.63	NA	0.53	0.9	0.83	0.28	0.58	0.49	0.57	0.78	0.6	0.59	0.59

Discussion

1. *C. fluminea* as a bioindicator of littoral contamination

As an invasive species and thus a highly widespread organism in freshwater ecosystems, autochthonous *C. fluminea* may provide useful information on the contamination patterns of lake littorals. In this study, mean PAH contamination of *C. fluminea* was low (21.5 ± 19.4 µg kg^{-1} DM) compared to polluted sites such as Lake Kentucky (171.5 µg kg^{-1} DM; (Lapviboonsuk and Loganathan, 2007)). In contrast, mean TM contaminations of *C. fluminea* were very similar to those measured in the *C. fluminea* from the littoral zone of Lake Bourget, located 20 kilometers from Lake Annecy (Table S3). Similar concentrations were also reported by Shoults and Wilson et al. (2010) from the Altamaha River (Georgia, USA), except for Cd for which the contamination in Lake Annecy was on average 10 times lower than in the Altamaha River and even lower than the detection threshold in the sediment. In this study, the magnitude of both TM and PAH contaminations of *C. fluminea* varied from 5 to 10 times among sites and the patterns of contamination were related to different contamination sources. These benthic organisms may therefore efficiently reflect the spatial differences in the magnitude of contamination that the littoral faces.

2. In-lake vs watershed sources of contamination

In this study, both the 200 m and 600 m buffers were expected to account for small and medium-scale constraints that may influence *C. fluminea* contaminations. The explanatory powers of the multiple linear regression models performed with the 600m buffer radii were higher in term of value and in number of significant variables, emphasizing the importance of selecting an appropriate buffer zone in such studies. The explanatory powers of the multiple linear regression models used to explain *C. fluminea* contamination were rather high although variable, suggesting that other non-considered parameters could also contribute to (i.e. sources) or influence (i.e. environmental variables) the contamination of organisms, such as bioturbation (Remaili et al., 2017; Schaffner et al., 1997).

The significant positive correlations of *C. fluminea* contamination by Cu, Pb, Sn and Zn with the drainage area in the lake watershed highlighted the potential role of stormwater as a major source of littoral biota contamination by TMs. This result is consistent with other studies that highlighted the influence of stormwater in lake contamination (McLellan et al., 2007; Zhang et al., 2016). Stormwater was also expected to explain the PAH contamination of *C. fluminea* (Brown and Peake 2005), although no significant correlation could have been identified. The influence of the total number of stormwater outlets was not consistent between the different TMs (i.e. positive and negative correlations). This result could have been influenced by the drainage area and watershed land cover, which could vary considerably between the outlets.

C. fluminea contamination was also positively correlated with the total engine power of boats in harbors for Pb and Zn, elements generally measured in high abundance in harbors (Guevara-

Riba et al., 2004). Clam As and Cd contaminations exhibited less significant correlations with the candidate variables. This result may be partly due to the fact that these elements are highly mobile between the different compartments (i.e. sediment, water and biota) (Frémion et al., 2017) and therefore possibly less directly related to point sources.

3. C. fluminea as an indicator of contaminant bioavailability

The lack of significant correlation between the TM concentrations in *C. fluminea* and those in the sediment, as well as the differences in BCF between the different contaminants, suggest substantial variability in contaminant bioavailability. These results show that chemical analyses performed on solely abiotic matrices do not provide robust evidence of the bioavailability of the contaminants and consequently their effective ecological risk (Guo and Feng, 2018). The molecular characteristics of contaminants can induce significant differences in their uptake (e.g. passive or active transfers), storage and excretion by the organism, as illustrated in our study by the higher bioconcentration of light PAHs compared to heavy ones. Such differential bioconcentration was already highlighted by previous studies (Meador et al., 1995; Noh et al., 2018). An explanation of such variability is that environmental variables, such as slope and wave energy in this study, influence the benthic organism exposure to littoral contamination. Indeed, these two variable could reflect the disturbance level at the sampling location leading to a transport and re-suspension of the sediment and so an increase in the exposure of benthic organisms to littoral contamination (Eggleton and Thomas, 2004; Frémion et al., 2016; Phelps, 2016). In addition, Cu contamination in *C. fluminea* was negatively correlated with the abundance of organic matter in the sediment, which was in agreement with the fact that Cu is highly bound to the organic matter fraction of the sediment (Frémion, 2016; Tiquio et al., 2017), which may reduce its bioavailability. These environmental variables can therefore be considered in the ecological risk assessment.

Conclusion

C. fluminea appeared to appropriately reflect the spatial heterogeneity of lake littoral contamination (both in magnitude and profile) and the target contaminated “hot-spots” locally. The identification of stormwater runoffs as potentially important sources of TM contamination for the littoral biota provided insights into the assessment of the ecological risk of the pollution in the littoral zone of Lake Annecy and useful information for identifying and suggesting remedial actions (e.g. stormwater management). However, regarding persistent organic pollutants such as PAHs, linking organisms and potential watershed sources was not possible in this study. This result underlines possible changes in the contamination pattern from the source to the biota for persistent organic pollutants. This study supports the need to consider littoral contamination as complementary to that at a single site in the deepest zone (i.e. management monitoring) to fully

appreciate the pressure of contamination on the lake. In view to continuing this work, it would be interesting to couple the variability of BCF between the contaminants with foodweb models to predict the preferential transfer of contaminants to patrimonial fishes such as whitefish and arctic char in Lake Annecy. In addition, measurements of enzymatic biomarkers in these autochthonous organisms could be performed to obtain bioindicators of the detrimental effects caused by their contamination and thus go further in the ecological risk assessment.

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Supplementary Information

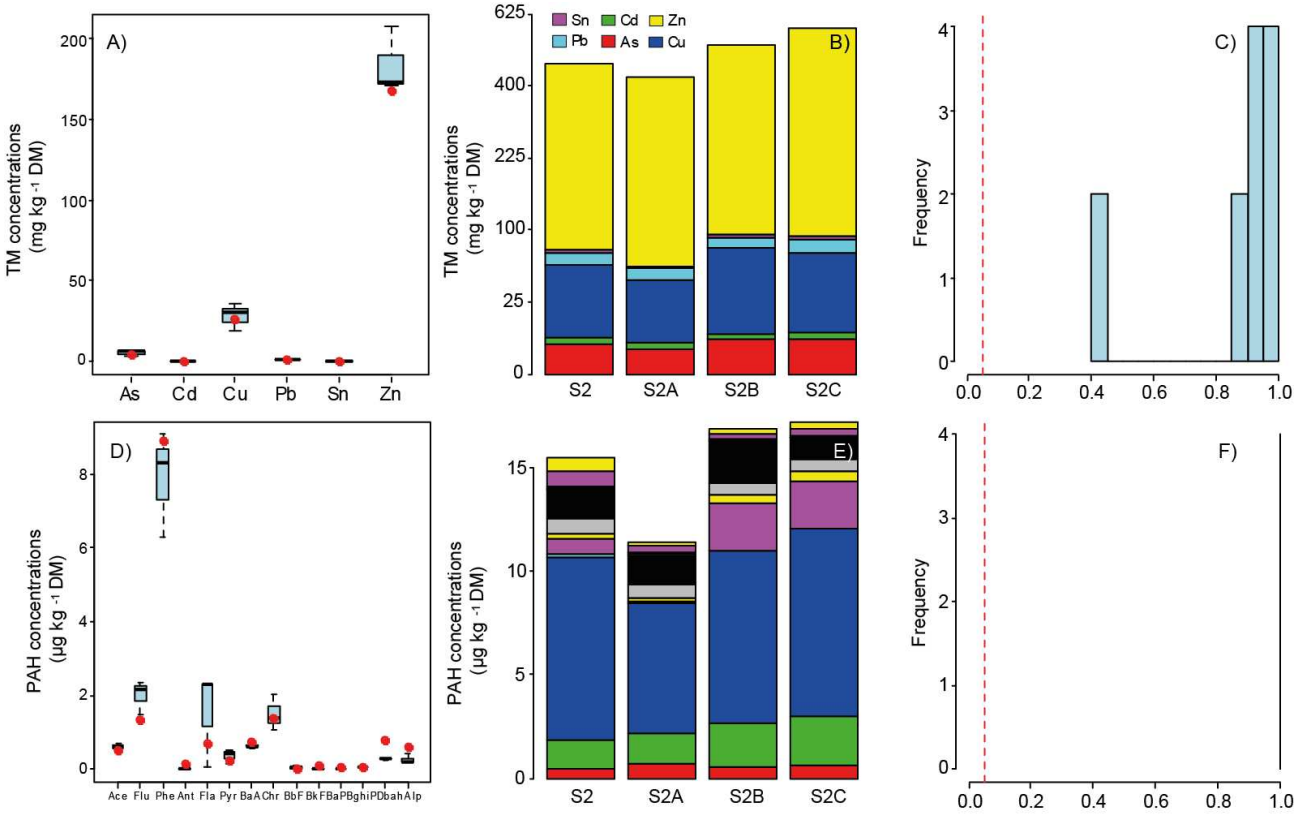


Figure S1. Intra-site (S2) spatial variability of C. fluminea contamination for the TMs (from A to C) and for the PAHs (from D to F). The box plots represent the concentrations for the different contaminants of the 3 additional replicate samples (S2A, S2B, S2C) and the red dots represents the concentrations of the study site (S2). Stacked diagrams allow for a direct qualitative and quantitative comparison of the variability of the contamination. The histograms represent the probability distribution of proportion comparison tests and the red dashed line indicates the 5% threshold considered to validate a significant difference in proportions of the contaminant profiles between the different samples.

S2: Estimating lipid contents the C. fluminea

The carbon and nitrogen concentrations of the Annecy and Bourget *C. fluminea* are positively correlated (Fig. S2A). C: N ratios show relatively low variability and follow a normal distribution (Shapiro test, p = 0.27) with an average of 4.62 ± 0.62 (Figure S2B). According to Post et al. (2007), the lipid levels of aquatic organisms can be estimated according to the following equation :

$$\%\, lipids = 7.24 \times C{:}N_{ratio} - 20.54$$

The mean lipids content in *C. fluminea* considered in this study was consequently equal to 12.9 %.

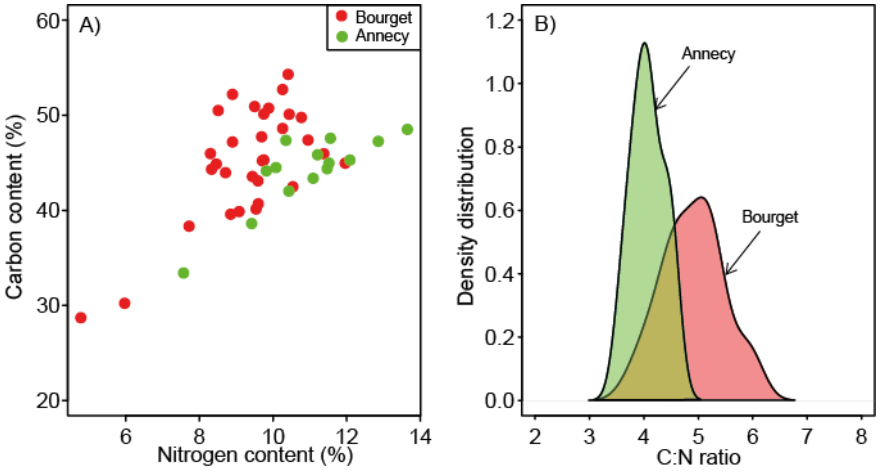
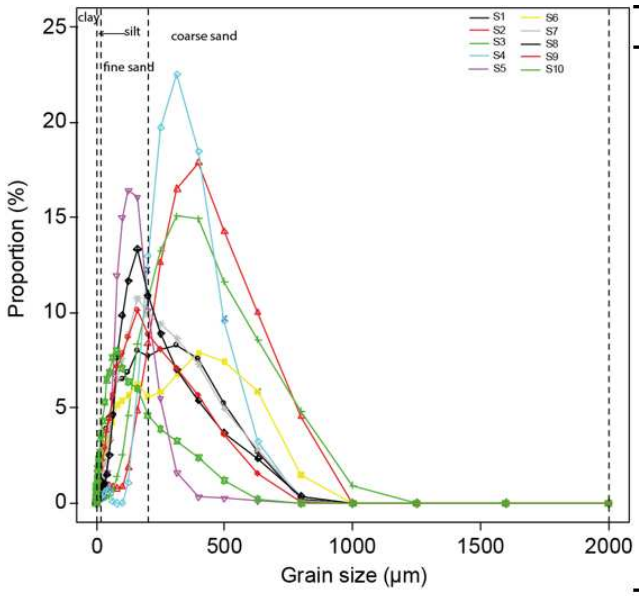


Figure S2. Plots of A) the relationship between carbon and nitrogen percentages in C. fluminea *sampled in Lake Annecy and Lake Bourget and B) the corresponding C: N ratios.*



Site	Organic matter (%)
s1	3.9
s2	2.7
s3	1.6
s4	1.7
s5	2.9
s6	3.8
s7	4.8
s8	2.7
s9	2.6
s10	4
s11	1.7
s12	2.1
s13	7.2
s14	3.4
s15	4.5
s16	6.8
s17	5.2
s18	14.6
s19	2.1
s20	2.7

Figure S3. Grain size distribution for the first 10 sediments on the left plot and organic matter content (%) in the sediments of the 20 sites on the right table. NB: There was not sufficient amount of sediment for the ten last sites to assess the grain size distribution.

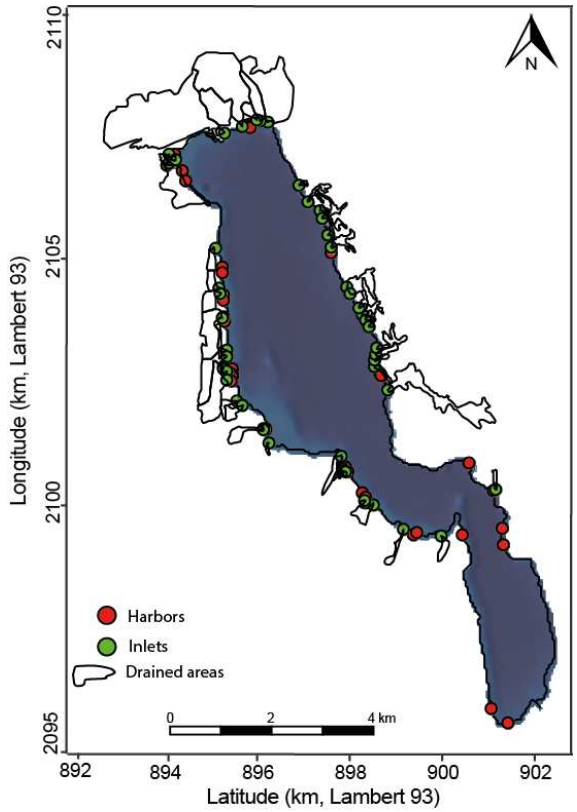


Figure S4. Spatial distribution of the various harbors and stormwater intlets of the watershed connected to the lake and associated with the drained areas.

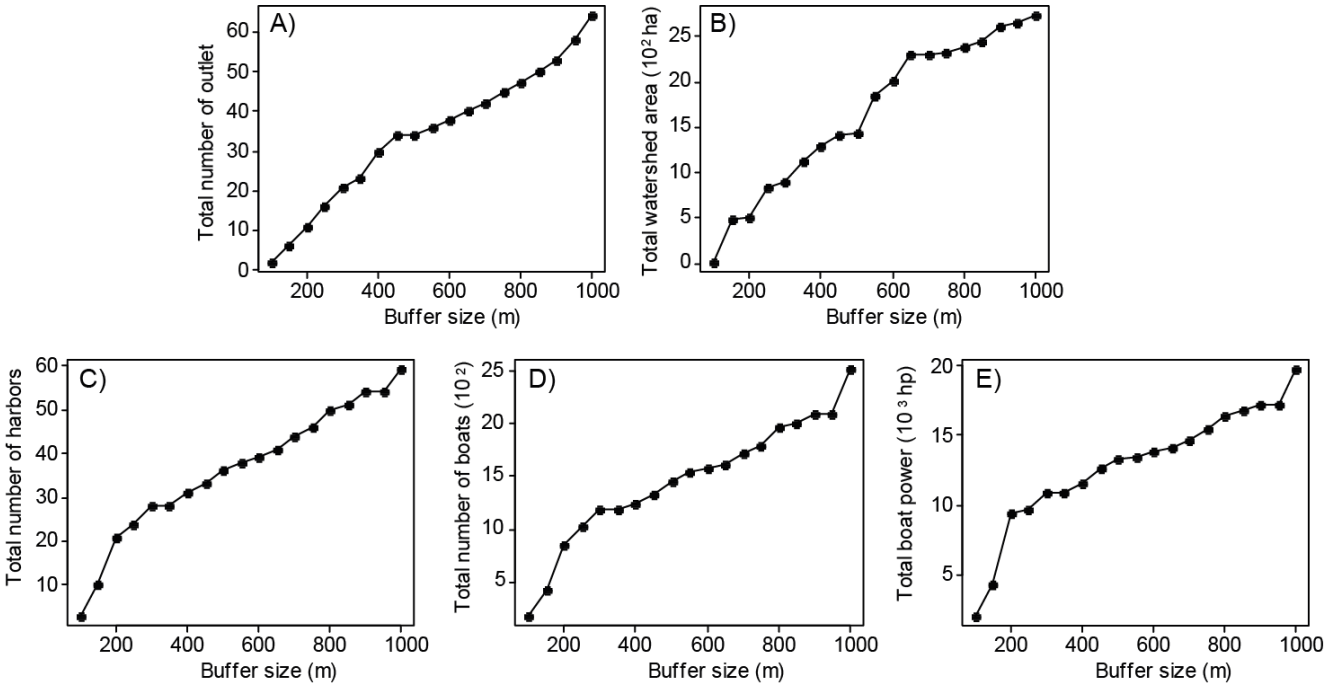


Figure S5. Relationship between the results of potential variables for the multiple linear regressions models and different buffer sizes (m) around the sampling points.

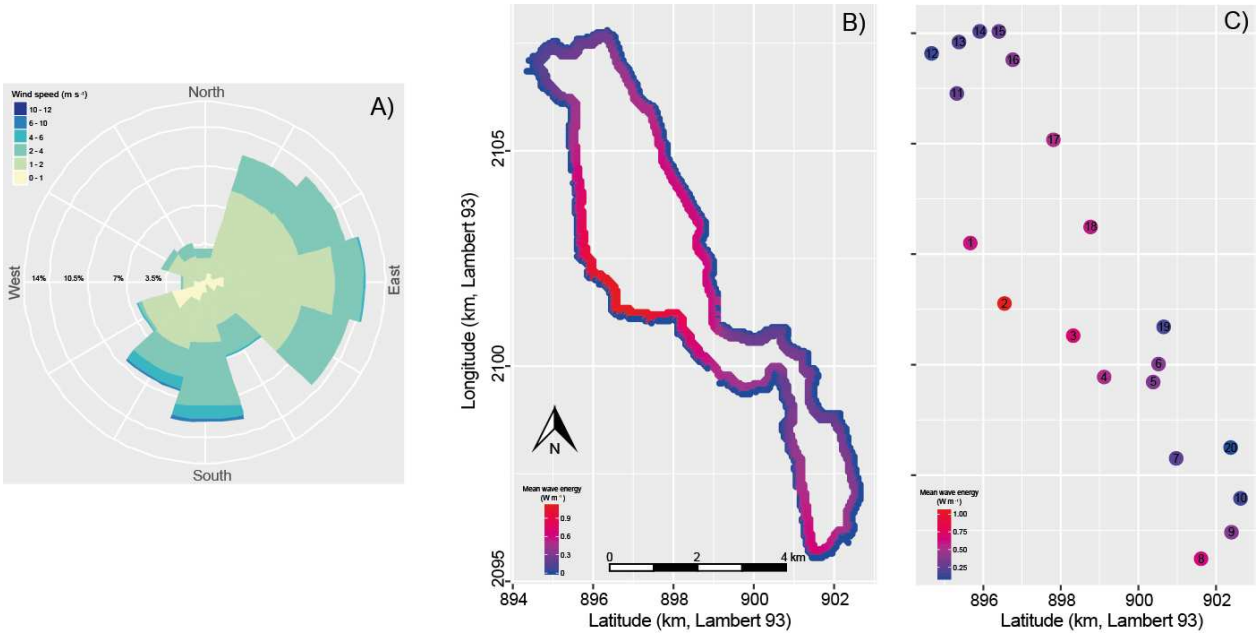


Figure S6. Hydrodynamics of the shoreline of Lake Annecy. A) Wind Rose taking into account the direction and speed of the winds at a daily frequency over the 2013-2016 period at the Météo-France Meythet station. The dominance of winds coming from the East and to a lesser extent from the South is noted. B) Results of estimates of average wave energy for the entire Annecy Lake coastal belt (200 m) and C) Estimates of average wave energy for each site by considering wave energies in a radius of 200 m around the sampling site.

Table S1. TMs and PAHs Concentrations in TMs (mg kg^{-1} DM) and PAHs (µg kg^{-1} DM) in sediments and C. fluminea of the 20 study sites. "ND" means Non-Detected values and "NA" Non-Available values.

Site	matrix	As	Cd	Cu	Pb	Sn	Zn	Ace	Flu	Phe	Ant	Fla	Pyr	BaA	Chr	BbF	BkF	BaP	BghiP	DbahA	Ip	Sum PAHs
s1	sediment	0.98	ND	ND	ND	1.18	32.40	8.67	1.01	34.68	0.90	24.47	21.70	12.36	26.33	17.00	9.03	14.84	13.41	0.36	8.01	192.78
s2	sediment	2.43	ND	ND	ND	0.44	19.00	1.07	ND	1.73	0.29	ND	0.69	ND	12.77	1.69	ND	0.09	0.11	ND	ND	18.62
s3	sediment	2.48	ND	ND	11.90	0.40	33.70	6.52	ND	ND	ND	10.05	18.05	6.74	52.04	18.75	10.11	24.54	11.80	2.76	14.31	175.70
s4	sediment	3.88	ND	ND	ND	0.39	25.70	7.62	0.28	ND	0.52	ND	0.63	0.77	9.30	0.25	ND	0.28	ND	ND	ND	19.88
s5	sediment	1.47	ND	ND	ND	0.59	23.10	15.31	3.11	16.76	0.46	36.76	38.03	29.28	35.58	29.09	16.49	34.91	31.68	1.93	20.48	309.87
s6	sediment	0.98	ND	ND	ND	ND	ND	0.69	11.77	39.87	0.46	3.83	5.63	0.51	60.65	3.58	0.22	2.50	112.78	0.73	0.56	243.33
s7	sediment	0.97	ND	ND	ND	0.63	14.60	34.43	12.50	31.81	ND	17.15	23.58	20.77	65.81	23.12	12.37	26.49	19.40	1.05	12.78	301.26
s8	sediment	3.32	ND	ND	ND	1.95	44.60	19.99	16.23	204.66	11.26	223.02	97.39	157.71	140.96	86.39	36.33	2.82	34.10	8.74	31.32	1070.91
s9	sediment	1.95	ND	ND	ND	0.39	22.90	6.56	ND	3.94	1.67	17.30	5.75	14.27	13.63	18.73	7.12	14.62	12.63	0.79	7.99	125.01
s10	sediment	0.98	ND	ND	ND	0.78	13.70	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.00
s11	sediment	1.92	ND	10.10	49.80	7.09	38.80	31.28	109.79	1965.74	575.46	5280.30	3526.03	3361.91	2781.38	2859.40	1641.11	3131.57	2050.68	262.21	1243.07	28819.91
s12	sediment	0.98	ND	27	ND	0.93	12.80	ND	9.87	60.28	3.26	62.26	26.92	34.03	29.91	38.71	18.84	37.21	75.20	3.31	26.07	425.86
s13	sediment	0.99	ND	ND	ND	4.45	22.80	25.65	1.95	2.84	ND	9.96	13.27	6.25	48.61	7.79	3.61	10.12	53.56	0.73	5.50	189.84
s14	sediment	0.97	ND	15.50	15.00	1.26	14.10	20.53	11.29	266.76	42.21	398.06	272.10	217.91	235.81	184.52	104.79	209.17	126.78	10.63	94.28	2194.85
s15	sediment	1.00	ND	12.00	ND	0.95	37.90	9.93	ND	31.86	0.24	12.10	11.42	5.47	23.79	16.83	5.97	11.07	18.57	0.38	6.02	153.65
s16	sediment	1.45	ND	ND	6.30	1.64	27.00	11.82	9.64	252.59	25.90	929.10	745.21	558.17	507.71	576.99	298.58	639.18	271.93	43.58	315.16	5185.56
s17	sediment	0.50	ND	10.40	ND	1.19	107.90	6.97	5.53	67.79	ND	68.52	57.18	29.00	67.07	40.68	18.91	39.15	66.43	10.42	29.96	507.62
s18	sediment	0.99	ND	15.80	7.90	2.41	48.80	13.55	11.65	172.96	5.00	417.12	312.38	248.51	287.82	265.03	133.06	223.39	165.43	27.14	114.35	2397.38
s19	sediment	3.47	ND	69.30	5.40	0.89	19.80	5.66	6.47	91.11	4.69	104.27	110.89	58.78	43.30	50.25	24.56	56.63	38.02	3.59	21.45	619.67
s20	sediment	1.91	ND	16.70	8.10	3.05	88.30	3.23	ND	10.85	0.78	35.19	30.44	21.75	24.65	20.94	10.90	24.43	18.97	0.98	8.35	211.44
s1	*C. fluminea*	5.58	0.20	36.56	1.42	0.08	230.99	0.42	1.11	6.54	0.23	0.61	0.48	1.18	2.23	0.16	ND	ND	0.13	0.29	0.24	13.64
s2	*C. fluminea*	5.85	0.23	39.60	0.56	ND	178.61	0.49	1.33	8.88	0.16	0.69	0.24	0.75	1.36	ND	0.10	0.04	ND	0.77	0.61	15.49
s3	*C. fluminea*	5.25	0.22	45.27	1.07	ND	201.29	0.42	1.02	4.45	ND	1.27	0.36	0.75	6.57	0.12	ND	ND	ND	0.23	0.20	15.47
s4	*C. fluminea*	5.41	0.20	35.69	0.73	ND	176.42	0.15	0.62	2.16	ND	0.67	0.19	0.19	0.43	0.07	ND	ND	ND	0.29	0.23	5.09
s5	*C. fluminea*	5.03	0.20	27.79	1.33	0.10	185.02	0.03	1.72	5.58	ND	1.65	0.34	0.49	0.84	0.10	ND	0.06	ND	0.29	0.23	11.41
s6	*C. fluminea*	5.88	0.33	39.24	0.66	0.05	180.77	0.11	1.50	4.49	ND	0.19	0.18	0.29	0.12	ND	ND	ND	ND	0.40	0.33	7.70
s7	*C. fluminea*	NA	NA	NA	NA	NA	NA	0.10	2.00	8.88	ND	5.45	1.37	2.03	4.47	0.66	0.24	0.31	0.38	0.33	0.26	26.48
s8	*C. fluminea*	NA	NA	NA	NA	NA	NA	0.35	4.53	14.89	ND	2.60	1.01	0.37	1.49	0.43	0.10	ND	0.14	ND	0.37	26.31
s9	*C. fluminea*	4.51	0.26	22.43	1.83	0.10	189.42	0.14	2.45	7.87	ND	2.26	0.93	0.25	2.22	0.43	0.13	ND	0.06	ND	0.39	17.19
s10	*C. fluminea*	NA	NA	NA	NA	NA	NA	0.10	2.14	8.60	ND	2.87	0.81	0.76	0.76	0.22	0.06	ND	0.03	ND	0.25	16.68
s11	*C. fluminea*	4.86	0.28	50.50	0.98	0.07	162.02	0.65	2.27	14.77	0.25	27.34	19.83	10.79	8.50	5.73	1.71	1.99	0.72	ND	0.56	95.14

Table S1. Continued.

Site	matrix	As	Cd	Cu	Pb	Sn	Zn	Ace	Flu	Phe	Ant	Fla	Pyr	BaA	Chr	BbF	BkF	BaP	BghiP	DbahA	Ip	Sum PAHs
s12	*C. fluminea*	4.45	0.16	26.04	0.56	0.06	167.50	0.20	3.83	14.26	ND	4.80	1.29	1.73	1.83	0.28	0.08	0.03	0.18	ND	0.26	28.81
s13	*C. fluminea*	NA	NA	NA	NA	NA	NA	0.18	1.32	7.23	ND	1.42	0.28	0.37	1.21	0.11	0.01	ND	0.10	ND	0.26	12.55
s14	*C. fluminea*	6.15	0.18	97.81	2.01	0.14	235.02	0.05	1.81	8.63	ND	1.98	1.64	0.75	5.08	0.40	0.16	0.23	0.36	ND	0.26	21.41
s15	*C. fluminea*	6.83	0.15	43.28	0.95	0.14	215.38	ND	1.07	4.07	ND	3.03	1.24	1.58	3.41	0.35	0.08	0.03	0.12	ND	0.19	15.24
s16	*C. fluminea*	NA	NA	NA	NA	NA	NA	0.37	2.84	10.13	1.22	11.52	6.70	5.47	5.01	0.24	0.74	0.57	0.21	ND	0.48	45.56
s17	*C. fluminea*	NA	NA	NA	NA	NA	NA	0.11	1.40	5.59	ND	2.27	0.80	0.67	1.81	0.21	0.05	ND	0.05	ND	0.20	13.23
s18	*C. fluminea*	NA	NA	NA	NA	NA	NA	0.17	1.74	7.60	ND	2.50	0.69	0.81	1.31	0.26	0.06	0.03	0.06	ND	0.20	15.51
s19	*C. fluminea*	7.09	0.34	53.62	0.62	ND	198.48	0.13	1.83	8.32	ND	1.17	0.41	0.49	0.53	0.06	0.01	ND	0.03	ND	0.26	13.30
s20	*C. fluminea*	NA	NA	NA	NA	NA	NA	0.09	1.60	7.97	ND	1.86	0.66	0.71	0.78	0.17	0.05	ND	0.02	ND	0.20	14.18

Table S2. BCFs for TMs and PAHs for the 20 study sites (ND values for the calculations were replaced as described in the Materials and Methods section of the manuscript).

	As	Cd	Cu	Pb	Sn	Zn	Ace	Flu	Phe	Ant	Fla	Pyr	BaA	Chr	BbF	BkF	BaP	BghiP	DbahA	Ip
s1	5.69	0.56	6.08	0.43	0.07	7.13	0.01	0.05	1.10	0.19	0.26	0.02	0.02	0.10	0.08	0.01	0.00	0.00	0.01	0.81
s2	2.41	0.66	6.59	0.17	0.08	9.40	0.10	0.46	234.41	5.13	0.57	14.61	0.35	62.06	0.11	0.01	8.24	0.41	0.42	16.34
s3	2.12	0.63	7.53	0.09	0.09	5.97	0.01	0.06	180.84	369.86	1.00	0.13	0.02	0.11	0.13	0.01	0.00	0.00	0.00	0.08
s4	1.40	0.55	5.94	0.22	0.09	6.86	0.00	0.02	2.17	180.02	0.02	14.23	0.30	0.25	0.05	0.28	1.00	0.04	1.00	6.10
s5	3.42	0.56	4.62	0.40	0.17	8.01	0.00	0.00	0.55	0.33	0.03	0.04	0.01	0.02	0.02	0.00	0.00	0.00	0.00	0.15
s6	6.00	0.94	6.53	0.20	0.29	52.17	0.05	0.16	0.13	0.11	1.00	0.05	0.03	0.57	0.00	0.00	0.06	0.00	0.00	0.54
s7	NA	NA	NA	NA	NA	NA	0.00	0.00	0.16	0.28	1.00	0.32	0.06	0.10	0.07	0.03	0.02	0.01	0.02	0.31
s8	NA	NA	NA	NA	NA	NA	0.00	0.02	0.28	0.07	0.00	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.01
s9	2.31	0.72	3.73	0.55	0.26	8.27	0.00	0.02	433.10	2.00	0.01	0.13	0.16	0.02	0.16	0.02	0.02	0.00	0.00	0.06
s10	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
s11	2.53	0.80	5.00	0.02	0.01	4.18	0.00	0.02	0.02	0.01	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
s12	4.54	0.45	0.96	0.17	0.06	13.09	5.73	35.36	0.39	0.24	0.00	0.08	0.05	0.05	0.06	0.01	0.00	0.00	0.00	0.01
s13	NA	NA	NA	NA	NA	NA	0.00	0.01	0.68	2.55	1.00	0.14	0.02	0.06	0.02	0.01	0.00	0.00	0.00	0.07
s14	6.34	0.50	6.31	0.13	0.11	16.67	0.00	0.00	0.16	0.03	0.00	0.00	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.00

Table S2. Continued.

	As	Cd	Cu	Pb	Sn	Zn	Ace	Flu	Phe	Ant	Fla	Pyr	BaA	Chr	BbF	BkF	BaP	BghiP	DbahA	Ip
s15	6.83	0.42	3.61	0.29	0.15	5.68	0.00	0.00	189.15	0.13	0.05	0.25	0.11	0.29	0.14	0.02	0.01	0.00	0.01	0.12
s16	NA	NA	NA	NA	NA	NA	0.02	0.03	0.29	0.04	0.05	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00
s17	NA	NA	NA	NA	NA	NA	0.01	0.02	0.25	0.08	1.00	0.03	0.01	0.02	0.03	0.01	0.00	0.00	0.00	0.00
s18	NA	NA	NA	NA	NA	NA	0.01	0.01	0.15	0.04	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
s19	2.04	0.96	0.77	0.12	0.04	10.02	0.00	0.02	0.28	0.09	0.00	0.01	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.01
s20	NA	NA	NA	NA	NA	NA	0.01	0.03	282.84	0.73	0.02	0.05	0.02	0.03	0.03	0.01	0.00	0.00	0.00	0.05

Table S3. Mean TMs (± SD) concentrations in C. fluminea *from Lake Annecy (n=20) and Lake Bourget (n=10) littoral zones. PAHs data were unavailable in Lake Bourget.*

		Lac d'Annecy	Lac du Bourget
	Reference	This study	From Lécrivain et al. (unpublished data)
TMs concentration (mg kg^{-1} DM)	As	5.6 ±0.8	NA
	Cd	0.2 ± 0.1	0.2 ± 0.1
	Cu	43.2 ± 19.6	34.0 ± 19.8
	Pb	1.1 ± 0.5	0.9 ± 1.4
	Sn	0.1 ± 0.0	NA
	Zn	193.4 ± 23.6	189.5 ± 36.1

3. Synthèse

La contamination de *C. fluminea* varie significativement entre les sites littoraux du lac d'Annecy, indiquant que ces organismes benthiques sont susceptibles de refléter l'influence variable de sources locales de contamination en zone littorale et sont ainsi de bons indicateurs de la contamination littorale lacustre. La population du bassin-versant du lac d'Annecy double en été sous l'affluence touristique. Nous attendions une influence forte des ports dans la contamination des Corbicules prélevées à la fin de l'été. Néanmoins, le transfert de contaminants par le réseau de drainage d'eaux pluviales semble jouer un rôle prépondérant dans la contamination du biote littoral, soulevant, comme pour le lac du Bourget, l'importance des sources urbaines diffuses dans la contamination de la zone littorale lacustre des grands lacs au bassin-versant urbanisé (Melymuk et al., 2014).

Les Corbicules du littoral du lac du Bourget ont également fait l'objet de dosage en concentrations internes en ETM (Tableau 3, résultats non publiées, voir Annexe 2 pour le détail des résultats) et présentent des concentrations similaires à celles des Corbicules du lac d'Annecy, comme évoqué dans l'Article 3.

Tableau 3. Concentrations moyennes en ETM des Corbicules et sédiments (mg kg^{-1} MS) du lac d'Annecy (n=20 sites littoraux) et du lac du Bourget (n=10 sites littoraux).

		Concentration moyenne (± écart-type)	
	Elément	Lac d'Annecy	Lac du Bourget
C. fluminea (mg kg^{-1} MS)	As	5,6 ±0,8	NA
	Cd	0,2 ± 0,1	0,2 ± 0,1
	Cu	43,2 ± 19,6	34,0 ± 19,8
	Pb	1,1 ± 0,5	0,9 ± 1,4
	Sn	0,1 ± 0,0	NA
	Zn	193,4 ± 23,6	189,5 ± 36,1
Sédiment (mg kg^{-1} MS)	As	1.7 ±1.0	NA
	Cd	0.4 ± 0.0	0.1 ± 0.0
	Cu	12.4 ± 14.5	3.9 ± 3.5
	Pb	7.4 ± 10.5	4.5 ± 2.3
	Sn	1.5 ± 1.7	NA
	Zn	32.6 ± 25.4	42.9 ± 26.4

Les divergences entre la contamination du sédiment et celle du biote benthique pour ces deux lacs pour chaque ETM soulignent la biodisponibilité variable des contaminants sédimentaires. Ces résultats mettent en exergue le besoin d'améliorer la compréhension des mécanismes régissant la mobilité et la biodisponibilité des polluants aux interfaces sédiment-eau-biote.

PARTIE II

Evaluation de l'écotoxicité des sédiments littoraux aux interfaces sédiment-eau-biote

La précédente partie a souligné la complexité des liens entre les contaminations du sédiment et du biote en zone littorale. Dans cette partie, l'étude à l'interface entre le sédiment, l'eau et le biote de l'écotoxicité des sédiments vise à apporter des éléments de compréhension sur les mécanismes régissant l'exposition et la biodisponibilité des contaminants sédimentaires littoraux. Ces derniers peuvent être à l'origine d'effets néfastes sur les organismes à la fois benthiques et pélagiques de la zone littorale lacustre. Les Chapitres qui composent cette partie portent tous sur l'étude des ETM (Cd, Cr, Cu, Ni, Pb et Zn) des sédiments littoraux du lac du Bourget.

Le Chapitre 4 porte sur l'évaluation des différences de biodisponibilité des ETM du compartiment sédimentaire littoral par l'exposition conjointe d'organismes pélagiques et benthiques. Les Chapitres 5 et 6 s'intéressent à l'évaluation des changements de mobilité et biodisponibilité des ETM des sédiments littoraux sous l'effet d'un marnage lacustre. Alors que le Chapitre 5 traite, par une approche laboratoire, des effets de l'assèchement puis remise en eau des sédiments de surface sur la contamination sédimentaire et du biote associé, le Chapitre 6 est consacré à une évaluation, par une approche *in situ*, des effets de la réduction de la hauteur d'eau sur la mobilité des ETM en lien avec l'abaissement de la cote dans le cadre du marnage de l'automne 2017.

Chapitre 4

Etude en laboratoire de la biodisponibilité de la contamination sédimentaire pour les organismes benthiques et pélagiques

1. Démarche générale

L'écotoxicité des sédiments d'eau douce s'évalue classiquement par approche matrice en tests monospécifiques normalisés sur des organismes benthiques (e.g. larves de *C. riparius* dans la norme NF T90-339-1 (AFNOR, 2010a), *Hyalella azteca* dans les normes NF T90-338-1 (AFNOR, 2010b) et NF ISO 16303 (AFNOR, 2014), *Heterocypris incongruens* dans la norme NF ISO 14371 (AFNOR, 2012)). Lorsque ces tests portent sur des organismes pélagiques, ce n'est plus le sédiment dans sa totalité auquel ils sont exposés, mais l'eau interstitielle ou le lixiviat (e.g. *D. magna* dans la norme NF EN ISO 6341 (AFNOR, 2012)), susceptibles alors de représenter un biais d'exposition dans l'évaluation de l'écotoxicité.

En zone littorale lacustre, les compartiments benthique et pélagique sont en interaction forte et les échanges de nutriments et micropolluants à l'interface eau-sédiment sont fréquents (cf I.3.1 de l'Introduction). La vision du sédiment comme « source de contamination » pour le compartiment pélagique est souvent abordée dans la littérature, mais l'évaluation des effets correspondants sur ce compartiment est rarement effectuée.

Ce chapitre vise donc à évaluer la biodisponibilité de la contamination en ETM du sédiment multi-contaminé de la zone littorale du lac du Bourget pour le compartiment benthique et pélagique sous la forme d'essais en microcosme de laboratoire. Les trois espèces choisies pour ces essais, *L. minor, D. magna* et *C. riparius*, évoluent dans des compartiments différents (i.e. pélagique et benthique), ont des voies d'exposition différentes de par leur guilde trophique (i.e. producteurs et consommateurs primaires et détritivores). La biodisponibilité pour ces organismes est évaluée au moyen des concentrations internes en ETM et de leur rapport avec celles du sédiment via le calcul du facteur de bioconcentration (Figure 16). Les effets sur les organismes sont mesurés par l'observation des réponses des traits de vie ; survie et taux de croissance individuelle pour *D. magna* et *C. riparius*, taux de croissance de la population pour *L. minor*)

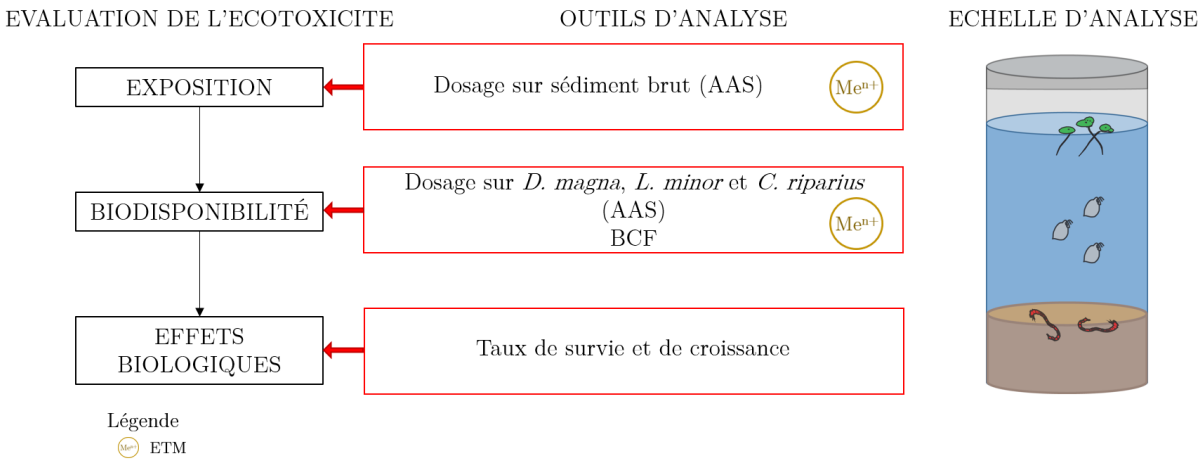


Figure 16. Schéma récapitulatif des outils et de l'échelle d'analyse pour l'évaluation de l'écotoxicité dans l'Article 4.

2. Article 4 - Contribution of trace metallic elements to weakly contaminated lacustrine sediments: effects on benthic and pelagic organisms through multi-species laboratory bioassays

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Abstract

Surficial sediments exhibit higher levels of contamination than overlying water, especially from persistent contaminants such as trace metallic elements (TMs). While sediments could in turn act as sources of contamination for the water column, their ecotoxicology is yet rarely assessed in a multi-compartments perspective. This study aims at assessing the response of benthic and pelagic organisms exposed to weakly contaminated sediments using a multi-species laboratory assay by focusing on TMs (Cd, Cr, Cu, Ni, Pb and Zn) contamination. *Chironomus riparius* larvae, *Daphnia magna* and *Lemna minor* were simultaneously exposed for ten days to six sediments sampled from the littoral of a large French lake (Lake Bourget). The endpoints consisted in the survival and growth rates and the bioconcentration factor (BCF). Significant negative relationships between sediment TM concentrations and survival rates of *C. riparius* and growth rates of *C. riparius* and *D. magna* suggested that both benthic and pelagic macro-invertebrates were impacted by sediment contamination, which was not observed in *L. minor*. Significant relationships of the sediment with the internal TM concentrations were positive while negative with the BCFs, suggesting an increase in biological regulation processes in all organisms with the increase of sediment TM concentrations. These results underline the importance of including both benthic and pelagic organisms in ecotoxicological assessment of low contaminated sediments and the relevance of the relationship BCFs/sediment contamination as prior biomarkers than higher life history traits.

Keywords

Heavy metal; bioconcentration factor; freshwater sediment; *Daphnia magna; Chironomus riparius, Lemna minor.*

Introduction

Lake littoral zones are particularly exposed to pollution coming from the watershed (Guyader et al., 2018; Johnson et al., 2018). In these areas, surficial sediment acts as an important sink of this pollution owing to its capacity of retaining contaminants, leading to levels many times higher than in the overlying water (Atkinson et al., 2007; Bryan and Langston, 1992). The ecotoxicity assessment of lake littoral sediment is therefore of concern, especially when considering the high ecological and economical importance of these areas (Décamps and Naiman, 1990; Raspopov et al., 1996).

Standard test protocols and consensus sediment quality guidelines (SQGs) can be used to assess the ecotoxicity of sediments (AFNOR, 2014b, 2014a, 2010, 2007; Burton, 2010; Burton Jr, 2002; Ingersoll et al., 1995), which do not usually fully consider the different compartments of aquatic ecosystems since they mainly focus on benthic invertebrate species. Assessing the ecotoxicity of contaminated sediments to organisms of different trophic behaviors from both benthic and pelagic compartments is likely to increase realism and seems to be relevant, especially for persistent and ubiquitous contaminants such as trace metallic elements (TMs), which do not undergo biodegradation (Triffault-Bouchet et al., 2005).

This study aims at assessing the contribution of sediment-borne TMs in the ecotoxicity of lake littoral sediments through laboratory multi-species assays including both benthic and pelagic organisms. Six natural surficial sediments were collected from the littoral of Lake Bourget (France) that exhibited low TM contamination (Lécrivain et al., 2018). Six TMs were considered for the experiment; Cd, Cr, Cu, Ni, Pb and Zn. Laboratory benthic *C. riparius* and pelagic *D. magna* and *L. minor* were simultaneously exposed to these sediments in a 10-day laboratory assay; survival and growth rates were considered as life history traits. Internal TM concentrations and bioconcentration factors (BCFs) - defined as the ratio between the TM concentration in the organisms and the TM concentration in the sediment (Mountouris et al., 2002) – were also selected to assess the sediment-borne TM bioavailability and raise potential regulation mechanisms following contamination exposure (Adams et al., 2000; McGeer et al., 2003). The hypothesis in the present study is that, despite low contamination, sediment-borne TM contamination may transfer to both benthic and pelagic organisms, which may be relevant conclusions in the prospect of studying pollution biomagnification in aquatic environments.

Material and methods

1. Sampling sites and method

The surficial sediments were sampled in the littoral zone of Lake Bourget located in Savoy on the northwest edge of the French Alps (45°43'N, 5°52'E). The 560 km^2 catchment area of this lake is covered by forests (45 %), agricultural areas (22 %), grazing fields (12 %), urban areas (13 %) and water bodies (8 %) (CISALB, 2009). More details, including a map of the lake and its watershed, are available in Lécrivain et al. (2018).

Six sites were selected along the littoral zone of the lake for the experiment (S3, S6, S7, S8, S9 and S10, Table 1) for their wide range of TM concentrations and ability to reach a gradient in pollution intensity.

At each site, surface (0-10 cm) sediment was collected at a water depth from 1.5 to 2.5 m using an Ekman grab from a boat. The sediment was then homogenized in a plastic tray and placed in pre-washed 2-L polyethylene bottles. The samples were transported to the laboratory in coolers and stored at 4°C during a maximum of 24 hours.

2. Sediment characterization

Grain size distribution, loss on ignition and heavy metal contamination were assessed according to the method described in Lécrivain et al. (2018). Briefly, 3 sub-samples of each sediment were dried at 105 °C for 24 hours. One was sieved at 1.6 mm for grain size measurements by laser diffractometry (Malvern Mastersizer 2000G), another was used for water concentration determination and ignited at 550 °C for 4 hours to determine the loss on ignition (LOI). The percentage of organic carbon (OC) in each sediment was calculated from the LOI using the relationship OC (%) = LOI (%)/2.13 (Dean Jr, 1974). The last sediment samples were sieved at 2 mm and 100 mg of the dried samples were mineralized in a microwave oven (CEM/MARS Xpress, 2 mL ultra-pure HNO3 + 6 mL ultra-pure HCl, 180 °C during 30 min, filtration on a 0.45-µm Whatman™ filter and dilution of the residue in 25 mL ultra-pure water). The resulting sample was analyzed by atomic absorption spectrometry (AAS). Cd, Cr, Cu, Ni and Pb were analyzed in a graphite furnace at 1500 °C and Zn with an air-acetylene flame (Perkin Elmer, model PinAAcle 900T, detection limits: Cd = 0.1 $\mu g.L^{-1}$, Cr = 0.040 $\mu g.L^{-1}$, Cu = 0.014 $\mu g.L^{-1}$, Ni = 0.07 $\mu g.L^{-1}$, Pb = 0.05 $\mu g.L^{-1}$, Zn = 0.02 $\mu g.L^{-1}$).

3. Laboratory microcosms and study endpoints

Laboratory organisms used for this experiment originated from a laboratory room exempt from possible contamination, at constant temperature (20 ± 2 °C) and under a light regime of 16 h light and 8 h darkness. *Daphnia magna* rearing was described in Lécrivain et al. (2018). *Chironomus riparius* midges were bred in plastic aquaria (34*18*19 cm) that contained a layer of artificial sediment that consisted in 2 kg of dry Fontainebleau sand (particle size 150–300 µm) (VWR Prolabo) mixed with 600 mg of finely ground fish food flakes (TetraMin®) submerged by

6 L of clean and aerated groundwater. Approximately 75 % of the water column was renewed weekly and midges were fed with finely crushed TetraMin®. The duckweed *Lemna minor* was axenically cultured in Erlenmeyer flasks containing 250 mL of a nutrient-rich synthetic medium (AFNOR, 1996), with starting new cultures every month.

For these bioassays, a formulated sediment (89 % of clean Fontainebleau sand (Sigma), 9 % of ignited sediment coming from the pristine Lake Aiguebelette (Savoy, France), 1.9 % of alpha-cellulose (Sigma Aldrich) and 0.1 % of TetraMin®) was used as control. The sediment was introduced in 3 replicates in acid-rinsed beakers that were then filled with a synthetic media (pH: 7.7, hardness: 60 mg $CaCO_3.L^{-1}$, alkalinity: 120 mg $CaCO_3.L^{-1}$, conductivity: 290 $\mu S.cm^{-1}$, phosphorous: 100 $\mu g.L^{-1}$, nitrogen: 1308 $\mu g.L^{-1}$, $FeEDTANa_2,6H_2O$: 109.4 $\mu g.L^{-1}$, oligo-elements and vitamins of M4 medium (Elendt and Bias, 1990)). The beakers were aerated and left seven days for stabilization and maturation in the dark at 20 °C.

Wet lacustrine littoral sediments were sieved with a mesh-size of 2 mm and 250 g of each sediment were introduced in an acid-rinsed beaker in triplicate for each site. Microcosms were then prepared as described in Lamonica et al. (2016).

Ten *D. magna* neonates under the age of 24 hours and homogeneous in individual size (i.e. coefficient of variation below 10 %) were introduced at the initial time (t0). Forty *C. riparius* first-instar larvae were also introduced into the beakers. Larvae were also homogeneous in individual size (i.e. coefficient of variation below 10 %). Two *L. minor* colonies, each of 2 fronds, two of 3 fronds, one of 4 fronds and one of 5 fronds, were introduced into the beakers. The colonies were chosen so that their shape (size and area of fronds) was homogenous between beakers.

During exposure, *D. magna* were daily fed with 10^6 cells/individual/day of a culture of *Pseudokirchneriella subcapitata* and *C. riparius* larvae with 0.33 ml per individual per day of a finely crushed suspension of 10 $g.L^{-1}$ TetraMin®. Half of the water column was gently renewed every other day to prevent abnormal high contaminant concentrations and its quality was monitored to prevent from bias in the fitness response of the organisms. Dissolved oxygen concentration ($mg.L^{-1}$), temperature (°C), conductivity ($\mu S.cm^{-1}$), pH and Na^+, K^+, Ca^{2+}, NH_4^+, Mg^{2+}, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-} dissolved concentrations ($mg.L^{-1}$) were measured in the beakers every 3 days following the methods described by Perrodin et al. (2016).

The organisms were all exposed for 10 days to prevent *D. magna* reproduction and *C. riparius* emergence. At the final time of the exposure, *L. minor* colonies were collected, rinsed with ultra-pure water and photographed. *D. magna* and *C. riparius* were collected, counted and placed 4 hours in beakers filled with fresh synthetic media in order not to include gut contents in the internal bioconcentrated TM concentrations.

Survival rate for the macro-fauna was expressed as the percentage of living individuals at the final time of the assays over the initial number of introduced individuals. The individual growth size (day^{-1}) for the macro-fauna was calculated according to the equation (1) (AFNOR, 2006),

where l_f and l_0 were respectively the final and initial individual body length (mm) and t the duration of the assays (days).

$$gr = \frac{ln(l_f) - ln(l_0)}{t} \quad (1)$$

The cephalic capsules of *C. riparius* were also measured to check that all larvae reached the fourth instar (Bour et al., 2015). Population growth rate for *L. minor* was assessed according to the equation (1) by replacing body length by total frond surface (mm^2) determined from the photographs using Mesurim software (Madre, 2006).

Internal TM concentrations were measured on dried *D. magna* (0.8 mL ultra-pure HNO_3, 4 hours, 60 °C + 0.8 ml ultra-pure water), *C. riparius* (CEM/MARS Xpress, 3 mL ultra-pure HNO_3 + 1 mL ultra-pure HCl + 1 mL H_2O_2, 180 °C, 30 min, dilution of the residue in 10 mL ultra-pure water) and *L. minor* (4 mL ultra-pure HNO_3 + 1 mL H_2O_2, 180 °C, 30 min, dilution of the residue in 10 mL ultra-pure water). Individuals from a same beaker were pooled for this measurement. In addition, samples of overlying water at day 0, 5 and 10 of the experiment were filtrated with 0.2-µm-nylon mesh and acidified with ultra-pure HNO_3. The biological and water samples were then analyzed by atomic absorption spectrometry (AAS) using the same method as for the sediment samples to assess Cd, Cr, Cu, Ni, Pb and Zn concentrations.

4. Data analysis

The differences of TM concentrations between sediments were compared using Chi^2-tests. The Bioconcentration Factor (BCF) for each TM was also calculated as the ratio between the internal TM concentration and the sediment TM concentration by organism (Jia et al., 2018; Mendoza-Carranza et al., 2016; Mountouris et al., 2002). The influences of the organisms and sediments TMs on internal TM concentrations were tested using two-way analyses of variance (ANOVA II) and post hoc Tukey's HSD tests.

Simple linear regressions were performed between the OC (%) in the sediments and the respective bulk sediment TM concentration ($mg.kg^{-1}$ DM) to assess whether the abundance of OC could exert a bias in the comparison between the sediment concentrations. Linear regressions between the biological endpoints and the sediment-borne TM concentrations were preferred to a site-by-site analysis in order to study the biological response to increasing sediment contamination.

The significance of the differences between the slopes of these linear regressions was assessed using the function "sma" of the *Smatr* package (Warton et al., 2012). All statistical analyses as well as graphical displays were carried out using R (Team, 2017). Throughout the manuscript, values following "±" correspond to the standard deviation of the data.

Results

1. Sediment characteristics

The littoral sediments were mainly sandy (Table 1, proportions of sand between 84.33 and 96.86 %) and poorly organic (OC proportions between 0.56 and 2.27 %), excepting for S7 that was mainly silty (54.15 % of silt) and exhibited a higher OC proportion (4.39 %).

Table 1. Main structural characteristics of the study sediments and the control.

		Sediment type			
Site	GPS coordinates	Sand (%)	Silt (%)	Clay (%)	OC (%)
Co	Artificial control	96.86	3.14	0.00	0.84
S3	45°47'57.228"N, 5°50'44.412"E	95.66	3.91	0.43	1.13
S6	45°41'40.452''N, 5°53'10.715''E	84.33	14.86	0.81	2.02
S7	45°41'33.828''N, 5°53'15.107''E	43.45	54.15	2.40	4.39
S8	45°41'19.032''N, 5°53'39.3''E	92.58	6.77	0.66	1.13
S9	45°40'3.288''N, 5°53'36.276''E	93.65	6.09	0.26	2.27
S10	45°39'7.92''N, 5°53'11.184''E	96.83	2.96	0.21	0.56

TM sediment concentrations ($mg.kg^{-1}$ DM) were positively correlated with OC (%), excepting for Cr (Figure 1, p-value < 0.01). As a consequence, to avoid organic carbon as a potential confounding factor when comparing TM concentrations between sediments (Chen et al., 2007; Lin and Chen, 1998; Loska and Wiechuła, 2003; Morillo et al., 2004; Rauret, 1998), the TM concentrations were expressed in $mg.kg^{-1}$ DM normalized to 1 % OC prior to data analyses. The OC-normalized TM concentrations (Table 2) significantly varied between the sediments (Chi^2-test, p-value < 0.01).

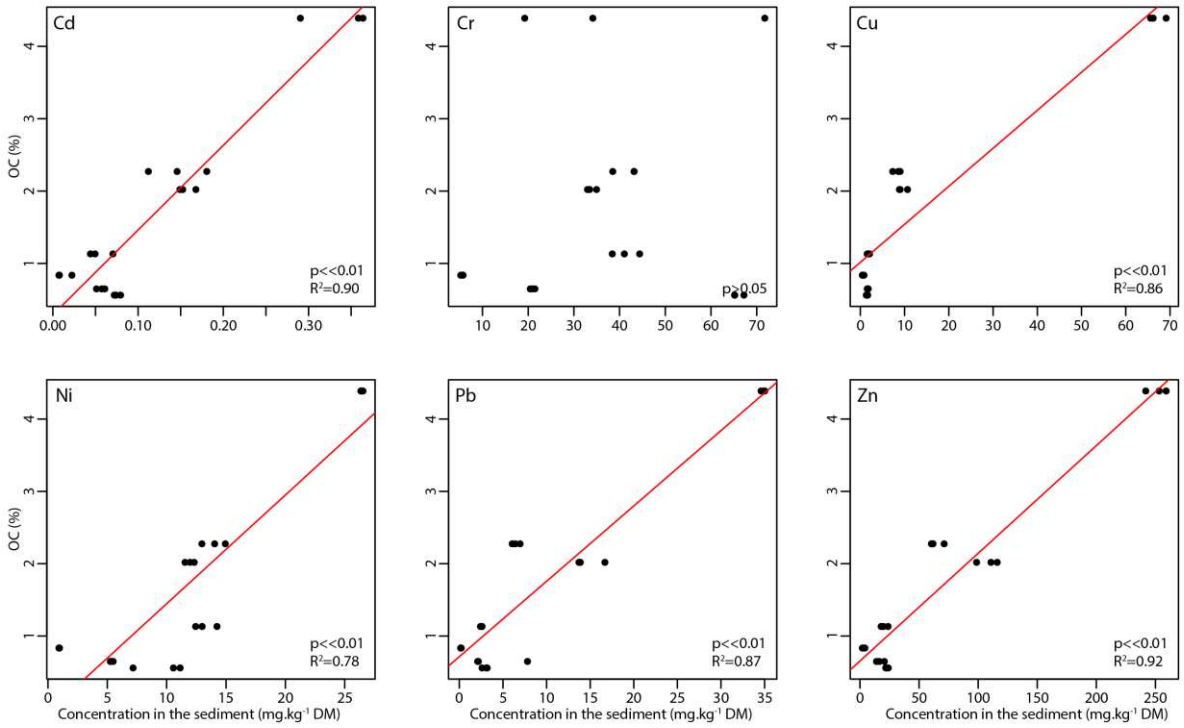

Figure 1. Linear regressions between percentage of organic carbon (OC) in the sediments and sediment TM content (mg.kg^{-1} DM). p represents the p-value of the significance of the linear regression and R^2 the adjusted R^2. Significant relationship is represented by a red line.

Table 2. Mean (± Standard deviation (SD)) TM sediment contents in mg.kg^{-1} DM normalized to 1% OC in the 6 study sites and in the control sediment Co. ND means "Non Detected" value.

Sediment concentrations (mg.kg^{-1} DM)						
Site	Cd	Cr	Cu	Ni	Pb	Zn
Co	0.01 ± 0.01	6.61 ± 0.32	0.72 ± 0.23	1.14 ± 0.02	0.21 ± 0.03	ND
S3	0.09 ± 0.01	32.30 ± 0.77	2.63 ± 0.20	8.24 ± 0.20	6.22 ± 5.04	26.32 ± 5.21
S6	0.08 ± 0.00	16.74 ± 0.52	4.70 ± 0.50	5.92 ± 0.19	7.31 ± 0.83	53.80 ± 4.43
S7	0.08 ± 0.01	9.50 ± 6.17	15.26 ± 0.43	6.02 ± 0.02	7.93 ± 0.05	57.28 ± 2.01
S8	0.05 ± 0.01	36.46 ± 2.66	1.61 ± 0.22	11.69 ± 0.80	2.21 ± 0.08	18.04 ± 2.64
S9	0.06 ± 0.02	18.31 ± 1.20	3.65 ± 0.40	6.15 ± 0.43	2.85 ± 0.20	28.40 ± 2.60
S10	0.13 ± 0.01	117.87 ± 2.17	2.75 ± 0.28	17.22 ± 3.84	5.32 ± 0.55	41.12 ± 1.85

2. Internal concentrations and BCFs

TM concentrations *in C. riparius* were on average 2.5 (Cd) to 6.4 (Cr) times higher than in *D. magna* and 1.6 (Ni) to 15.2 (Cr) times higher than in *L. minor* (Table 3). Only Cu concentrations in *L. minor* significantly exceeded those in *C. riparius*. Cu and Ni concentrations in *L. minor* were also significantly higher than in *D. magna*. Only Cr concentrations were significantly higher in *D. magna* than in *L. minor*. There was no significant difference between the Zn internal concentrations of the three species.

Table 3 *Mean internal TM concentrations (± SD) in mg.kg^{-1} DM and mean BCF (± SD) for each study organism. Different letters (a, b and c) indicate significant differences of the internal concentrations and the BCFs between the organisms.*

	Mean internal concentration (± SD) in mg.kg^{-1} DM					
Species	Cd	Cr	Cu	Ni	Pb	Zn
C. riparius	1.05 ± 1.00^{a}	33.52 ± 11.02^{a}	29.52 ± 12.59^{a}	11.17 ± 4.37^{a}	5.10 ± 3.63^{a}	150.25 ± 35.28^{a}
D. magna	0.42 ± 0.26^{b}	5.21 ± 3.03^{b}	11.63 ± 6.47^{b}	2.36 ± 2.11^{b}	1.33 ± 1.29^{b}	107.22 ± 115.53^{a}
L. minor	0.42 ± 0.19^{b}	2.20 ± 1.74^{b}	35.39 ± 7.40^{c}	7.00 ± 5.64^{c}	0.87 ± 1.51^{b}	147.57 ± 230.19^{a}
	Mean BCF (± SD)					
Species	Cd	Cr	Cu	Ni	Pb	Zn
C. riparius	14.17 ± 7.88^{a}	2.34 ± 2.33^{a}	12.38 ± 11.83^{a}	2.84 ± 3.81^{a}	2.03 ± 2.54^{a}	7.58 ± 7.26^{a}
D. magna	13.04 ± 21.47^{a}	0.36 ± 0.35^{b}	4.86 ± 4.07^{b}	0.46 ± 0.44^{b}	0.60 ± 0.86^{b}	4.82 ± 4.93^{a}
L. minor	8.45 ± 7.64^{b}	0.19 ± 0.24^{b}	15.97 ± 14.30^{c}	1.45 ± 1.33^{c}	0.18 ± 0.26^{b}	4.40 ± 7.07^{a}

The BCFs for *C. riparius* were on average 2.5 (Cu) to 6.5 (Cr) times higher than in *D. magna* and 2 (Ni) to 11.3 (Pb) times higher than in *L. minor* (Table 3). Similarly to the internal concentration, only the BCFs for Cu in *L. minor* significantly exceeded the BCFs in *C. riparius*. The BCFs for Zn did not exhibit significant difference between the organisms.

The internal Cd, Cu, Pb and Zn concentrations in *C. riparius* were significantly and positively correlated to sediment concentrations. *L. minor* presented significant positive correlations for Cu and Zn, whereas for *D. magna* such a relationship was only identified for Pb (Figure 2). Two negative relationships could also be identified; from Cr for *L. minor* and Cd for *D. magna*. Except for Zn, the slopes of the positive linear regressions were significantly higher (from 1.7 to 4 times higher), excepting for Zn, and more numerous for *C. riparius* than for the other organisms.

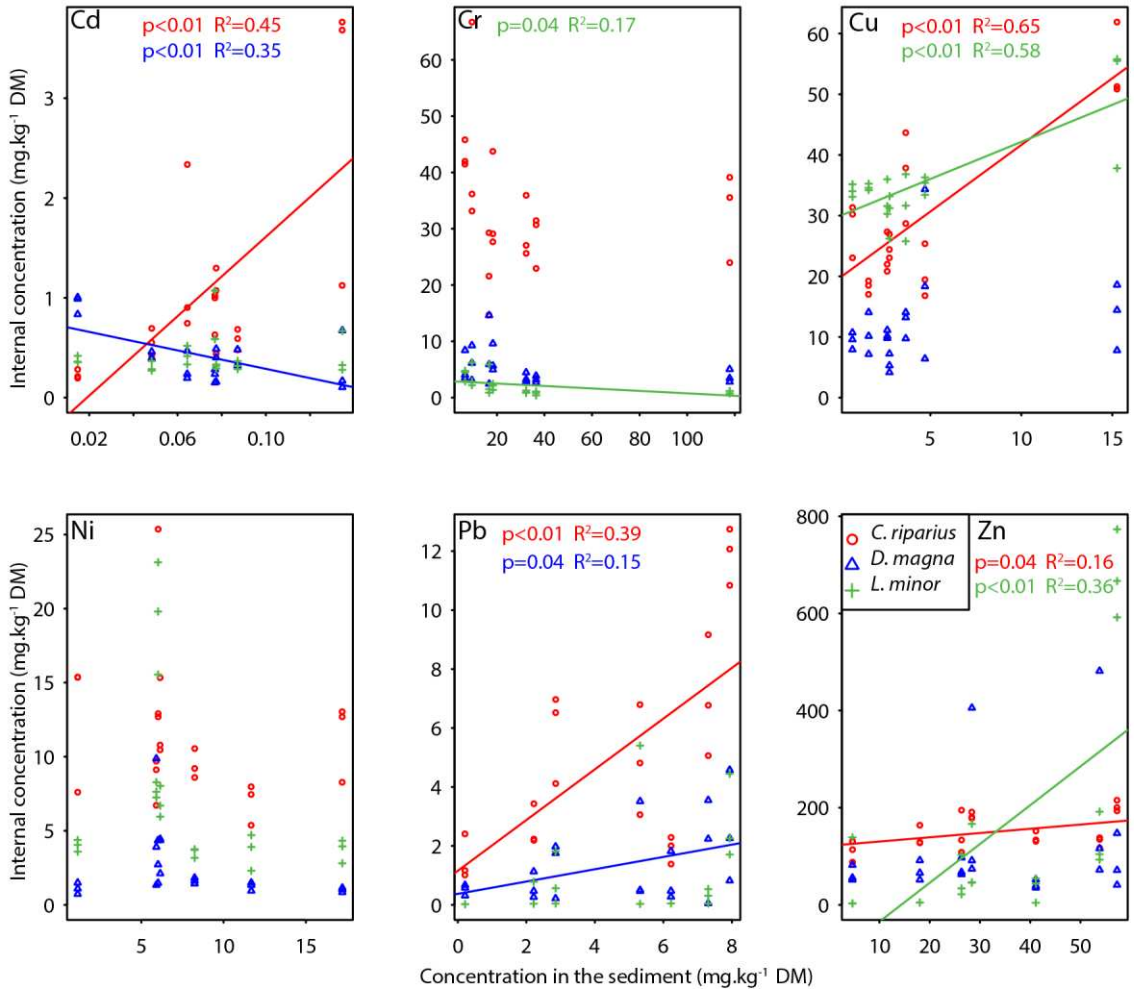

*Figure 2. Relationships between heavy metal (Cd, Cr, Cu, Ni, Pb, Zn) concentrations in organisms (*C. riparius, L. minor and D. magna*) in mg.kg^{-1} DM and in the sediments in mg.kg^{-1} DM normalized to 1% OC. Colored lines represents the fitted values of the linear regressions with red for* C. riparius, *blue for* D. magna *and green for* L. minor. *p represents the p-value of the statistical test and R^2 the adjusted R^2.*

When significant, the relationships between the BCFs and sediment-borne TM concentrations were all negative (Figure 3). These negative slopes were significantly higher for *C. riparius*, from 2 (Zn) to 11 (Cr) times, except for Cu for which the slope for *L. minor* was 1.4 times higher than for *C. riparius*.

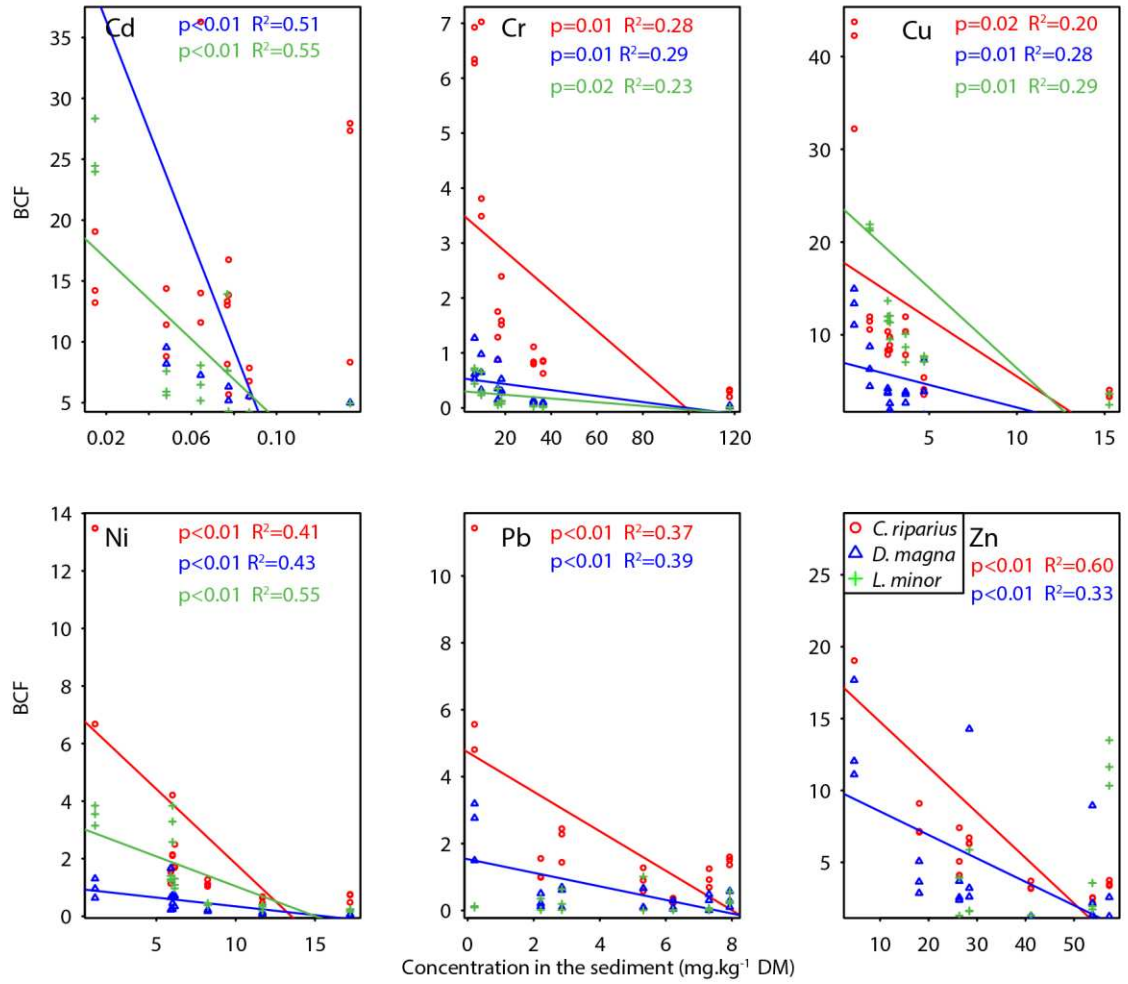

Figure 3. Linear regressions between BCF of organisms (C. riparius. L. minor and D. magna) *and heavy metal (Cd, Cr, Cu, Ni, Pb, Zn) concentrations in sediments in mg.kg*$^{-1}$ *DM normalized to 1% OC. p represents the p-value of the statistical test and* R^2 *the adjusted* R^2*. Colored lines represents the fitted values of the linear regressions with red for* C. riparius, *blue for* D. magna *and green for* L. minor.

3. Life history traits

The mean survival rates of *C. riparius* and *D. magna* in the control sediments were of 100 ± 0.00 % and 95.2 ± 3.29 % respectively. *C. riparius* in sediment S10 were the only ones to exhibit a significantly lower survival rate (48.75 ± 5.30 %) than in the control, while there was no significant difference in the survival rates of *D. magna* between the sediments (mean survival rate 82.43 ± 20.28 %). Mean growth rates were significantly lower for *C. riparius* in S3 (0.21 ± 0.001 day-1) and S10 (0.20 ± 0.003 day-1) compared to the control (0.23 ± 0.003 day-1), while there was no significant difference between *D. magna* growth rates (mean growth rate = 0.09 ± 0.004 day^{-1}) and a significantly lower population growth rate for *L. minor* in S8 (0.19 ± 0.02 day^{-1}) compared to the control (0.21 ± 0.01 day^{-1}).

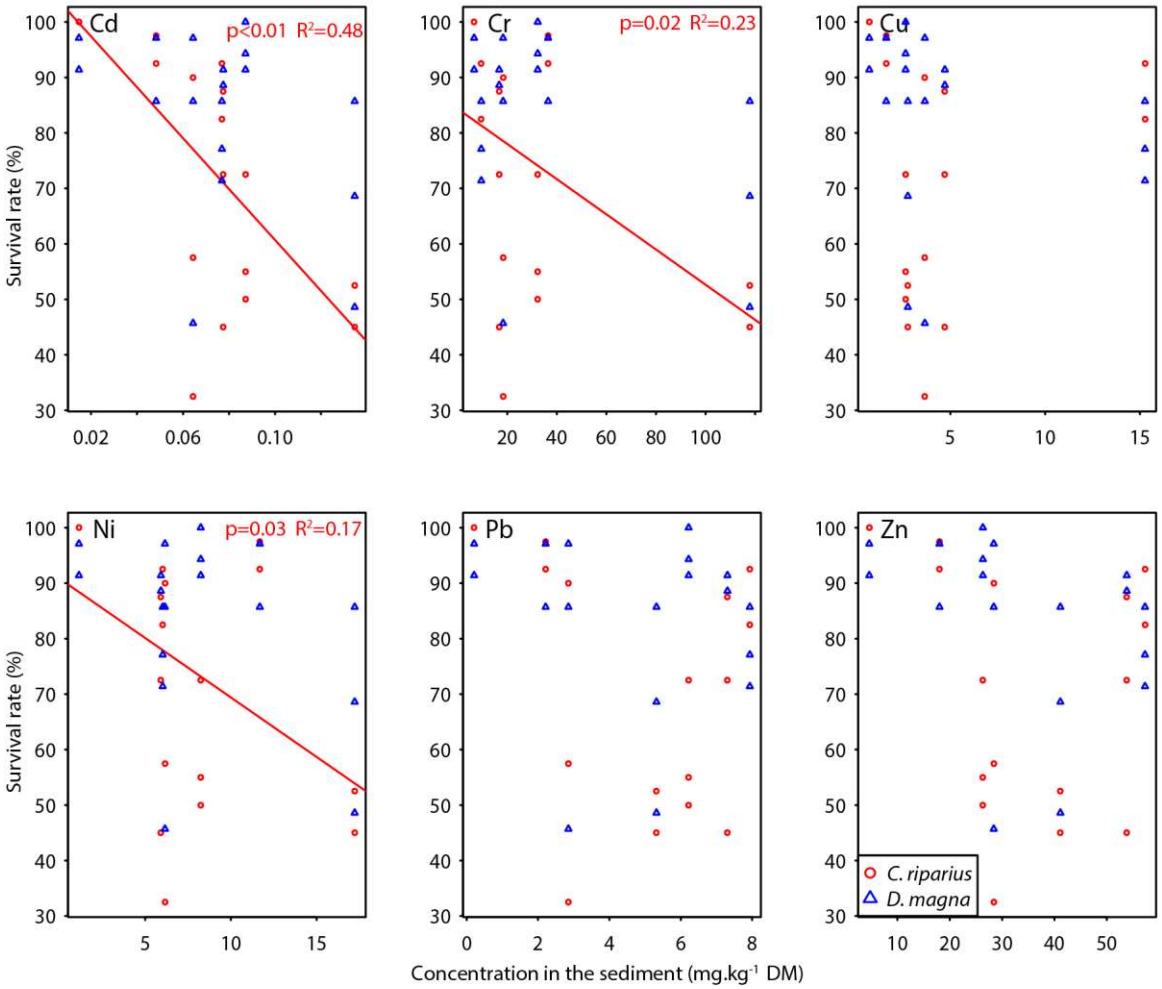

Figure 4. Linear regressions between the survival rates (%) of C. riparius *and* D. magna *and TM concentrations in sediments in mg.kg⁻¹ DM. p represents the p-value of the statistical test and R^2 the adjusted R^2. Colored lines represents the fitted values of the linear regressions with red for* C. riparius, *blue for* D. magna.

Survival and growth rates for *C. riparius* exhibited a significant negative relationship with sediment TM concentrations for Cd, Cr and Ni (Figure 4 and 5), while no significant relationship between the survival rates of *D. magna* and the sediment TM concentrations was observed (Figure 4). Growth rate of *D. magna* was nevertheless significantly negatively related to Cd, Cr and Ni sediment concentrations (Figure 6). No significant relationship was observed between the growth rates of *L. minor* population and the TM sediment concentrations (Figure 7). However, the relationships for Cu (p-value = 0.07, adj-R^2 = 0.12) and Pb (p-value = 0.05, adj-R^2 = 0.15) are likely to raise a positive trend between the two variables.

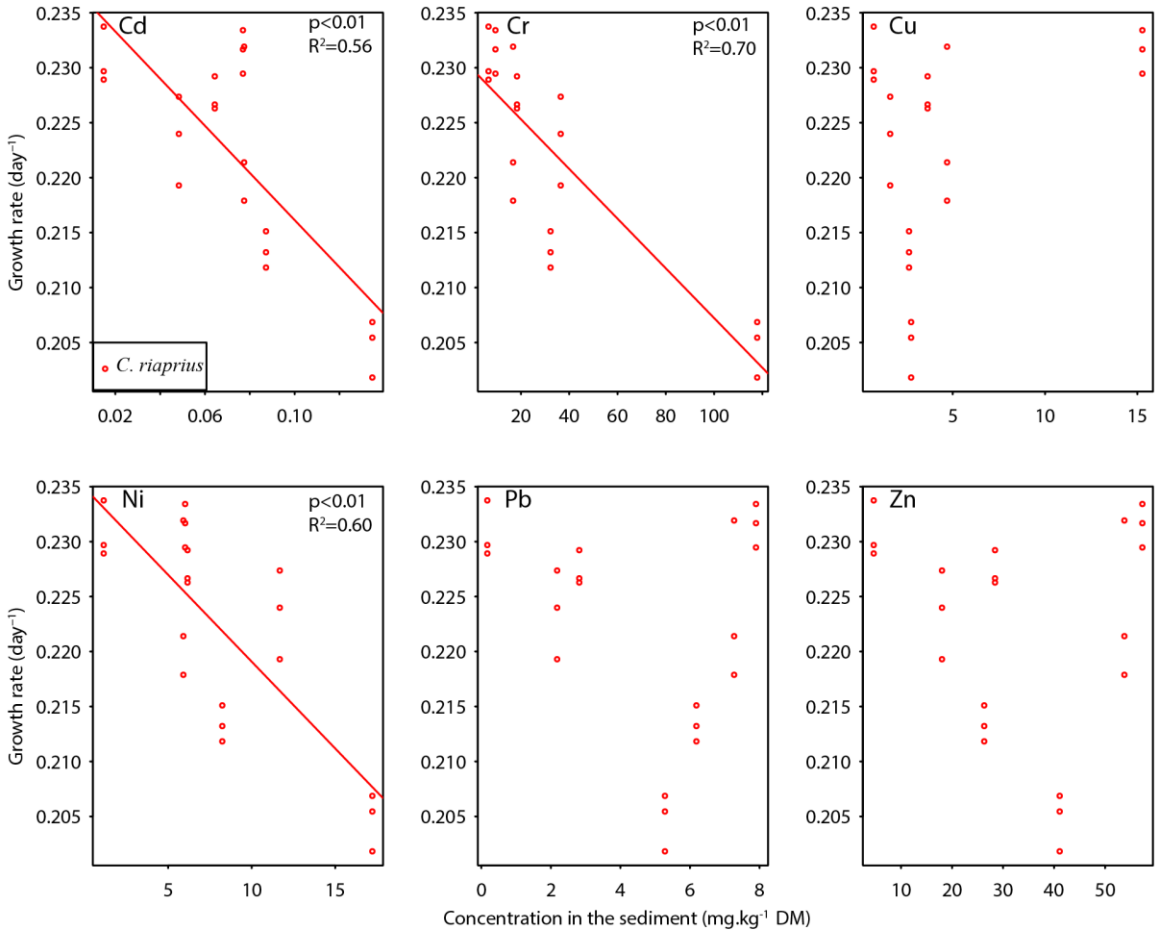

Figure 5. Linear regressions between the growth rate (day^{-1}) of C. riparius *and TM concentrations in sediments in $mg.kg^{-1}$ DM. p represents the p-value of the statistical test and R^2 the adjusted R^2. Significant relationship is represented by a line.*

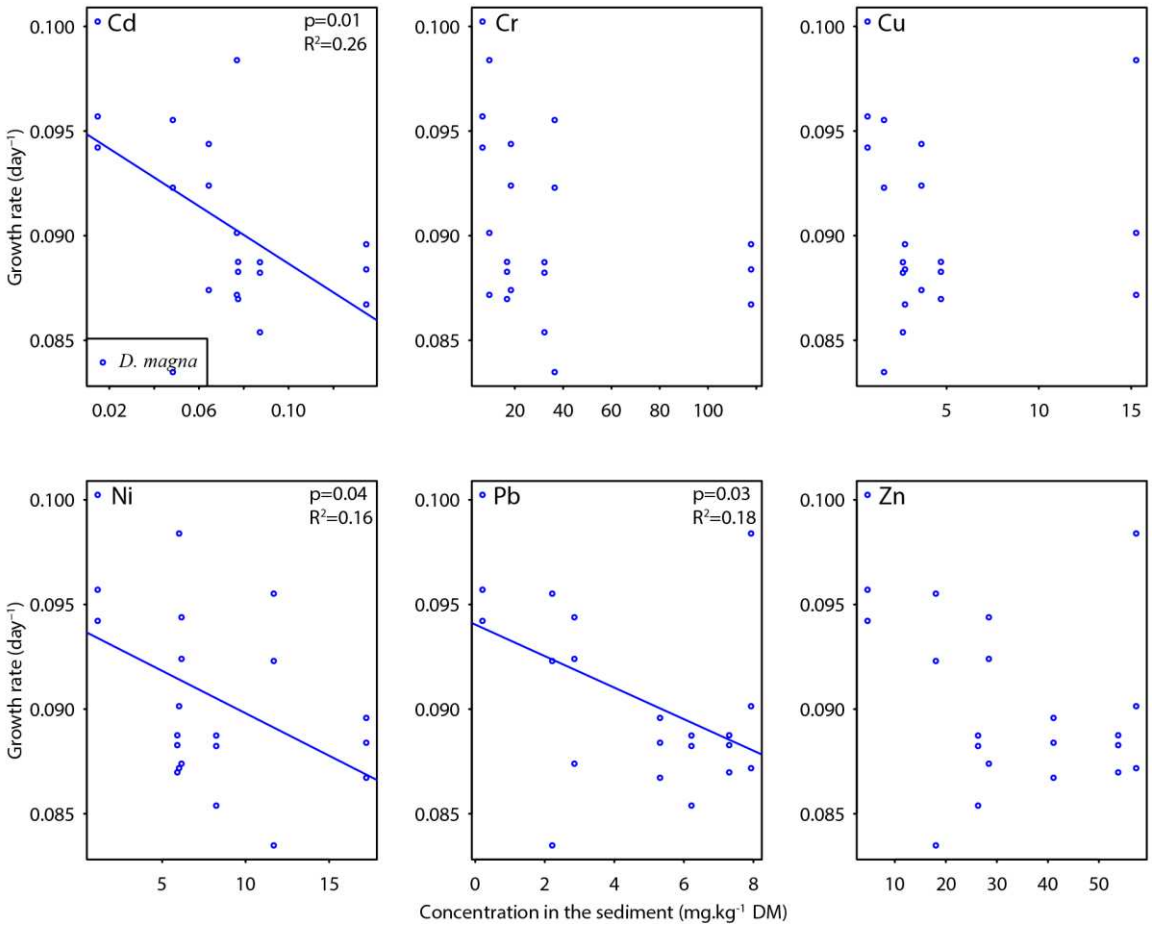

Figure 6. Linear regressions between the growth rate (day^{-1}) of D. magna *and TM concentrations in sediments in mg.kg^{-1} DM. p represents the p-value of the statistical test and R^2 the adjusted R^2. Significant relationship is represented by a line.*

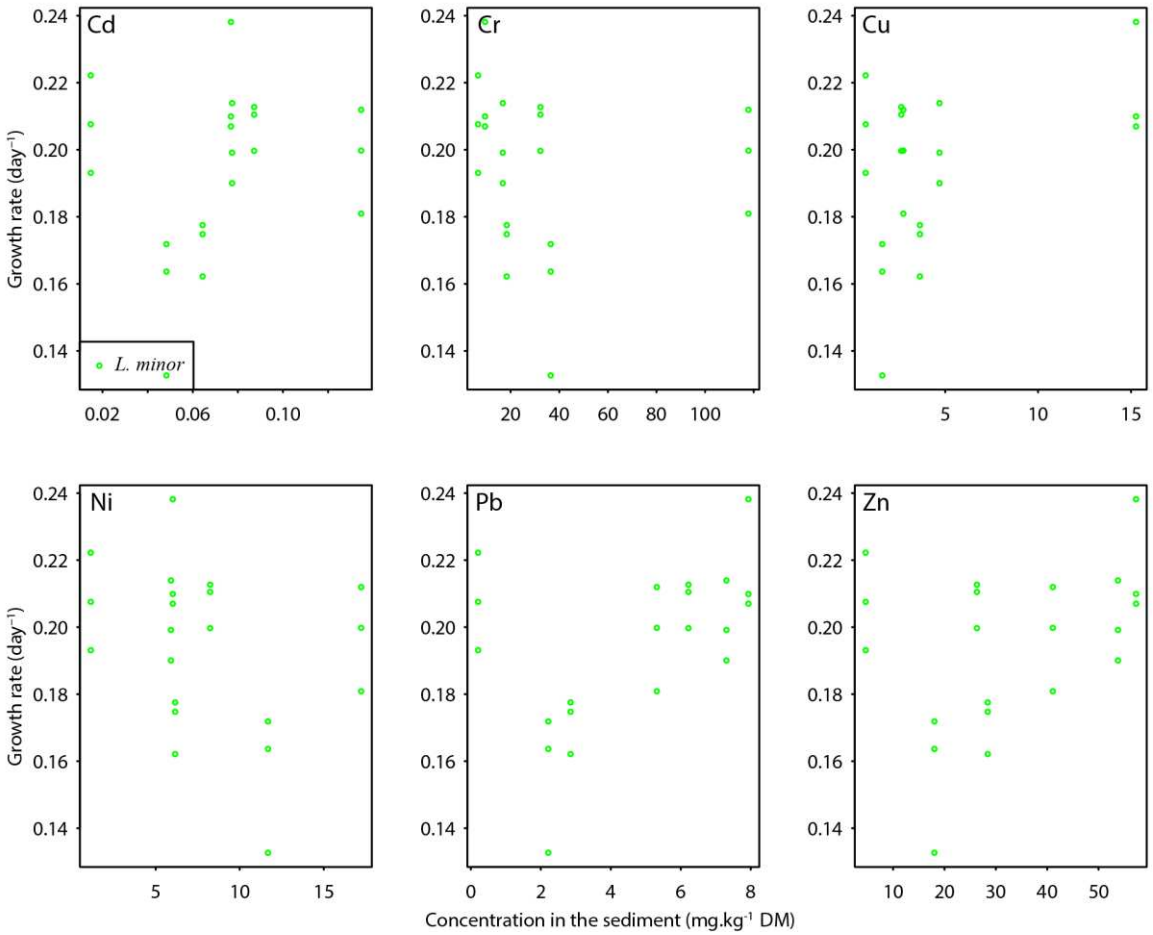

Figure 7. Linear regressions between the growth rate (day^{-1}) of L. minor *and TM concentrations in sediments in mg.kg^{-1} DM. p represents the p-value of the statistical test and R^2 the adjusted R^2.*

Discussion

Sediment-borne TM bulk concentrations were in the same order of magnitude as other worldwide large deep lakes with diversified activities on their catchment area (Duman et al., 2006; Fytianos and Lourantou, 2004; Ikem and Adisa, 2011; Katip et al., 2011; Liu et al., 2014; Özmen et al., 2004; Pertsemli and Voutsa, 2007; Scheibye et al., 2014; Yuan et al., 2011). Mean *C. riparius* internal concentrations were in the same order of magnitude as those exposed to low contaminated sediments in Roosa et al. (2016), even if the comparison should be made with caution because of differences in the experimental design (e.g. exposure time, renewal of the overlying water). Metal pollution is often linked to urban sources such as vehicles, roof and road runoffs and industrial effluents (Jung, 2009). Other sediment-borne chemicals were found in the same littoral sites, such as polycyclic aromatic hydrocarbons (PAHs) (the average sum of 15 PAHs listed by the US EPA was equal to 772.6 ± 1355.5 µg.kg^{-1} for the 6 sites) and polychlorinated biphenyls (PCBs) (the average sum of the 7 indicator congeners was equal to 21.0 ± 20 µg.kg^{-1} for the 6 sites) (Lécrivain et al., 2018), that could have exerted harmful effects on exposed organisms. Pesticides are not excluded as well, even if the agricultural practices in

the lake watershed are not intensive. Indeed, the littoral sediment are likely to exhibit a multi-contamination mostly reflecting the influence of point in-lake (e.g. harbours) and watershed sources (Poté et al., 2008). These chemicals may induce a biological response individually or as a mixture (Harrahy and Clements, 1997). Nevertheless, TMs were all detected in the exposed organisms and the significant negative relationships obtained between TMs sediment contamination and biological responses in this study suggest that TMs at least contribute to a significant part of these effects, whatever the contributions of the other contaminants.

A significant decrease in *C. riparius* survival and growth rates was observed along with the increase in sediment Cd, Cr and Ni concentrations. This result is in accordance with the fact that Cr and Ni exhibited high contents in every sediment. The life history traits response to Cd exposure might be explained by the high bioavailability of this TM, whose uptake is facilitated via the transporters of the resembling divalent Ca (Adams et al., 2011). In addition to its own toxic effect, Cd can thus inhibit the uptake and transportation of other essential elements like Ca, Mn and Fe, which can contribute to adversely affecting the survival and growth rates of *C. riparius* (Hou et al., 2007). Contrary to *C. riparius*, no significant impairment of sediment TM contamination was observed on *D. magna* and *L. minor* survival and only *D. magna* growth rate significantly decreased with an increase in Cd, Ni and Pb sediment concentrations. For *L. minor* a positive trend between Cu and Pb sediment contamination and the growth rate could even lead to the hypothesis of a hormesis phenomenon (Juang et al., 2012).

The observed disparities in life history traits responses between the organisms might be due to differences in exposure to the sediment-borne TMs. Except for Cu, the slopes from the linear regressions between internal and sediment TM concentrations were 2 to 4 times higher for *C. riparius* than for the other organisms. That was consistent with the assumption that benthic organisms were exposed to a higher extent than pelagic organisms to the sediment contamination in laboratory multi-species bioassays. Moreover, the BCFs were 1.7 to 12.3 times higher in *C. riparius* than in *D. magna* and *L. minor* for Cr, Ni and Pb. However, Cd, Cu and Zn were found at the same concentrations or even significantly higher in the pelagic than in the benthic organisms, suggesting a high bioavailability of these TMs to the pelagic organisms. The fact that the littoral sediments were mainly sandy and poorly organic may have facilitated the diffusion of TMs towards the water column (de Haas et al., 2004; Eggleton and Thomas, 2004; Mountouris et al., 2002), possibly enhanced by the bioturbation activity of *C. riparius* (Galar-Martinez et al., 2008; Geiszinger et al., 2009). Measurements of the dissolved fraction of TMs in the overlying water were performed at day 0, 5 and 10 of the experiments and concentrations were all under the limits of detection (data not shown), excepting for Cu (mean = 2.94 ± 1.15 µg.L^{-1}). Negligible to non-detected TM concentrations in the overlying waters were also obtained in such assays from pas studies (Harrahy and Clements, 1997; Triffault-Bouchet et al., 2005) and did not allow to assert the assumption of an increase in dissolved TM.

The different life history traits responses between the organisms might also be linked to dissemblance in ecological sensitivity. In this study, *C. riparius* exhibited internal Pb

concentrations on average 3.9 times higher than in *D. magna*. However, *D. magna* growth rate significantly decreased when Pb sediment concentrations increased while no significant response was observed for *C. riparius*, suggesting that *D. magna* may display a higher sensitivity to Pb exposure than the benthic *C. riparius* as it was already demonstrated for Ni (Leonard and Wood, 2013).

Both differences in bioconcentration and life history traits responses from these three species underline the importance of studying different species from different compartments and trophic behaviors to adequately assess the ecological risk of sediments (Bourioug et al., 2018; Jakimska et al., 2011; Rainbow, 2007). Indeed, even if lethal responses may not be observed in the water column overlying weakly contaminated sediments, individual growth rate impairments may result in a decline in population growth (Sibley et al., 1997) and has important ecological consequences, especially in a productive area like the lake littoral zone (Décamps and Naiman, 1990; Raspopov et al., 1996).

The BCFs of both benthic and pelagic organisms decreased along with an increase in sediment-borne TM contamination. Since sediment TM concentrations were normalized to 1 % of organic carbon and internal TM concentrations were positively correlated with sediment concentrations, the differences in bioavailability between the sediments could not explain the negative relationship between BCF and sediment contamination. This relationship might be explained by the control of bioconcentration by regulatory mechanisms activated to limit the uptake or increase the excretion of TMs, such as metallothioneins as along with an increase in sediment-borne TMs (Adams et al., 2000; Bodar et al., 1990; DeForest et al., 2007; McGeer et al., 2003). Inverse relationships between BCFs and TM contamination has already been observed in highly contaminated contexts, both in the field (Velez et al., 2015) and in the laboratory (Figueira et al., 2012). The present results underline that this negative relationship may occur in a low contamination context. At the least contaminated sediment concentrations, BCFs were the strongest suggestion that regulation processes may not have occurred. *In natura*, this relationship may consequently lead to observe the highest biological contaminant transfers through biomagnification in both benthic and pelagic compartments in the least contaminated environments (Chen et al., 2000).

Furthermore, regulatory mechanisms may exert a bias when the intention is to use the BCF to assess the organism exposure to a contamination (Goldberg et al., 1983; Kraak et al., 1991; Zweig and Rabeni, 2001). Conversely, the change in BCF along a sediment contamination gradient could be combined with relevant molecular biomarkers in order to provide insights on potential biological responses to exposure, even in the absence of higher life history traits response (Teisseire and Guy, 2000).

Conclusion

The present study was aimed at assessing the toxicity of six slightly contaminated sediments to benthic and pelagic organisms through laboratory 2-L microcosm assays. TMs were detected in both benthic and pelagic whole-body organisms and seemed to exert lethal and sub-lethal (individual growth rate) impacts on *C. riparius* and only sub-lethal impacts on *D. magna*. The organisms did not always seem to be impacted by the same TMs while exhibiting similar internal concentrations, suggesting a disparity in sensitivity. The negative relationships between BCFs and sediment contamination levels suggested that all organisms actively regulated their TM internal concentrations. The laboratory bioassays suggested that low-dose sediment contamination, in addition to the benthic biota, may impact pelagic macro-fauna and floating macrophytes. These results consequently underline the importance of including pelagic organisms in the ecotoxicological assessment of surficial sediments, especially in lake littoral zones where pelagic macro-fauna and flora are of ecological importance. Assessing BCFs in sentinel organisms along a pollution gradient could be a relevant tool to detect stressful effects of pollutants in situations where higher life history traits would not exhibit significant responses, especially in low contamination contexts, as it was the case in this study for *L. minor*.

Compliance with Ethical Standards:

Funding: This work was funded by Ministère de la Transition Ecologique et Solidaire.

Conflict of Interest: The authors declare that they have no conflict of interest.

Ethical approval: This article does not contain any studies with human participants or vertebrate animals performed by any of the authors.

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3. Synthèse

Même dans un contexte de faible multi-contamination, ces résultats indiquent que la pollution sédimentaire est biodisponible pour les organismes du compartiment pélagique. Nous pouvons alors nous questionner sur le transfert trophique de cette contamination initialement contenue dans le compartiment sédimentaire, véhiculée par des organismes pélagiques davantage mobiles que les organismes endobenthiques, d'autant que la vaste majorité des espèces de poissons se nourrissent des invertébrés et macrophytes de la zone littorale (Vadeboncoeur et al., 2011).

Ces essais de laboratoire montrent également une relation négative entre BCF et contamination sédimentaire. Ces résultats indiquent que la fraction de polluants sédimentaires bioconcentrée, pour l'ensemble des organismes d'étude, n'augmente pas linéairement avec la pollution sédimentaire à laquelle ils sont exposés. Ceci pourrait s'expliquer par l'implication croissante de mécanismes de régulation intrinsèques aux organismes pour faire face à une exposition de plus en plus importante aux micropolluants (Adams et al., 2011; McGeer et al., 2003). En perspective de ce travail, il serait par conséquent intéressant de mettre en évidence les mécanismes biochimiques en jeu par l'utilisation de biomarqueurs enzymatiques plus spécifiques que l'AChE et la GST (cf Article 1), tels que les métallothionéines (Drira et al., 2017).

Chapitre 5

Effets du marnage lacustre sur la mobilité et la biodisponibilité des contaminants sédimentaires : étude en laboratoire de l'assèchement et ré-immersion du sédiment littoral

1. Démarche générale

Le marnage lacustre engendre en zone littorale d'une part l'exondation des sédiments les plus proches de la berge et d'autre part un abaissement de la colonne d'eau au-dessus des sédiments littoraux plus profonds. Dans le premier cas, une combinaison de plusieurs facteurs (e.g. météo favorable, durée d'exposition à l'air libre, granulométrie du sédiment) est nécessaire pour assister à l'assèchement complet du sédiment, qui sera par la suite ré-immergé lors de la remontée du niveau de l'eau. Ces changements abiotiques que subit le sédiment de surface sont susceptibles de modifier la mobilité des ETM sédimentaires. Le terme « mobilité » dans ces travaux est défini comme la capacité de l'ETM à passer du sédiment avec lequel il est initialement lié à sa forme dissoute, dans l'eau interstitielle ou colonne d'eau dans lesquelles il sera davantage biodisponible. La mobilité de l'ETM dépend donc de la nature des liaisons avec le sédiment (de la fraction la moins mobile dite « résiduelle » à la plus mobile dite « échangeable ») et ces laisons peuvent changer selon les conditions abiotiques (e.g. pH, redox, force ionique) (Figure 17).

L'oxydation provoquée par la mise à l'air libre ou l'assèchement de sédiment anoxique semble entrainer une redistribution de la fraction résiduelle vers celles échangeables des ETM (De Jonge et al., 2012; Stephens et al., 2001). Cependant, les connaissances sur les changements de mobilité des ETM du sédiment littoral lacustre, sub-oxique à oxique, sous l'effet d'un assèchement et remise en eau restent encore aujourd'hui partielles. D'un côté, Nedrich et Burton (2017) ont observé une augmentation des concentrations en Zn dans l'eau interstitielle de sédiments littoraux sub-oxiques à oxiques asséchés puis ré-immergés. D'un autre côté, Frémion et al. (2017) ont observé une réduction de la mobilité du Cd, Cr, Ni, Pb et Zn au profit de la fraction résiduelle lors de l'assèchement de sédiment d'une retenue de barrage soumise à des vidanges régulières.

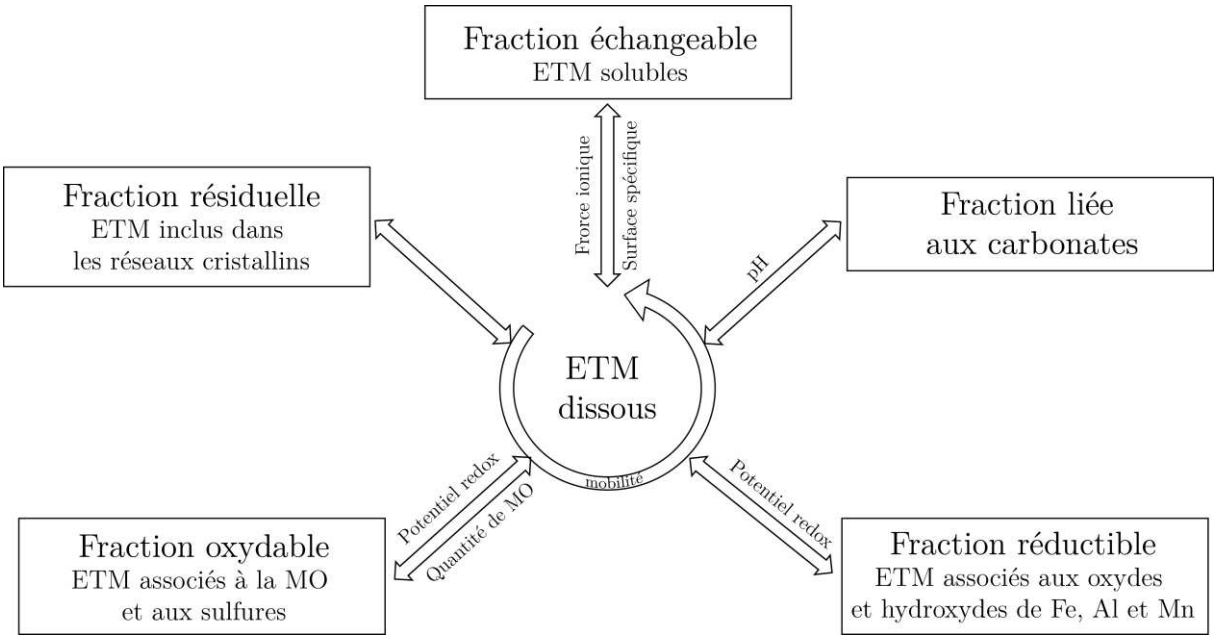

Figure 17 Principales fractions sous lesquelles se trouvent les ETM cationiques du sédiment et exemple de facteurs abiotiques qui facilitent les changements de mobilité avec la forme dissoute (modifié d'après Smith et Huyck (1999) et Qasim (2015)).

Dans le cas des grands lacs péri-alpins, dont le niveau d'eau a été stabilisé depuis les années 80, comment évolue la mobilité des ETM du sédiment littoral suboxique à oxique soumis à un assèchement puis une ré-immersion sous l'influence du marnage ? Si cette mobilité croît lors de ces phénomènes, les ETM sont-ils susceptibles d'impacter le biote benthique exposé ?

Ce Chapitre vise à apporter des éléments de réponse à ces questions en se basant sur les sédiments d'un site littoral du lac du Bourget. Ce site a été sélectionné pour sa bathymétrie (cf Chapitre 6) et sa contamination en ETM (cf Chapitre 1) intéressantes pour l'étude en laboratoire et *in situ* des effets du marnage sur la mobilité et la biodisponibilité des ETM sédimentaires (présent Chapitre et suivant).

Dans cette étude en laboratoire, les sédiments ont été asséchés et ré-immergés dans des microcosmes pour y exposer des larves de *C. riparius*. La mobilité des ETM sédimentaires liée à l'assèchement et la ré-immersion a été évaluée au moyen de tests de lixiviation simples et de tests d'extractions séquentielles. La biodisponibilité et les effets biologiques ont été respectivement mesurés via la concentration interne des larves de chironomes en ETM et les réponses de traits de vie comme la croissance et survie (Figure 18).

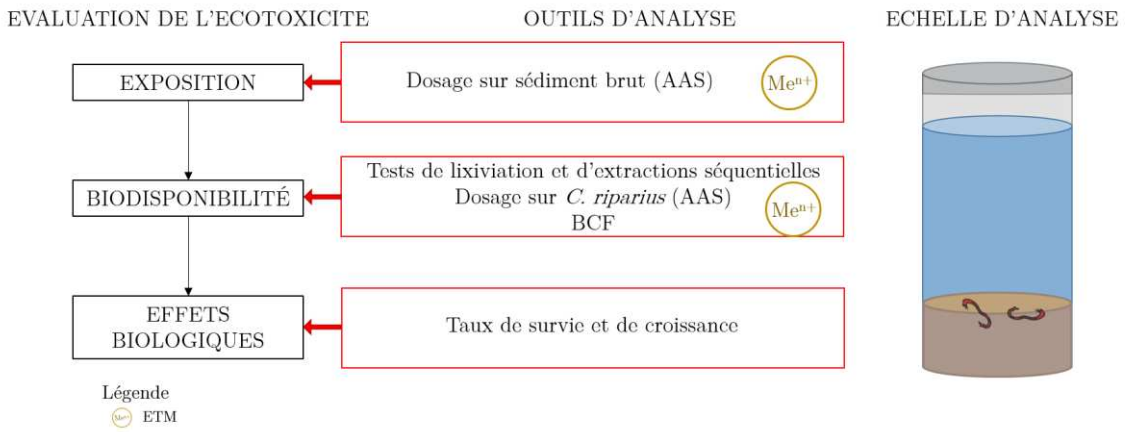

Figure 18. Schéma récapitulatif des outils et de l'échelle d'analyse pour l'évaluation de l'écotoxicité dans l'Article 5.

2. Article 5 – Simulating lake water level fluctuations in the laboratory: what is the fate of sediment-borne trace metals?

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Abstract

Alterations in the timing, frequency, and magnitude of water level fluctuations (WLFs) in lakes may result in important changes in abiotic parameters that can affect sediment-borne contaminant mobility and bioavailability in littoral zones. This study aims to assess the mobility of trace metals (TMs) – Cd, Cr, Cu, Ni, Pb and Zn - under laboratory-simulated WLFs through a three-pronged approach. One surficial sediment was sampled from the shoreline of a large French lake exhibiting an artificially limited WLFs. A sample was enriched with a solution of TMs to ensure significant measurements of mobility. The spiked and naturally contaminated sediments were dried and re-immersed. The first approach consisted of measuring the mobility of TMs from the sediment to the water column under re-suspensions of particles through leaching tests. The second approach assessed the partitioning of TMs between the different binding forms within the sediments through sequential extraction tests. The last approach tested the changes in TM bioconcentration in organisms exposed to sediment through microcosm assays. The hypothesis was that WLFs may increase mobility from the sediment to the water column relative to mobility from the residual to mobile fractions within the sediments and consequently increase the bioconcentration of less inert trace metals, mostly Cd and Zn. This hypothesis was partly confirmed as Cd and Zn exhibited the greatest mobility following WLFs. However, this mobility increased toward the residual fraction instead, except when WLFs included great resuspension of particles. The study also provides insights into the complex relationships among contaminant mobility, bioavailability and bioconcentration, especially in the context of large abiotic disturbances such as WLFs. These findings may be useful for further management strategies for WLFs-regulated lakes and reservoirs.

Keywords

Heavy metal, laboratory microcosm, sequential extractions, leaching test, lake littoral, mobility, bioavailability.

Introduction

Alterations of the timing, frequency and magnitude of water level regimes may result in important changes in the ecological structure and functioning of littoral habitats (Adams, 2002; Evtimova and Donohue, 2014, 2016; Strayer and Findlay, 2010). The impacts of water level regulations on the abiotic characteristics of littoral zones and the negative consequences on biological productivity and diversity have been widely studied (Hirsch et al., 2017; Leira and Cantonati, 2008). Restoring natural water-level fluctuations (WLFs) in artificially regulated lakes is hence increasingly considered as a tool for ecological restoration (Coops et al., 2003; Coops and Hosper, 2002; Geest et al., 2005). However, little attention has been paid to the influence of these changes on abiotic parameters, e.g., sediment-borne contaminants and their mobility at the sediment-water interface (SWI) (Frémion et al., 2017, 2016). WLFs induce the drying and re-flooding of shoreline surficial sediments, which may affect biogeochemical cycling in sediments through changes in temperature, pH, redox potential, particle resuspension and microbial activity. These alterations can affect the lability, solubility and speciation of contaminants, potentially resulting in toxicity of an originally non-toxic SWI. The mobility of sediment-borne contaminants under sediment drying has been often studied in the context of management of dredged sediments (Charrasse et al., 2018; Guevara-Riba et al., 2004; Kim et al., 2018), but little is known about the mobility and bioavailability of contaminants from shoreline surface sediments that undergo WLFs after immersion by standing waters for a long period (Skoulikidis et al., 2008).

Lake Bourget (Savoy, France) is a large deep lake for which WLFs was artificially reduced to 30 $cm.year^{-1}$ in the early 1980s for hydroelectricity generation (Miquet, 1997); the restoration of larger WLFs is currently being argued for ecological rehabilitation purpose. Among other contaminants, trace metals (TMs) have been measured in littoral surficial sediments at low to moderately toxic levels (Lécrivain et al., 2018).

The aim of this study is to assess the mobility and bioavailability of six TMs (Cd, Cr, Cu, Ni, Pb and Zn) from a littoral surficial sediment of Lake Bourget through laboratory WLFs simulations. The simulations consisted of drying and re-immersing these sediments and assessing the mobility of sediment TMs following three approaches. The first approach consisted of assessing the mobility of TMs between the sediment and the water column under re-immersion, including vigorous resuspension of particles simulated through leaching tests. The second approach was based on sequential extraction tests to appraise the potential changes in the binding forms of TMs within the sediment under re-immersion without mechanical resuspension of particles. The third approach used microcosm bioassays in which laboratory aquatic organisms were exposed to these sediments to determine the changes in TM bioconcentration after WLFs. Half of the naturally contaminated sediment was spiked with TMs to ensure the detection of contaminant mobility via these three approaches since littoral sediments are coarse sediments and are likely to adsorb less metal on particle surfaces than fine offshore sediments (Lécrivain et al., 2018; Nedrich and Burton, 2017).

Past studies have shown a redistribution of most TMs from the residual to mobile fractions following drought of anoxic sediments (Stephens et al., 2001). Other studies have demonstrated that the speciation of TMs depends on their concentrations in the sediment (Fan et al., 2002). Others have only shown slight changes in oxid to suboxic sediments (Frémion et al., 2017).
Following these past results, this study hypothesizes that sediment drying and re-flooding may increase mobility from the sediment to the water column (Approach 1) related to mobility from the residual to mobile fractions (Approach 2) and consequently increase the bioconcentrations (Approach 3) of the less inert TMs, mostly Cd and Zn (Tiquio et al., 2017; Wu et al., 2011).
The results are expected to increase knowledge of the behavior of sediment-borne contaminants under controlled WLFs and provide broader perspectives for management tools related to WLFs in lake ecological restoration.

Materials and methods

1. Sampling sites and method

2 kg of wet surface (0-5 cm) sediment was sampled in the southeastern littoral of Lake Bourget (45°40'3.3''N, 5°53'36.3''E) at a water depth of 1 m using an Ekman grab in an area with a gentle slope. The sediment was then homogenized in a plastic tray and placed in pre-washed 2-L polyethylene bottles. The samples were transported to the laboratory in coolers, sieved through 2-mm mesh to remove debris and macrofauna and stored at 4 °C.

2. Sampled sediment characterization

The grain size distribution, loss on ignition and total content of trace metals of the sediment were assessed according to the method described in Lécrivain et al. (2018). Briefly, 3 sub-samples of sediment were dried at 105 °C for 24 hours. One sub-sample was used for grain size measurements by laser diffractometry (Malvern Mastersizer 2000G). The second sub-sample was used for water content determination and further ignited at 550 °C for 4 hours to determine the loss on ignition (LOI). The percentage of organic carbon (OC) was calculated from the LOI using the relationship OC (%) = LOI (%)/2.13 (Dean Jr, 1974). The last sediment sample was dried and mineralized in a microwave oven (CEM/MARS Xpress, 2 mL of ultra-pure HNO_3 + 6 mL of ultra-pure HCl, 180 °C for 30 min, filtration on a 0.45-µm Whatman™ filter and dilution of the residue in 25 mL of ultra-pure water). The resulting sample was analyzed by atomic absorption spectrometry (AAS). The total sediment contents of Cd, Cr, Cu, Ni and Pb were measured in a graphite furnace at 1500 °C, and the total sediment content of Zn was measured with an air-acetylene flame (Perkin Elmer, model PinAAcle 900T, detection limits: Cd = 0.1 $\mu g.L^{-1}$, Cr = 0.040 $\mu g.L^{-1}$, Cu = 0.014 $\mu g.L^{-1}$, Ni = 0.07 $\mu g.L^{-1}$, Pb = 0.05 $\mu g.L^{-1}$, Zn = 0.02 $\mu g.L^{-1}$).

3. Sediment spiking

Half of the sediment was spiked with Cd (added as $Cd(NO_3)_2,4H_20$; Merck), Cr (added asCrO_3, Merck), Cu (added as $CuCl_2,2H_2O$, Sigma-Aldrich), Ni (added as $NiSO_4$, $7H_2O$, Acros Organics) and Zn (added as $Zn(CH_3COO)_2$, Prolabo) to achieve the following respective final concentrations: 2, 75, 90, 30 and 200 $mg.kg^{-1}$ DM. These nominal concentrations were chosen as the means of the respective Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) (MacDonald et al., 2000b) to increase the probability of observing biological effects of sediment contamination on the exposed organisms. The final sediment concentrations of Cd, Cr, Cu, Ni and Zn were 1.30 ± 0.22, 62.39 ± 14.53, 60.20 ± 11.19, 13.18 ± 2.47 and 150 ± 30 $mg.kg^{-1}$ DM, respectively. Throughout this study, the non-spiked sediment will be called Sediment A, and the spiked one will be called Sediment B.

4. WLFs simulation

Sub-samples of sediments A and B were dried in an oven at 40 °C for 6 days to ensure slow, total drying. The other sub-samples remained wet and were stored at 4 °C for use as controls in the simulation.

Approach 1

Leaching tests were performed on the dried and control (always wet) sediments according to the European standard (EN 12457-2, 2002) to assess the leachate concentrations of the TMs that could be transferred from the sediment to the water column after re-flooding with mechanic particle re-suspension. The leachate dissolved TM concentrations were measured using atomic absorption spectrometry (AAS) as previously described.

Approach 2

Another sub-sample of the dried sediments was slowly re-wetted until water saturation with a synthetic medium (pH: 7.7, hardness: 60 mg $CaCO_3.L^{-1}$, alkalinity: 120 mg $CaCO_3.L^{-1}$, conductivity: 290 $\mu S.cm^{-1}$, phosphorous: 100 $\mu g.L^{-1}$, nitrogen: 1308 $\mu g.L^{-1}$, $FeEDTANa_2,6H_2O$: 109.4 $\mu g.L^{-1}$, oligo-elements and vitamins of M4 medium (Elendt and Bias, 1990)). Then 250 g of FM of the sediments, with a height of approximately 2 cm, were introduced in acid-rinsed beakers (4 replicates for each sediment (spiked and non-spiked)) and submerged in 2 L of the same synthetic medium. The beakers were aerated and left to stand for seven days for stabilization and maturation in the dark at 20 °C.

Sequential extraction tests were performed according to the method of Pueyo et al. (2001). Tests were performed on wet (sequential extraction test "SE1"), dried (sequential extraction test "SE2") and re-wetted (sequential extraction test "SE3") sediments to assess the mobility of the trace metals along the WLFs simulation between the 4 fractions: (F1) exchangeable metal; (F2) Fe-Mn oxides and hydroxide-bound metal; (F3) organic matter and sulfide-associated metal; and

(F4) residual metal. For each sediment, the extractions were performed in triplicate, and a cleaning step with ultra-pure water was introduced between each fraction. The supernatants were separated by centrifugation (20 min at 8000 g), filtered with a 0.2-µm nylon mesh and acidified with concentrated nitric acid. The TM concentrations in the sediment fractions were measured by atomic absorption spectrometry (AAS) as previously described.

Approach 3

Microcosm assays were performed using the previously cited beakers containing sediments that always remained wet throughout the whole study as controls.

The laboratory organisms used for this experiment originated from a laboratory room exempt from possible contamination at constant temperature (20 ± 2 °C) and under a daily light regime of 16 h of light and 8 h of darkness. *Chironomus riparius* midges were bred in plastic aquaria (34*18*19 cm) containing a layer of artificial sediment comprising 2 kg of dry Fontainebleau sand (particle size 150–300 µm) (VWR Prolabo) mixed with 600 mg of finely ground fish food flakes (TetraMin®) submerged in 6 L of clean and aerated groundwater. 75 % of the water column was renewed weekly, and the midges were fed finely crushed TetraMin®. Forty *C. riparius* first-instar larvae were introduced into the microcosms. The larvae were homogeneous in individual size (i.e., coefficient of variation of less than 10 %). During exposure, the larvae were fed 0.33 ml per individual per day of a finely crushed suspension of 10 $g.L^{-1}$ TetraMin®. Half of the water column was gently renewed every other day to prevent abnormally high contaminant concentrations, and the water column quality was monitored to prevent bias in the fitness response of the organisms. The dissolved oxygen concentration ($mg.L^{-1}$), temperature (°C), conductivity ($\mu S.cm^{-1}$), pH and Na^+, K^+, Ca^{2+}, NH_4^+, Mg^{2+}, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-} dissolved concentrations ($mg.L^{-1}$) were measured in the beakers every other day following the methods described by Perrodin et al. (2016).

The larvae were exposed for 10 days to prevent emergence. At the final time (tf) of exposure, the larvae were collected, counted and placed for 4 hours in beakers filled with fresh synthetic media to exclude gut contents from the internal bioconcentrated TM concentrations.

The survival rate was expressed as the percentage of living individuals at the final time of the assays over the initial number of introduced individuals. The individual growth size (day^{-1}) was calculated according to equation (1) (AFNOR, 2006), where l_f and l_0 are the final and initial individual body lengths (mm), respectively, and t is the duration of the assays (days).

$$gr = \frac{ln(l_f) - ln(l_0)}{t} \quad (1)$$

The cephalic capsules were also measured to check that all larvae reached the fourth instar (Bour et al., 2015).

Internal TM concentrations were measured on dried and pooled individuals from the same beaker (CEM/MARS Xpress, 3 mL of ultra-pure HNO_3 + 1 mL of ultra-pure HCl + 1 mL of H_2O_2, 180 °C, 30 min, dilution of the residue in 10 mL of ultra-pure water). The samples were then analyzed by atomic absorption spectrometry (AAS) using the same method as for the sediment samples.

5. Data analysis

The sediments that remained wet during the whole study were used as a control for these tests, called “Control”, and the tested sediments that had undergone WLFs simulations following the three approaches were called “WLF-sediments”.

For sequential extraction tests, the sum of the first three fractions (F1+F2+F3) is often considered the most mobile fraction (Kartal et al., 2006; Liu et al., 2016). This fraction will be called the “mobile fraction” in the study.

The influence of WLFs simulations on TM mobility in the three approaches was statistically assessed using Type III Sum of squares analysis of variance (ANOVA) (on TM concentrations (in leachate for Approach 1, in sediment fractions in Approach 2 and in organisms in Approach 3), with treatment (control and WLFs) and sediments (A and B) as fixed factors. For all variables, the normality and the homoscedasticity of the residues were tested using the Shapiro-Wilk's test and the Levene's test, respectively.

Following the ANOVA results in Approach 2, the repartition within the fractions of each TM was also statistically compared between the sequential extraction tests SE1-SE2 and SE1-SE3 using the function prop.test from the *pgirmess* package (Giraudoux and Giraudoux, 2018).

For all approaches, the ratios of the TM concentrations (in leachate for Approach 1, in the mobile fraction in Approach 2 and in organisms in Approach 3) measured in the WLF-sediments to those in the controls were calculated to illustrate the evolution (increase or decrease) of the mobility/bioavailability of the TMs following WLFs simulations and compare the evolution among the three approaches; these ratios were called $Ratio_{leaching}$, $Ratio_{extraction}$ and $Ratio_{organism}$, respectively.

All statistical analyses as well as graphical displays were performed using R (Team, 2017). Throughout the manuscript, values following “±” correspond to the standard deviation of the data.

Results

1. Main sediment characterization

The sampled sediment was mainly sandy (94.5 ± 1.0 %) and poorly organic (1.8 ± 0.2 %) (Table 1), which is characteristic of a surficial sediment exposed to hydrodynamic regimes in the littoral zone (Lécrivain et al., 2018).

The TM concentrations in the Sediment A were always under the TEC, whereas those of the sediment B were always above, except for Ni and Pb. Both sediments exhibited TM concentrations under the PEC.

Table 1. GPS coordinates, grain size distribution (%), organic carbon (OC) content (%) and mean TM contents (± standard deviation (SD)), and TEC and PEC in mg.kg^{-1} DM (dry mass) of the two sediments (n=3).

	Sediment A	Sediment B	TEC*	PEC*
GPS coordinates	45°40'3.3''N, 5°53'36.3''E		-	-
Sand (%)	94.5 ± 1.0		-	-
Silt (%)	5.3 ± 1.0		-	-
Clay (%)	0.2 ± 0.0		-	-
D50 (µm)	551.9 ± 11.4			
OC (%)	1.8 ± 0.2		-	-
Cd (mg.kg^{-1})	0.09 ± 0.01	1.30 ± 0.22	0.99	4.98
Cr (mg.kg^{-1})	25.35 ± 4.08	62.39 ± 14.53	43.4	111.00
Cu (mg.kg^{-1})	6.33 ± 0.17	60.20 ± 11.19	31.6	149.00
Ni (mg.kg^{-1})	14.23 ± 7.24	13.18 ± 2.47	22.7	49.00
Pb (mg.kg^{-1})	5.81 ± 0.85	5.64 ± 0.67	35.8	128.00
Zn (mg.kg^{-1})	46.86 ± 0.24	149.12 ± 25.60	121.00	459.00

* from (MacDonald et al., 2000b)

2. Approach 1

An increase in Cu, Ni and Pb leachate concentrations was observed for WLF-sediments compared to the control and was significant for Ni in Sediment A and Cu in Sediment B (Figure 1).
The TM concentrations in the leachates from both the control and WLF-sediments were significantly higher in Sediment B than in Sediment A, even when the total sediment concentrations were similar (e.g. Ni), except for Pb. This may be due to the higher TM mobility linked to the spiking of Sediment B, which did not undergo the same aging process of TM contamination as Sediment A.

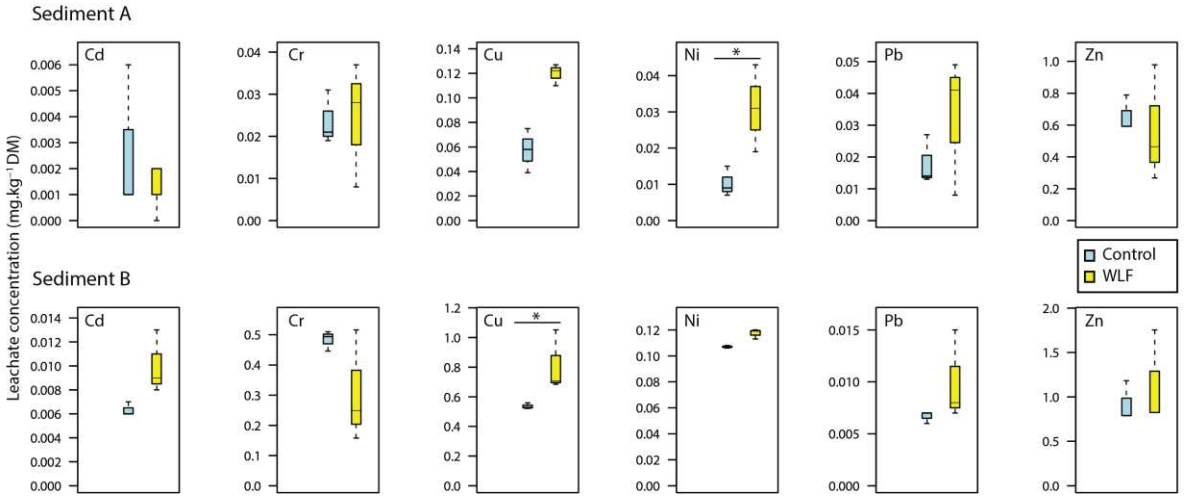

Figure 1. Leaching test results for the control sediments (blue) and WLF-sediments (yellow) for the natural (A) and spiked (B) sediments (n=3). The stars indicate significant differences between the control and WLF-sediments.

3. Approach 2

Type III Sum of Squares ANOVA revealed significant differences in the distributions between fractions according to both the sequential extraction test (SE1, SE2 and SE3) and the TM. Following these results, a prop.test was performed for each TM to test the differences between the sequential extraction tests in the distributions between the fractions.

The WLFs simulation was assessed by comparing the results of the sequential extraction tests SE1 and SE3 and was characterized by an upward trend of the residual fraction (F4) in both sediments (Figure 2), which was more or less marked according to the TM and significant for Zn in both sediments and for Cr in Sediment B (Table 2).

Table 2. Prop.test results to assess significant differences between the sequential extraction tests (SE1, SE2 and SE3) in the distribution of each TM between the 4 fractions.

	Element	Cd	Cr	Cu	Ni	Pb	Zn
Sediment A	Chi SE1-SE2	0.13	1.24	1.95	0.27	1.42	12.41
	p-value SE1-SE2	0.99	0.74	0.58	0.97	0.70	**0.01**
	Chi SE1-SE3	0.06	0.37	0.92	0.35	0.53	31.44
	p-value SE1-SE3	1.00	0.95	0.82	0.95	0.91	**0.00**
Sediment B	Chi SE1-SE2	0.41	5.10	1.64	0.38	0.63	4.50
	p-value SE1-SE2	0.94	0.16	0.65	0.95	0.89	0.21
	Chi SE1-SE3	0.53	12.38	2.18	1.78	0.86	23.33
	p-value SE1-SE3	0.91	**0.01**	0.54	0.62	0.84	**0.00**

More precisely, drying (comparison between the sequential extraction tests SE1 and SE2) was also characterized by an upward trend of F4 in both sediments and was significant for Zn in Sediment A (Table 2).

Exploring the fraction analysis further, Cd and Zn exhibited the greatest abundance in F2, Cu and Pb were highly bound to organic matter as they were abundant in F3, and Cr and Ni exhibited the greatest abundance in F4.

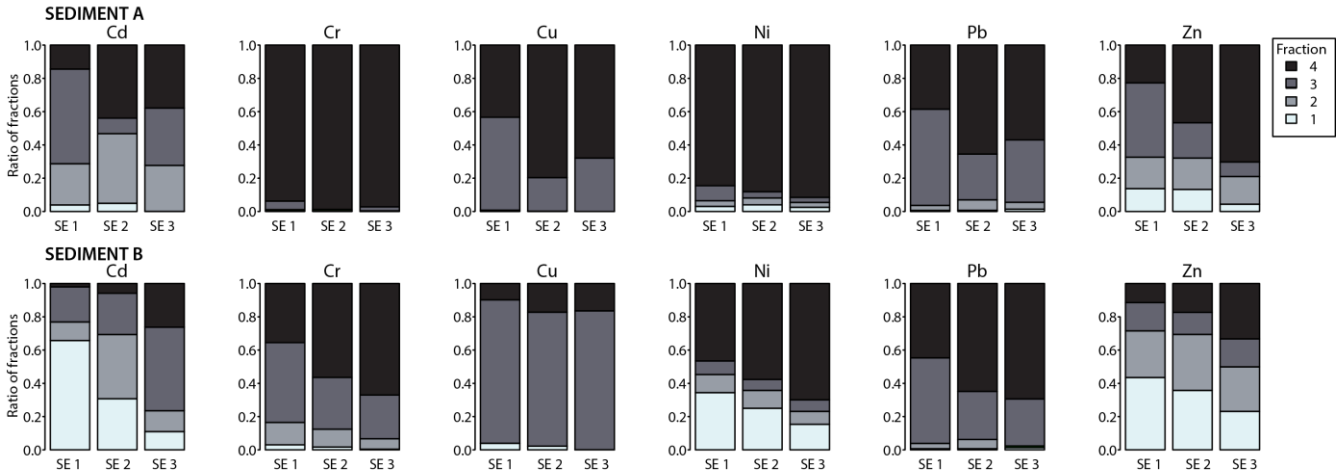

Figure 2. Fractionation of Cd, Cr, Cu, Ni, Pb and Zn according to the BCR protocol. The results are expressed as the mean percentage of the contribution of each fraction (concentrations in mg.kg^{-1} DM converted in ratios over the total concentration, n=3). SE1, SE2 and SE3 correspond to extraction tests performed on the control (wet), dried and WLF-sediments respectively.

Overall, the WLFs simulation was characterized by a reduction of the mobile fraction (F1+F2+F3), which might results in reduced bioavailability of the sediment-TMs.

4. Approach 3

There was no significant difference between the WLFs and control sediments or between Sediments A and B in terms of the survival (mean = 78 ± 9 %) and growth rates (mean = 0.30 ± 0.005 day^{-1}) of *C. riparius*.

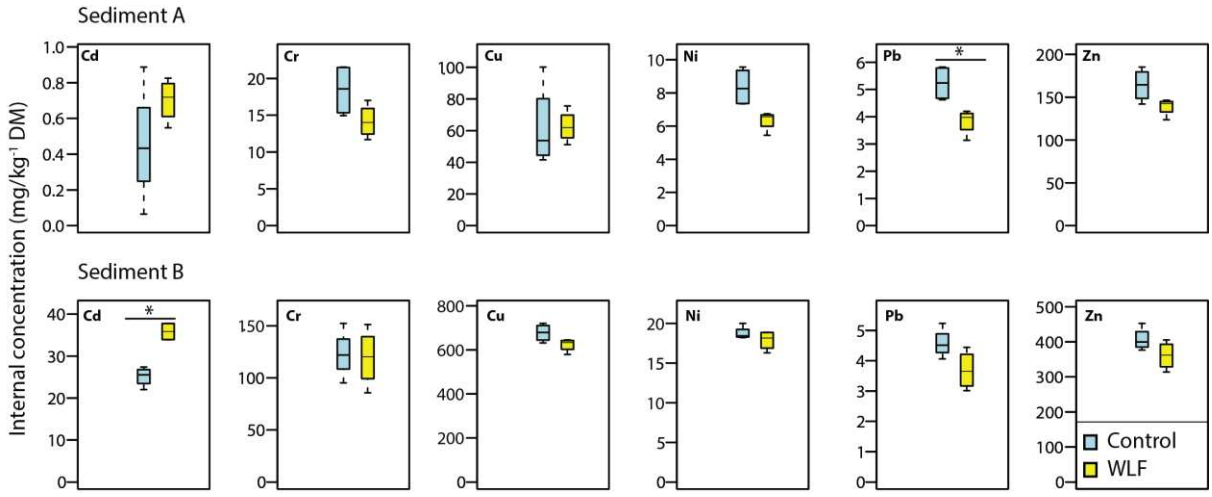

Figure 3. TM internal concentrations (mg.kg^{-1} DM) in C. riparius *(n=4) exposed to the control (blue) and WLF-sediments (yellow) from sediments A and B.*

A downward trend was observed in internal concentrations between the organisms exposed to the control and WLF-sediments, with a significant decrease in Pb in Sediment A (Figure 3). By contrast, Cd concentrations significantly increased in organisms exposed to WLF-sediment B.

5. Comparison of TM mobility among the three approaches

$Ratio_{leaching}$ was greater than 1 (Table 3) except for Cd in Sediment A and Cr in Sediment B, suggesting that hydrodynamic flows related to WLFs may increase TM mobility from the sediment to the water column.

By contrast, $ratio_{extraction}$ was less than 1, suggesting a decrease in the mobile fraction in the sediment following WLFs simulation.

$Ratio_{organisms}$ was less than or close to 1, except for Cd for both sediments. These results are in agreement with $ratio_{extraction}$ as the internal TM concentrations decreased with a decrease in the more mobile fractions in the sediment following the WLFs simulation. The variations in the $Ratio_{organism}$ values were less important compared to $ratio_{extraction}$ and $ratio_{leaching}$.

Table 3. $Ratio_{extraction}$ (n=3), $Ratio_{leaching}$ (n=3) and $Ratio_{organism}$ (n=4) for each TM and sediment. (+) and (-) symbolize an increase or decrease in the concentration, respectively, between the control and WLF-sediments

	TM	Cd	Cr	Cu	Ni	Pb	Zn
Sediment A	$Ratio_{extraction}$	0.10 (-)	0.66 (-)	0.31 (-)	0.64 (-)	0.40 (-)	0.19 (-)
	$Ratio_{leaching}$	0.50 (-)	1.03 (+)	2.09 (+)	3.00 (+)	1.81 (+)	0.87 (-)
	$Ratio_{organism}$	1.55 (+)	0.77 (-)	1.01 (+)	0.76 (-)	0.73 (-)	0.85 (-)
Sediment B	$Ratio_{extraction}$	0.16 (-)	0.60 (-)	0.50 (-)	0.58 (-)	0.38 (-)	0.46 (-)
	$Ratio_{leaching}$	1.58 (+)	0.64 (-)	1.52 (+)	1.10 (+)	1.50 (+)	1.23 (+)
	$Ratio_{organism}$	1.43 (+)	0.97 (-)	0.92 (-)	0.95 (-)	0.81 (-)	0.89 (-)

Discussion

WLFs in lake littoral zones are complex phenomena that can induce the mobility of sediment-borne pollutants following drastic changes in abiotic parameters. In this study, the mobility of TMs following WLFs simulations was observed within the sediment fractions, between the sediment and the water column and between the sediment and the biota. However, the mobility pattern varied greatly according to the TM.

The sequential extraction tests showed that Cd and Zn exhibited the highest mobile fraction. In particular, F1 and F2 had greater abundances of these elements compared to the other TMs in both the controls and WLF-sediments. A general decrease in this mobile fraction was observed in the sediments following WLFs for all TMs. However, the highest decreases were observed for Cd and Zn, which may be due to the fact that these two TMs are naturally reactive and mobile

elements (Frémion et al., 2017; Liu et al., 2016). The decrease in the mobile fraction was consistent with the decrease in the Cd and Zn concentrations in the leaching tests following WLFs observed in the naturally contaminated sediment (Sediment A). However, the increase in the mobile fraction observed in the spiked sediment underlines the high reactivity of these elements under drastic abiotic changes such as WLFs with resuspension of particles, especially for spiked sediment, for which the aging time (i.e., the time during which the speciation and availability of metals change within the sediment (Ghoveisi Hossein et al., 2018)) may not be comparable with that of naturally contaminated sediments (Ardestani and van Gestel, 2016; Costello et al., 2016). Moreover, the decrease in the bioconcentration of Zn following the bioassays was consistent with the decrease in the mobile fraction and, by extension, the bioavailability of this TM. Again, a contradictory increase in bioconcentrated Cd was observed following WLFs, highlighting the complex relationship among TM mobility, bioavailability and bioconcentration. By contrast, Cr, Cu, Ni and Pb are more inert TMs (Calmano et al., 1993; Frémion et al., 2017; Liu et al., 2016; Tiquio et al., 2017; Wu et al., 2011), consistent with their higher abundance in the residual fraction for both the control and WLF-sediments in the sequential extraction tests. F3 was fraction with the second greatest abundance of these elements, which are known to naturally bind to organic matter and sulfides, especially Cu (Frémion, 2016; Tiquio et al., 2017). A decrease in the mobile fraction following WLFs was also observed for these TMs, albeit to a lesser extent than for Cd and Zn, and was consistent with a decrease in the bioconcentration observed in the bioassays. However, strong increases in the dissolved concentration of these TMs in the leachate following WLFs were observed in the leaching tests. By re-suspending particles into oxygen-rich water, the leaching tests may have increased the oxidation of the organic matter and sulfides that the sediment drying had probably initiated (Nedrich and Burton, 2017; Simpson et al., 2000; Wu et al., 2011). This reaction may have led to the release of dissolved Cr, Cu, Ni and Pb in the water column.

In addition, opposing results (increase vs decrease) were obtained for some TMs in terms of $ratio_{extraction}$, $ratio_{leaching}$ and $ratio_{organism}$, further indicating the complex relationships among contaminant mobility, bioavailability and bioconcentration, especially in the context of specific abiotic disturbances such as WLFs. As an example, the differences obtained among the TMs in $ratio_{extraction}$ and in $ratio_{leaching}$ were higher than the differences in $ratio_{organism}$, suggesting that *C. riparius* larvae might regulate TM bioconcentration by reducing assimilation, enhancing excretion or both (Adams et al., 2000; McGeer et al., 2003).

Conclusion

Laboratory experiments partially confirmed the study hypothesis as the most reactive TMs (Cd and Zn) exhibited the greatest mobility following WLFs. The hypothesis was also partly invalidated as this mobility seemed to increase toward the residual fraction instead of the more bioavailable fractions, except when WLFs included extensive resuspension of particles. In this

case, the assumption was that the oxidation of the organic matter and sulfides may have played a role in the release of the more inert TMs to the water column. The results also provided insights on the complex relationships among contaminant mobility, bioavailability and bioconcentration, especially in the context of large abiotic disturbances such as WLFs.

These findings may provide useful preliminary conclusions for further management strategies of dam reservoirs that undergo large WLFs with sediment re-suspensions as well as standing waters for which WLFs restorations are planned for ecological considerations.

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3. Synthèse

Ces résultats mettent en lumière les mobilités variables entre ETM sous l'effet de l'assèchement et remise en eau des sédiments et internalisation par le biote. Conformément à la littérature, le Cd et le Zn semblent être les éléments les plus facilement mobiles et donc potentiellement à risque en cas d'assèchement et de ré-immersion des sédiments. Néanmoins, cette mobilité tend à décroitre sous l'effet de l'assèchement du sédiment, conforté par l'étude de Frémion et al. (2017). La ré-immersion semble favoriser la mobilité des ETM, mais dans une moindre mesure puisque les écarts de mobilité avant et après la simulation de marnage (i.e. assèchement puis ré-immersion) ne sont pas significatifs dans l'ensemble à l'exception du Zn pour lequel la fraction résiduelle augmente significativement. Ainsi, l'ensemble du phénomène (assèchement et remise en eau) semble présenter un risque limité, comme en atteste l'absence d'écart significatif dans le taux de croissance des larves de chironomes exposées. Leur concentration interne en métaux reste inchangée, à l'exception du Cd qui augmente d'un facteur 1,5 suite aux fluctuations du niveau d'eau. En revanche, les tests de lixiviation mettent paradoxalement en évidence des mobilités accrues pour les ETM les plus inertes habituellement, à savoir le Cr, Cu, Ni et Pb. Les changements abiotiques forts liés à la remise en suspension forcée des particules sédimentaires peuvent être à l'origine de cette mobilité, peut-être par une oxydation importante des composés chimiques. Ce dernier point nous amène, dans le Chapitre suivant, à aborder la question de l'influence de la remise en suspension en lien avec l'abaissement de la colonne d'eau lors du marnage lacustre sur la mobilité et biodisponibilité des ETM du sédiment.

Chapitre 6

Effets du marnage lacustre sur la mobilité et la biodisponibilité des contaminants sédimentaires : étude *in situ* de l'abaissement du niveau d'eau en zone littorale

1. Démarche générale

Alors qu'un grand nombre de lacs européens ont vu leur marnage artificiellement réduit depuis les années 80 (Coops et al., 2003), certains gestionnaires de ces lacs visent au travers de grands projets de restauration écologique à augmenter le marnage annuel des grands lacs pour se rapprocher des conditions naturelles (Coops and Hosper, 2002). C'est le cas par exemple des lacs d'Annecy (SILA, 2011) et du Bourget (CISALB, 2017). De plus, les événements météorologiques extrêmes supposés plus fréquents dans les années à venir laissent penser que les déficits/excédents hydriques que connaîtront les lacs résulteront en des marnages intensifiés (Milly et al., 2005). A ce jour, les effets écotoxiques de ces fluctuations de niveau d'eau font l'objet d'un nombre très faible d'études scientifiques. A titre d'exemple, en 2008, la méta-analyse de Leira et Cantonati ne relevait que 12 % des études sur les marnages lacustres depuis 1991 incluant une notion de contamination. Le but de ces deux derniers chapitres est donc d'évaluer le risque écotoxicologique des sédiments littoraux lacustres sous l'effet de nouvelles fluctuations du niveau d'eau.

Dans ce Chapitre, les variations temporelles et spatiales de la contamination en ETM des sédiments et du biote pélagique exposé ainsi que celles des paramètres physico-chimiques sont évaluées en zone littorale lacustre sous l'effet du marnage du lac du Bourget d'une amplitude de 80 cm (Figure 19). L'objectif est ici **d'évaluer l'impact du marnage *in situ* sur la mobilité et la biodisponibilité des ETM sédimentaires**. Nous faisons l'hypothèse que l'abaissement de la colonne d'eau au-dessus du sédiment en zone littorale est susceptible d'accroître la contamination de la colonne d'eau et par conséquent celle du biote pélagique. Cet abaissement devrait en effet (1) modifier le régime hydrodynamique, ce qui augmenterait le taux de particules en suspension (Cantwell et al., 2002; Fetters et al., 2016; Kalnejais et al., 2007; Richards et al., 2018; Zoumis et al., 2001), et (2) modifier certains paramètres abiotiques de la colonne d'eau (e.g. pH, potentiel d'oxydo-réduction), pouvant ainsi conduire à un accroissement de la mobilité des ETM sédimentaires (Arnott et al., 2001; Bhattacharyya and Gupta, 2008; Hofmann et al., 2008; Meyer, 2007).

La plupart des travaux cités dans les lignes précédentes visaient à améliorer la compréhension mécanistique des phénomènes liés aux fluctuations du niveau d'eau et furent par conséquent majoritairement réalisés en laboratoire sous conditions contrôlées. Néanmoins, compte tenu de la

complexité de la zone littorale lacustre dans sa structuration spatiale (e.g. agencements complexes d'habitats, interactions biotiques fortes) et temporelle (e.g. fluctuations journalières de la température et du taux d'oxygène dissous de la colonne d'eau peu profonde), une évaluation de la mobilité et de la biodisponibilité *in situ* semble appropriée dans le cadre d'une évaluation des risques écotoxicologiques réaliste.

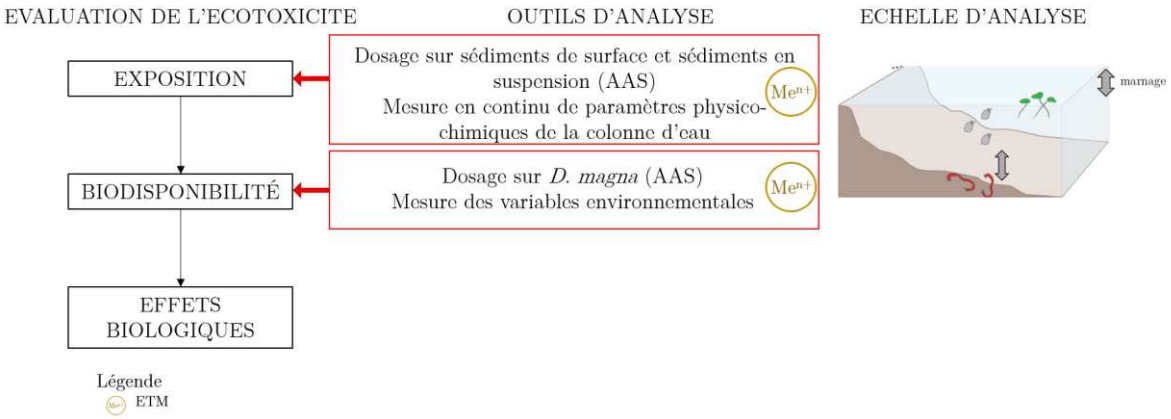

Figure 19. *Schéma récapitulatif des outils et de l'échelle d'analyse pour l'évaluation de l'écotoxicité dans l'Article 6.*

2. Article 6 – Effects of water-level fluctuations on the littoral aquatic environment and metallic contamination of a large peri-Alpine lake (Lake Bourget)

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Article en préparation pour soumission à Hydrobiologia

Abstract

Water-level fluctuation (WLF) is a management action in many large lakes whose effects on contaminant behavior have seldom been investigated. We monitored both environment and trace metals (TMs) within three matrices (i.e. surficial and trapped sediment and encaged *Daphnia magna*) among three littoral sites in Lake Bourget (France) during a WLF event (Δdepth = 0.8 m) that occurred from September to November 2017. Oxygen, temperature and conductivity displayed important hourly variations and differed among the three sites despite their close vicinity. pH and oxido-reduction potential were more stable although several abrupt changes could be recorded. The effects of wind speed, river discharge and precipitations (i.e. external forcings) on turbidity and water velocity, used as proxies for contaminants dynamics and / or dispersal, were modeled using generalized additive models (GAM) and the possible effect of WLF at modulating these relationships was considered using tensor product smooths. WLF had a high influence on the relationships between the external forcings and turbidity while it remained marginal for water velocity. Specifically, WLF tended to increase the effects of the external forcings on these two variables. The explanatory power of GAM (i.e. deviance explained) decreased over successive hourly time-lags highlighting the short time-scale response of turbidity and water velocity to external forcings. Most variability in normalized TM concentrations was associated to site-specific variations and TM-specific distributions. Nonetheless, normalized TM concentrations were higher before than during and after the WLF in surficial sediment and was lower after the WLF in trapped sediment. Together, our results highlight the large environmental fluctuations impacting the littoral of Lake Bourget that can modulate contaminant behavior and suggest that WLF could influence contaminant mobility and transfer to the biota.

Keywords

water-level fluctuation, littoral, high-frequency time series, hydrodynamic, trace metal.

Introduction

Water-level fluctuation (WLF) is currently developed as a management tool in many large lakes. It can have different purposes not directly related to ecological management such as limiting the flooding risk of downstream cities (e.g. winter drawdown (Carmignani and Roy, 2017)) or optimizing electric production. In several large European lakes, it has also recently been expected to foster the development of reeds in the littoral which may help at conserving such habitats of important conservation concerns (Coops and Hosper, 2002; Evtimova and Donohue, 2016).

The effects of WLF have been investigated toward diverse biological groups such as fish or invertebrate (Baumgärtner et al., 2008; Sutela and Vehanen, 2008). Both direct and indirect effects have been reported mostly related to direct mortality and spatial changes in habitat use respectively. For instance, Werner and Rothhaupt (2008) reported mass mortality of Asian clams in Lake Constance after a WLF while Rogers and Bergersen (1995) reported that fall drawdown increased daily movement of largemouth bass likely related to changes in habitat occupancy due to the loss of littoral vegetation.

Apart of these ecological implications, WLF can also affect littoral hydrodynamic possibly cascading up to contaminant mobility. The decrease in water-level within shallow littoral areas during a WLF event can, not only, increase sediment resuspension and consequently increase the water column contamination (Cantwell et al., 2002; Fetters et al., 2016; Kalnejais et al., 2007; Zoumis et al., 2001) but also change the proportion of mobile and bioavailable fractions of contaminants (Arnott et al., 2001; Bhattacharyya and Gupta, 2008; Hofmann et al., 2008; Meyer, 2007). WLF could therefore affect contaminant behavior and transfer within the littoral foodweb (Weltens et al., 2000). In this study, we address the possible effects of a WLF event of 80 cm occurring in early autumn 2017 on the trace metals (TMs) contamination of the littoral zone of a large peri-Alpine lake (Lake Bourget, France). First, the physical and chemical environment (i.e. oxygen, temperature, conductivity, pH and oxido-reduction potential) was monitored at high frequency (i.e. hour-scale) among three sites to appreciate the extent of the environmental fluctuations that could possibly condition the TMs chemical mobility. Second, high-frequency (i.e. hour-scale) turbidity and water velocity were considered as proxies for the TM physical mobility. TMs are often adsorbed on sediment particles whose variability constraints water turbidity, hence, variations in turbidity were expected to be directly related to the changes in TMs contamination within the water column. Complementarily, water velocity was expected to represent the possibility for TMs to spread and disperse within the littoral zone. Different models were considered to capture the influence of three external forcings (i.e. precipitation, river discharge and wind speed) on the two variables previously cited and specific investigations were conducted to identify the way WLF could modulate these relationships. Third, TM concentrations in two sedimentary (i.e. surficial sediment, suspended sediment) and one biological (i.e. encaged *Daphnia magna*) matrices were measured at three occasions (i.e. before, during and after the WLF) to assess the possible implication of WLF in TMs littoral contamination.

The investigations conducted were expected to provide insights regarding the influence of WLF on contaminant mobility that is often an overlooked effect of WLF within lake littorals. The high frequency measurements offer the opportunity to fully appreciate the complexity of the littoral environment that is a prerequisite to infer contaminant behavior. WLF was hypothesized to enhance the influence of external forcings on TM mobility proxies (i.e. turbidity and water velocity) leading to higher TMs mobility as the water-level decreases (Cózar et al., 2005). Finally, we expected that TMs within the different matrices would increase both in variability (i.e. coefficient of variation) and concentrations when the water-level was low due to an enhancement of transport-deposition processes.

Methods

1. Lake Bourget and study sites

Lake Bourget is a large French natural lake with a surface area of 42 km^2 sheltered between the limestone mountains of the Epine and Bauges (44.5 km^2, 45.699N-5.873E; Figure 1A). The catchment area of the lake is 560 km^2 and covered by forests (45 %), agricultural areas (22 %), grazing fields (12 %), urban areas (13 %) and water bodies (8 %) (CISALB, 2009). The two main cities developed at the vicinity of the lake are Chambéry (220,000 inhabitants) and Aix-les-Bains (30,000 inhabitants). Following a eutrophication period during the second part of the 20^{th} century, the water quality has been restored over the last decades (Berthon et al., 2013) and the lake is currently oligo-mesotrophic (i.e. total phosphorus in the water column ranging between 8 and 12 µg L^{-1}; Jacquet et al. (2017)).

The study area was located in the southeastern part of the lake close to the outlet of a small arm of the Tillet River, one of the main tributary of the lake (Figure 1B). It was selected for its appropriate gentle slope (i.e. ~ 5 %) enabling the study of WLF over a 40-meters long transect (Figure 1C). This study area was also selected due to the non-negligible TME concentrations (Lécrivain et al., 2018) and its restricted access from the shoreline, limiting potential visitors to disturb continuous data measurements.

Three study sites were retained along a littoral transect and were distant from about 20 m to each other (Figure 1C). The shallowest site ($S_{0.5}$) was located ~ 10 m far from the shoreline at 0.5 m depth and the two other points ($S_{1.5}$ and $S_{2.5}$) at ~ 30 m and ~ 50 m of the shoreline at depths of 1.5 and 2.5 m respectively.

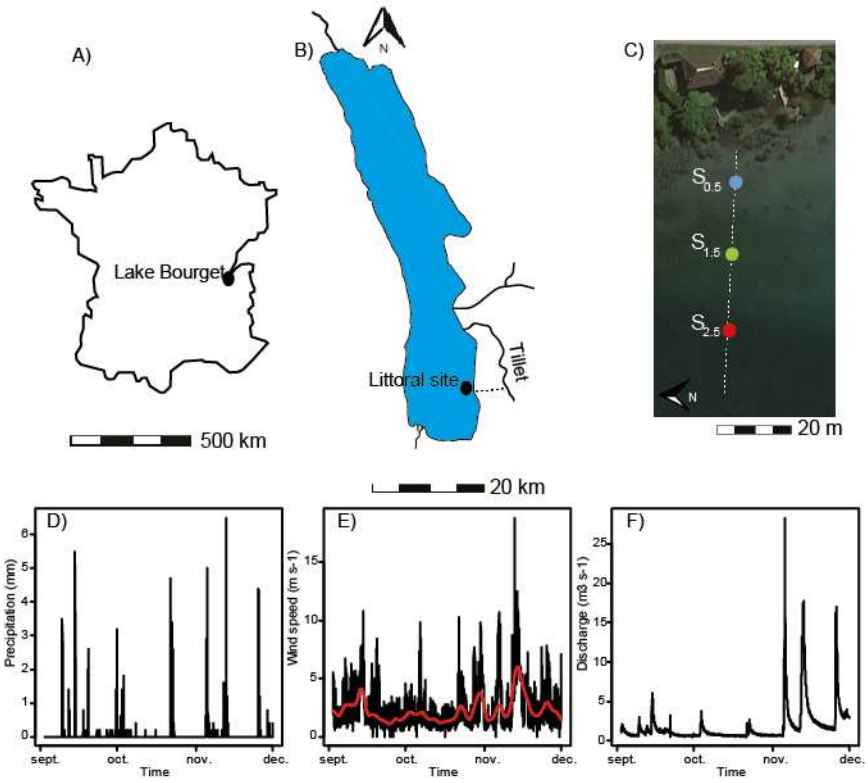

Figure 1. Location of Lake Bourget in France (A) and sites in the littoral of the lake, (B). Sites repartition along the littoral (C). External forcings considered to be implicated in TM mobility and spread: precipitation (mm) (D), wind speed (m s^{-1}) (E) and Leysse discharge (m^3 s^{-1})(F).

2. Environmental screening

The experimental design for screening the environmental variations consisted in high-frequency monitoring of environmental data spanning the entire WLF event from 02/09/2017 to 30/11/2017. At the three sites, temperature and conductivity were measured using CTD probes while oxygen temperature was measured using Minidots. At site $S_{1.5}$, an Aqua Troll 600 multiparameter probe was used to record turbidity, pH and oxido-reduction potential. At site $S_{2.5}$, an acoustic Doppler current profiler (ADCP) was used to estimate water current and water-level (i.e. pressure). The CTD and Aqua Troll 600 multiparameter probes were configured to measure the parameters hourly. The ADCP set up was configured to account for 3 vertical windows of 40 cm height. For each window, the mean particle velocity over one minute at a second-scale each hour was estimated and averaged over the three vertical windows to get the mean hourly water velocity. Details regarding the environmental setup and the probes are provided in Table 1.

Hourly measurements for wind speed and precipitation were provided at the meteorological station of Météo-France Chambéry-Aix-73329001 (Figures 1D-E). Hourly discharges of the Leysse River were extracted from the national hydrographic monitoring website (http://hydro.eaufrance.fr/) and corresponded to the hydrologic station of La Motte-Servolex-

V1315020 (Figure 1F). The flood plume of the Leysse River typically flows North-Est toward the studied area and the discharges of both the Leysse and the Tillet rivers exhibit similar hydrological regimes. Consequently, discharge of the Leysse River was expected to influence either directly or acting as a surrogate of the discharge of the Tillet River.

3. Contamination assessment

TM measurements were performed at three occasions (steps) during the WLF event: on the 31/08/2017 before the water-level dropped in October (step1), on 19/10/2017 when the water-level was low (step 2) and on 24/04/2018 after the water-level stabilized (step 3).
Triplicates of TM measurements were performed on surficial, trap sediments and encaged *D. magna* among each of the three sites (Figure 2B). At each site, sediment traps and *D. magna* caging were deployed respectively two weeks and one week prior sampling sessions to ensure sediment accumulation and *D. magna* contamination. *D. magna* originated from a breeding room exempt of contamination, at constant temperature (20 ± 2 °C) and under a light regime of 16 h light and 8 h darkness. Rearing and caging procedures were described in Lécrivain et al. (2018). The sampled surficial and trapped sediments were placed in pre-washed polyethylene bottles, transported to the laboratory in coolers, sieved at 2 mm to remove macro-debris and stored at 4°C during a maximum of 24 hours. LOI was estimated according to Afnor (2007).
Prior measurements, bulk sediments were mineralized in a microwave oven (CEM/MARS Xpress, 2 mL of ultra-pure HNO_3 + 6 mL of ultra-pure HCl, 180 °C for 30 min, filtration on a 0.45-µm Whatman™ filter and dilution of the residue in 25 mL of ultra-pure water), and *D. magna* were dried and mineralized (0.8 mL ultra-pure HNO_3, 4 hours, 60 °C + 0.8 ml ultra-pure water). TM concentrations were then estimated by atomic absorption spectrometry (AAS). The total sediment contents of Cd, Cr, Cu, Ni and Pb were measured in a graphite furnace at 1500 °C, and the total sediment content of Zn was measured with an air-acetylene flame (Perkin Elmer, model PinAAcle 900T). The detection limits were as follows: Cd = 0.1 µg L^{-1}, Cr = 0.040 µg L^{-1}, Cu = 0.014 µg L^{-1}, Ni = 0.07 µg L^{-1}, Pb = 0.05 µg L^{-1}, Zn = 0.02 µg L^{-1}). Raw concentrations (mg kg^{-1} DM) for surficial, trap sediments and encaged *D. magna* on the three sites and steps are given in Table S1 (Supplementary data).

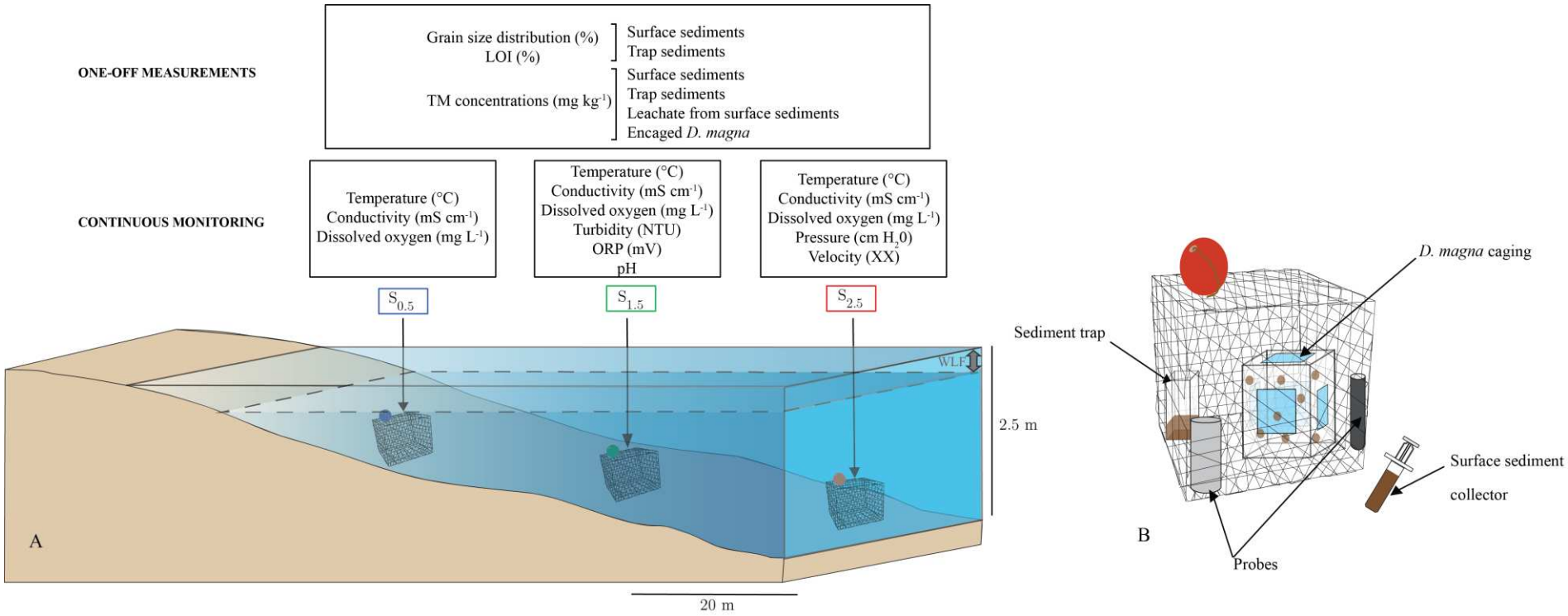

Figure 2. Experimental design with the measurements performed for each study point $S_{0.5}$, $S_{1.5}$ and $S_{2.5}$ (A) and an example of the device arrangement in a site (B).

Table 1. Summary of the continuous and point sampling measurements performed in this study including the measured parameters, the matrix on which they were measured, the device, method used, and the study sites where measurements were performed.

Measured parameter	Compartments	Device/method/reference	Localization	Measurement frequency
Temperature (°C) Conductivity (mS cm^{-1})	water	CTD probes	$S_{0.5}$, $S_{1.5}$ and $S_{2.5}$	Continuous monitoring, each 1 hour, from 02/09/2017 to 30/11/2017
Dissolved oxygen (mg L^{-1})	water	miniDOT probes		
Turbidity (NTU) ORP (mV) pH (pH unit)	water	Aqua Troll 600 multiparameter probe	$S_{1.5}$	
Pressure (cm H_20) Velocity (mm s^{-1})	water	Doppler acoustic profiler (ADCP)	$S_{2.5}$	
Rain intensity (mm) Wind speed (m s^{-1}) Tributary discharge (m^3 s^{-1})	atmosphere			
Grain size distribution (d50) LOI (%) TM concentrations (mg kg^{-1} DM)	surface and trap sediments	Malvern Mastersizer 2000G Afnor, 2007 AAS	$S_{0.5}$, $S_{1.5}$ and $S_{2.5}$	3 sampling: before (31/08/17), during (19/10/17), after (24/04/18) WLF 15 days exposure for trap sediment and 7 days exposure for *D. magna*.
Leachate concentrations (mg kg^{-1} DM)	surface sediments	EN 12457-2 2002		
TM concentrations (mg kg^{-1} DM)	*D. magna*	*in situ* caging (Lécrivain et al. 2018)		

4. Data analysis

The variability of the environmental context (i.e. temperature, oxygen, conductivity) among the three sites was characterized at the hour-scale using Kernel density functions of the first differences of the variables (i.e. X_{t+1}-X_t) and at a week-scale by considering standard deviations over seven days of the time series of each variable (n = 168).

Two variables were considered to be implicated in the contamination mobility; the turbidity as it relates to the amount of particles on which may be bounded contamination and water velocity that condition the transport and dissemination of contaminant. Generalized additive models (GAM, Hastie and Tibshirani (1993); Wood (2006)) were used to analyze the influence of the external forcings on these two variables. GAM are flexible non-parametric models that accommodate for nonlinear relationships between variables and can support different distributions of the response variable. A Gamma distribution was considered for both responses variables as they were continuous and clearly diverging from a normal distribution by their right-skewness. WLF was expected to modulate the responses of the turbidity and water velocity to environmental variables. In order to account for this possible modulation, interactions between external forcings and water-level were considered in the GAM using tensor product smooths (Wood, 2004). The tensor product smooths allow to make the smooth relationship between the response (i.e. either turbidity or water velocity) and the external forcings to change nonlinearly with water-level. In other words, the tensor product interaction terms in the GAM reflect the amount by which the response variable is adjusted from the external forcing relationships for any water level condition. Tensor product interaction terms are also suitable to model responses to interactions of variables with different units which is the case in this study and have been shown to provide fruitful insight among complex ecological interactions (e.g. (Bacheler et al., 2009; Kvile et al., 2016)). In order to assess the possible time-lag responses of turbidity and water velocity to the external forcings, full GAM with tensor product interaction terms were fitted by delaying external forcings from 0 to 48 hours (i.e. responses variables were modeled against external forcings previously recorded from 0 hour (instantaneous) to 48 hours).

A three ways analysis of variance (ANOVA) was performed to estimate the implication of TMs, WLF (i.e. steps) and sites on the variability of the TMs contamination for the different matrices (i.e. surficial and trapped sediment and *D magna*). Prior the ANOVAs, each TM concentration was normalized to the TM maximal concentration in the matrix so that TM concentrations ranged between]0:1]. This allows accounting for the different inherent concentrations of the TMs. Three ways ANOVA were conducted on both normalized data to estimate changes in TM concentrations and their coefficient of variations for changes on their variability (i.e. local spatial variability).

All statistical analyses as well as graphical displays were performed using R 3.5.0 (R Core Team Development, 2017) and the packages *network* (Butts, 2008), *mgcv* (Wood, 2011, 2006). Throughout the manuscript, values following "±" correspond to the standard deviation of the data. The significance rates are symbolized as following: "." for 0.1 > p-value > 0.05; "*" for

0.05 > p-value > 0.01; "**" for 0.01 > p-value > 0.001 and "***" for p-value < 0.001. The adjusted R-squared is written "Adj-R^2".

Results

1. Environmental context

The environmental variables exhibit different dynamics. Temperature was characterized by clear nycthemeral variations as well as a general decreasing trend leading from ~24 °C in early September to ~7°C in late November (Figure 3A). Oxygen concentrations also exhibited important nycthemeral variations and were almost always higher than 5 mg L^{-1} except at several occasions for $S_{2.5}$ and at $S_{1.5}$ for which the occasional collapses in oxygen concentrations may be related to inconsistent measurements (Figure 3B). Oxygen concentrations also reached especially high concentrations at the three sites with oxygen concentrations reaching more than 15 mg L^{-1}. The conductivity mostly differed between $S_{2.5}$ that exhibited higher conductivity (~ 0.44 mS cm^{-1}) than the two other shallower sites with a mean conductivity of 0.22 mS cm^{-1} and 0.27 mS cm^{-1} (Figure 3C). The conductivity was rather steady at $S_{0.5}$ and $S_{1.5}$ while it tended to increase over time at $S_{2.5}$ from September to October and decrease in November. Hourly variations in these three parameters tended to decrease with depth for temperature as shown by the Kernel density distributions although most variations usually ranged within a ± 1°C range (Figure 3D). Maximal hourly temperature variations could nonetheless reach up to 2.9 °C at $S_{0.5}$ while they were ~ 1.5 °C for the two other sites. Oxygen hourly variations were also substantial although very similar among the three sites with most variations ranging within a ± 2 mg L^{-1} range (Figure 3E). Differently, for conductivity, the site $S_{2.5}$ differentiated from the two other sites with important hourly variations than could reach up to 0.5 mS cm^{-1} (Figure 3F). The temporal changes in the fluctuations of these three parameters highlighted similar trends at a week-scale for temperature for $S_{1.5}$ and $S_{2.5}$ (Figure 3G). Temperature at $S_{0.5}$ mostly differentiated from the two other sites by the higher standard deviations observed during October. For oxygen, the three sites exhibited similar temporal patterns in their fluctuations with an oxygen variability that tends to decrease overtime (Figure 3H). For conductivity, the higher variations observed at $S_{2.5}$ were labeled in the temporal changes in standard deviations with a strong increase during November while it remained rather steady for the two other sites (Figure 3I). pH and oxido-reduction potential (ORP) could only be measured at $S_{1.5}$. pH exhibited clear nycthemeral variations and tended to slightly increase during October from 8.2 to 8.4 before suddenly decrease to ~ 8 during several days early November. Such sharp decreases occurred several times over the studied period especially around mid-November (Figure 3J). ORP was characterized by small temporal variations until mid-November remaining at ~ 270 mV although several hourly decreases could be noticed (Figure 4K). The 12 and 13 November a specific event over sudden decrease of ORP occurred leading to negative ORP during 17 hours before re-increase at ~ 220 mV for several

days. In late November, ORP increased to reach similar values compared to those measured at the beginning of the survey (Figure 3K).

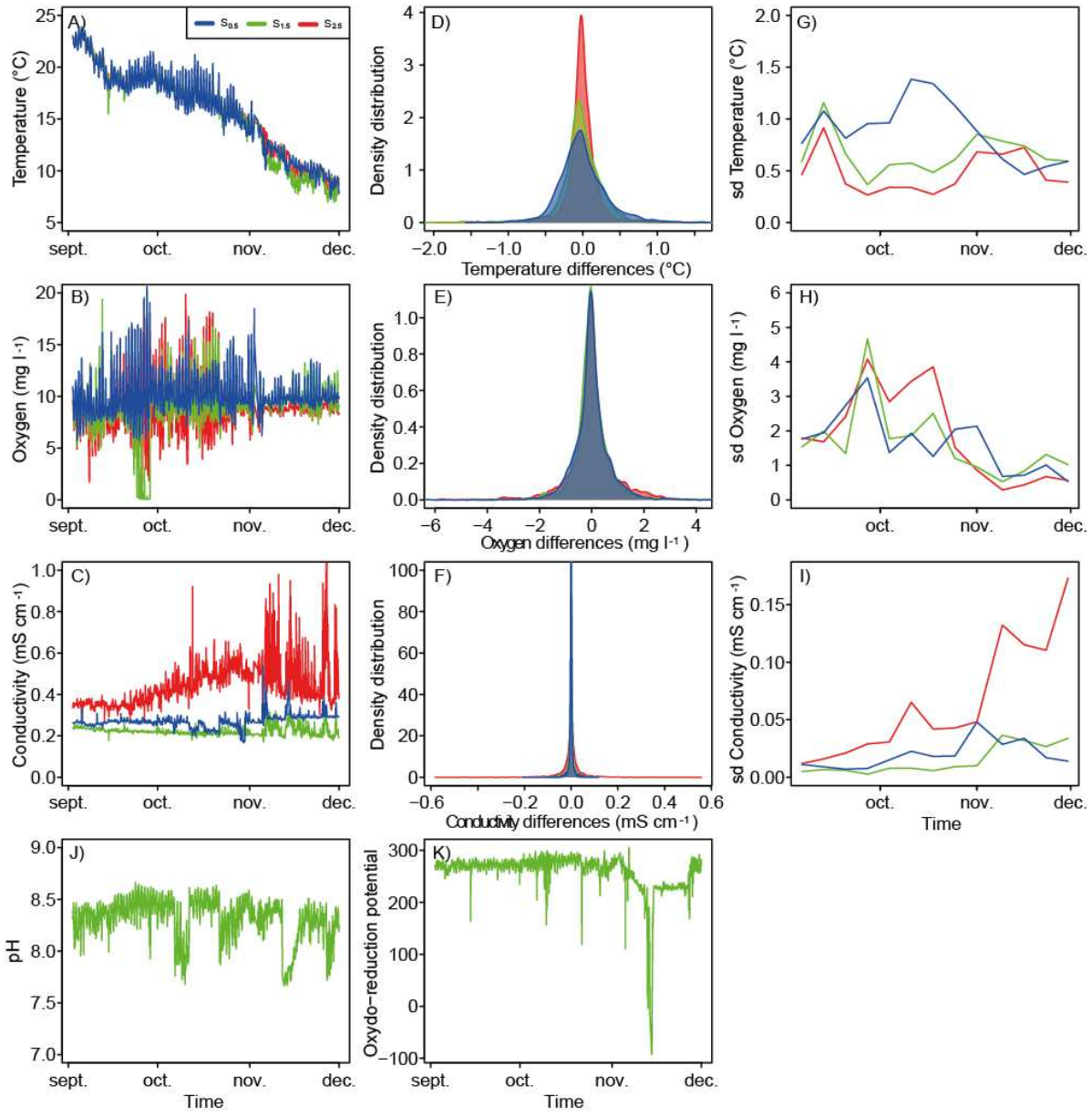

Figure 3. Hourly dynamics of temperature (A), oxygen (B) and conductivity (C) at the three study sites; red for the site at 2.5 m depth ($S_{2.5}$), green for the site at 1.5 m depth ($S_{1.5}$), and blue for the site at 0.5 m depth ($S_{0.5}$) (n = 2122). The hourly variations of the three variables are represented using Kernel density functions (D to F). The weekly changes in temporal variability are assessed using standard deviations over seven days (n = 168) (G to I). pH and oxido-reduction potential (ORP) were measured only at $S_{1.5}$ (J and K).

The extent of WLF expressed as the water pressure at $S_{2.5}$ was 83 cm (Figure 4A). The decrease of water-level mostly occurred during September although the minimal water-level was reached at mid-October followed by a low level period of several weeks prior starting to increase again during the first week of November. Turbidity was highly variable over the studied period

characterized by an alternation of low turbidity and high turbidity occurring very suddenly over only few hours (Figure 4B). The mean water velocity was characterized by short term fluctuations (i.e. hour-scale) that mostly remained below 0.1 cm s^{-1} excepted for several occasions. Nonetheless, during the first two weeks of November higher water velocity and fluctuations were recorded with velocity maxima higher than 0.15 cm s^{-1} (Figure 4C).

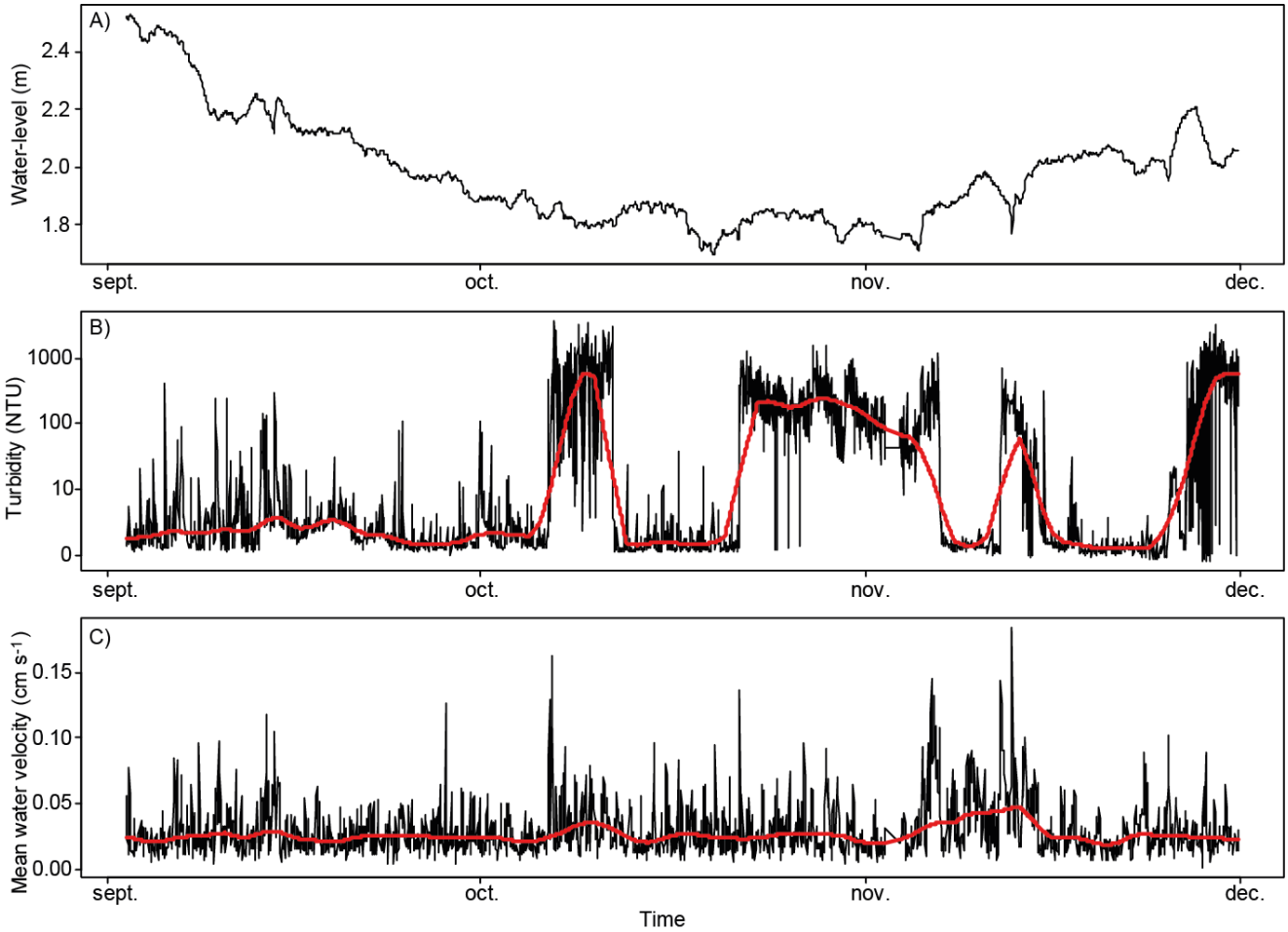

Figure 4. Hourly dynamics of water-level (A), turbidity (B) and mean water velocity (C). Red lines represent lowess-smooth trends (span window = 5% in the data, n= 2122). Note the logarithmic-scale for turbidity.

The GAMs were able to capture significant proportions of the variability for turbidity and water velocity (Table 2). The consideration of tensor product smooths to account for the effect of WLF was especially important for turbidity (i.e. increase of 43.9 % in deviance explained) while it remained more marginal for water velocity (i.e. increase of 4.9 % in deviance explained). For turbidity, the 3D tensor maps highlight the fact that the effect of precipitation and wind speed increased as long as the water level decreased while for discharge the effect was mainly pronounced only when the water level was the highest (Figures 5A-C). For water velocity, the highest effects of precipitations and discharge were also identified when water level was low while it was the opposite for wind speed (Figures 5E-F).

The deviance explained by the full GAM considering tensor product smooths varied with the different time-lags for the two variables (Figure 6). Specifically, these latter tended to decrease as time-lag increased. The decreasing pattern was more regular for turbidity than for water velocity. Furthermore, for water velocity, the deviance explained increased over two time lags.

Table 2. Summary statistics of the GAMs accounting or not for the water level fluctuations (WLF).

		Turbidity			Water velocity		
	Smooth terms	edf	p-value	Deviance explained	edf	p-value	Deviance explained
Generalized additive models without WLF	s(Precipitation)	1.53	0.31	5.6 %	1.00	0.14	13.8 %
	s(Wind_speed)	1.00	6.1×10^{-10}		2.42	$<1.10^{-10}$	
	s(Discharge)	1.00	1.4×10^{-4}		1.00	8×10^{-3}	
Generalized additive models accounting for WLF	te(Precipitation, pressure)	9.95	8.5×10^{-3}	49.5 %	3.00	0.06	18.7 %
	te(Wind_speed, pressure)	12.21	$<1.10^{-10}$		6.48	$<1.10^{-10}$	
	te(Discharge, Water-level)	19.76	$<1.10^{-10}$		9.67	$4.3<1.10^{-8}$	

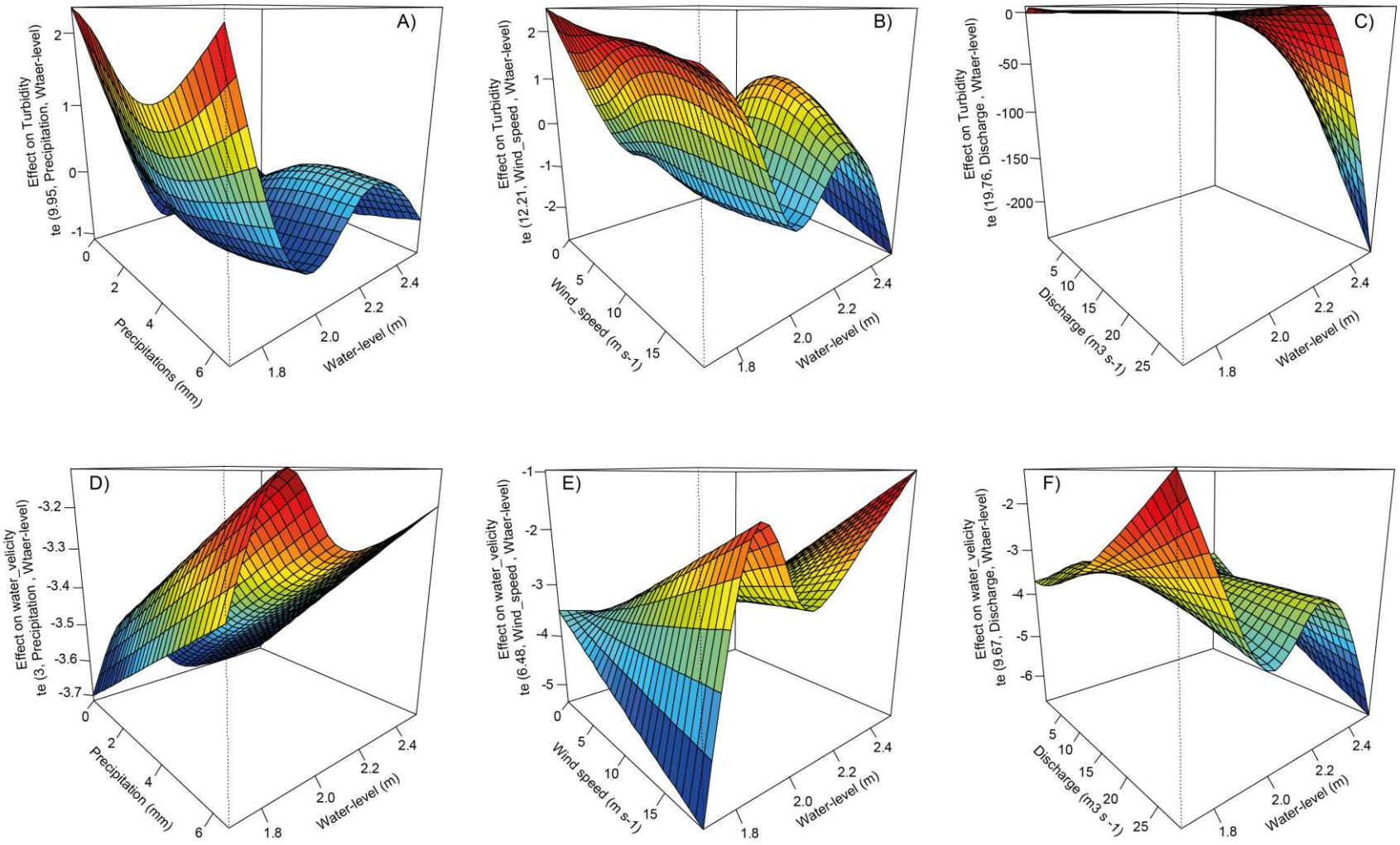

Figure 5. 3D-tensor product maps (i.e. interaction smooth functions) highlighting the implication of water-level the modulating the relationships between the environmental variables and turbidity (A to C) and water velocity (D to F).

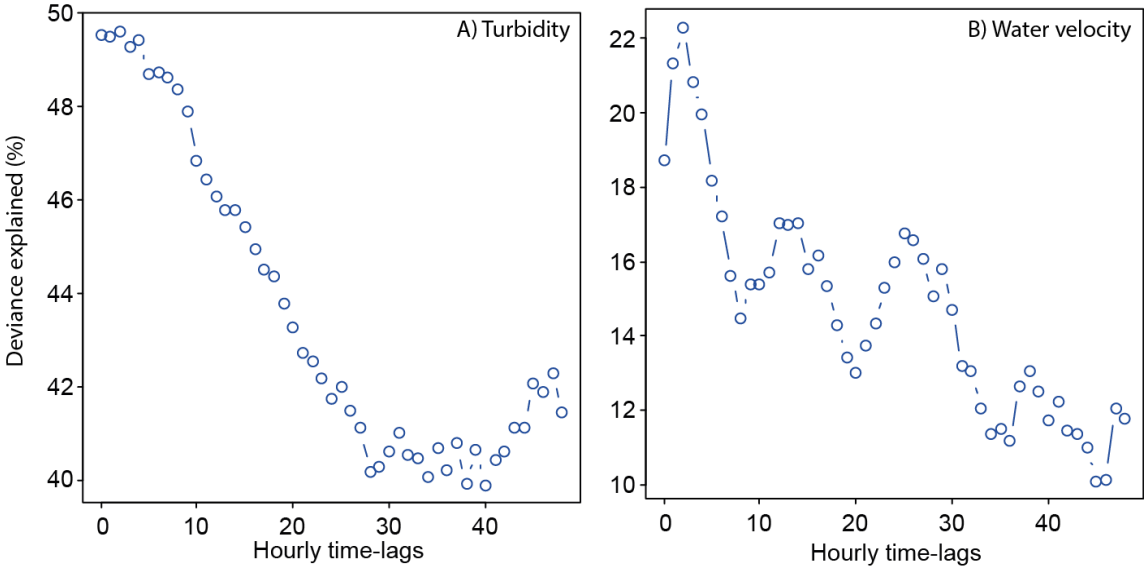

Figure 6. Changes in deviance explained over different time-lags of the full GAM for turbidity (A) and water velocity (B).

2. Fluctuations in TM contaminations

The surficial sediment concentration did not significantly vary among sites while it differed significantly among steps of WLF and among most TMs (Figures. 7A to C and Table 3). TMs of surficial sediment were higher before the WLF than during and following this event. A major proportion of variance explained was specific of TMs indicating that their distribution highly differed ((Figure 7C). For the trapped sediment, the three explaining variables explained significant variations in TM normalized concentrations although these variations were mostly related to sites and TMs (Figures 7D to E, Table 3). Specifically, $S_{0.5}$ had lower TM concentrations than the two other sites and step 3 (i.e. following the WLF) exhibited. Similarly to the surficial sediment, the distributions of normalized concentrations also importantly differed among TM for the trapped sediment. For *D. magna*, the site-specific variations explained the major proportion of variance explained with especially low concentrations at $S_{1.5}$ followed by $S_{2.5}$ and the highest concentrations measured at $S_{0.5}$ (Figure 7G, Table 3). WLF did not have a significant effect on normalized concentrations although they tended to be more variable at step 1 (i.e. before the WLF) than during and following this event (Figure 7H). The distribution of normalized concentrations significantly differed among TM with lower variability for Cr and Cu than for the other TMs (Figure 7I).

The coefficient of variations of the normalized concentrations were not significantly correlated to the three variables (ANOVA, $p > 0.05$) for any matrices except for the trapped sediment for which coefficients of variations were higher during the WLF than previous and after the event and Pb and Zn that exhibited higher coefficient of variations than the other TMs.

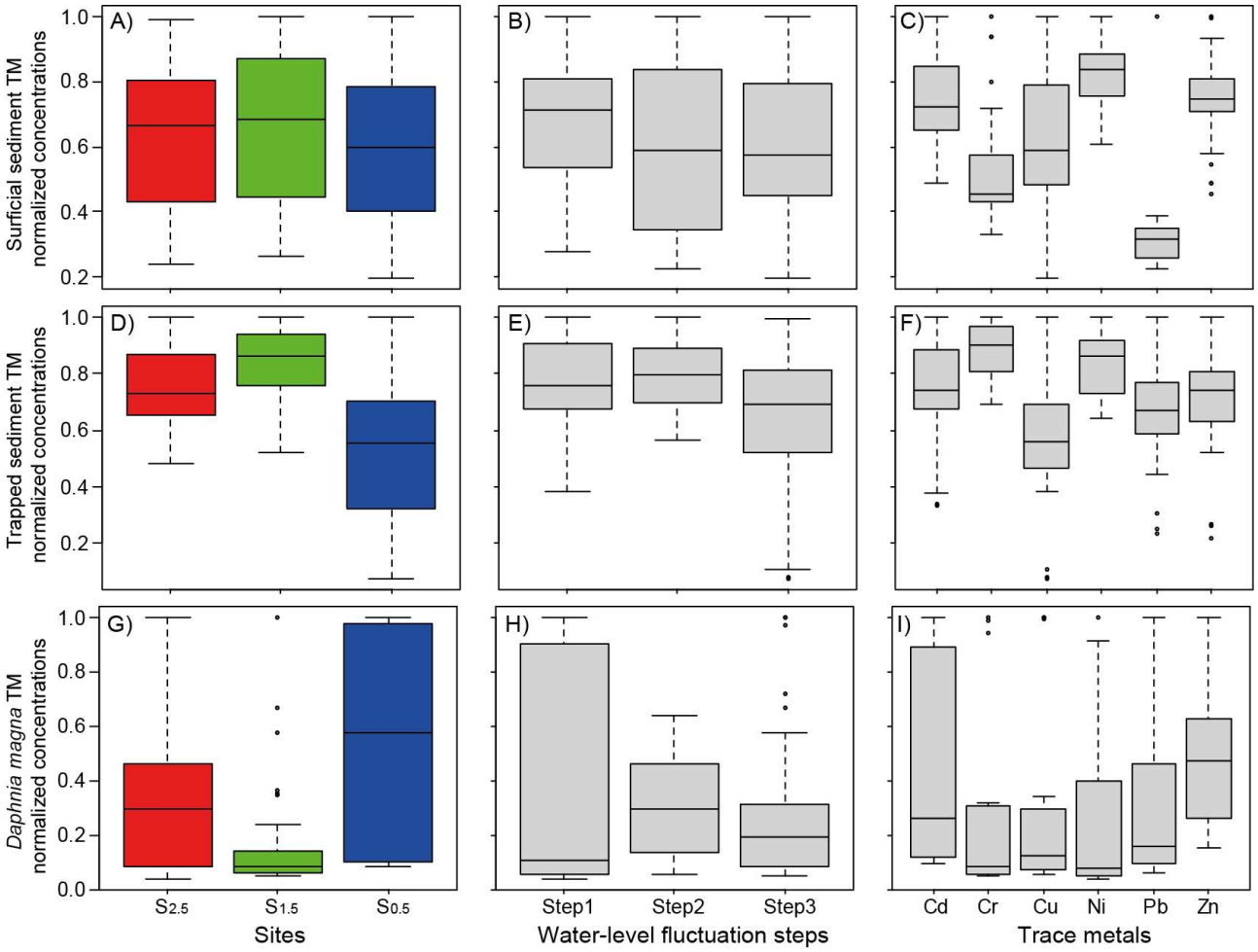

Figure 7. Boxplots highlighting the variability of TM concentrations among sites, steps of water-level fluctuations and trace metals for surficial sediment (A to C), the trapped sediment (D to F) and D. magna (G to I).

Table 3. Summary of the statistics for the three-ways ANOVA partitioning the TM concentration changes among sites, steps of WLF and trace metals.

	Surficial sediment				Trap sediment				*Daphnia magna*			
	Sum of squares	Variance explained	p-values	Adj-R^2	Sum of squares	Variance explained	p-values	Adj-R^2	Sum of squares	Variance explained	p-values	Adj-R^2
Sites	0.078	0.009	0.218		1.958	0.322	<0.001		2.953	0.242	<0.001	
Steps	0.133	0.016	0.023		0.477	0.078	<0.001		0.189	0.015	0.099	
TM	4.276	0.511	<0.001	0.512	1.681	0.277	<0.001	0.658	1.088	0.089	0.010	0.301
Residuals	3.8779				1.963				7.994			

Discussion

1. Fluctuating littoral environment

Despite their proximity, significant environmental differences have been identified among sites both among raw data (e.g. different temperature or oxygen concentrations among sites) as well as their associated fluctuations (e.g. differences in weekly standard deviations). These results allow to appreciate the differences in environmental conditions at rather short spatial-scale (i.e. few dozen of meters) that may support spatial differences among contaminant mobility and transfer within littoral foodwebs. For instance, changes in temperature, that can reach several degrees Celsius between sites and successive hours, can foster changes in contaminant chemical binding forms under abiotic reactions (e.g. dissolution of compounds bound to trace metals) and biological transformations (e.g. increase in the biodegradation of the organic matter) (Eggleton and Thomas, 2004), as well as changes in biological metabolism possibly cascading to contaminant uptake and excretion (Becker, 2018; Prato et al., 2009; Schulte, 2015). Similarly, although oxygen concentrations remained quite high, their variations, likely due to benthic primary production (i.e. oxygen saturation $> 200\%$), could induce the oxidation of suspended sediments or drive surface-overlying water exchanges (Atkinson et al., 2007) leading to change in metal bioavailability (Nedrich and Burton, 2017; Simpson et al., 2000; Wu et al., 2011). In addition, increase of brightness for the water column and the surface sediment due to a lower depth of water could lead to an increase of UV exposure for the biota, leading to possible phototoxicity of contaminants such as polycyclic aromatic hydrocarbons (Ankley et al., 1995; Barron, 2007; Swartz et al., 1997).
Complementarily, fluctuations of pH and ORP can also modify the partitioning of contaminants (i.e. changes in the sorption coefficient Kd). The episodic and sudden variations of these two variables were likely to affect contaminant sorption on sediment and consequently their bioavailability (Cloran et al., 2010; Lee and Lee, 2005). Characterizing environmental variations at short spatial and time-scale hence appeared especially informative to address the constraints that both contaminant and organisms are facing within the lake littoral.

2. Water-level fluctuation as a littoral driver

Among the three external forcings considered, wind speed and river discharge explained significant variations in both turbidity and water velocity while precipitations remained non-significant when not accounting for interactions with WLF. This result was expected as both wind speed and discharge can either trigger sediment resuspension or support the input of sediments from the watershed (Hofmann et al., 2008; Williams, 2006). Interestingly, the consideration of WLF at modulating the effect of the three external forcings on turbidity drastically increased the deviance explained by the external forcings indicating that WLF strongly modulate the effects of external forcings on turbidity. The tensor products maps highlighted that the effects of these forcings tended to increase as water level decrease, supporting

the hypothesis that WLF could enhance the mobility of contaminant by increasing the effects of external forcings on turbidity. The interactions between WLF and the external forcings were much lower for water velocity as the increase in deviance explained was marginal when considering WLF interactions in the GAM. Therefore, WLF seemed to have a minor influence on water velocity and consequently contaminant dispersion and spread.
The decrease of deviance explained over successive time lags suggests that both turbidity and water velocity respond over short time-scale (i.e. hour) to environmental variations. This result supports the relevance for accounting for short-time scale to appreciate the extent of contaminant response to external forcings. Complementarily, the maintaining of rather high deviance explained at larger time-lags indicate that environmental fluctuations could also influence these two variables at longer time-scale (i.e. several days). Explicitly, these results suggest that change in external forcings would almost instantaneously impact the mobility and spread of contaminant and that environmental variation will continue to affect these responses several days after they occur, leading to exposure durations high enough to potentially impair living organisms.

3. Littoral contamination characterization and variations under WLF

The variations of TM normalized concentrations differed among matrices, suggesting differences in TM behavior among these matrices. For the three matrices, a significant variability of TMs normalized concentration was TM-specific indicating that their distribution differed among TMs. For instance, in surficial sediment, Pb had similar normalized concentrations expected for one measurement while those for Cu were much more spread. These differences could provide insight regarding the spatial distribution of TMs (i.e. aggregative structures) within surficial and trapped sediment as variance of a sample can be related to its spatial structure (Taylor, 1961). For *D. magna*, the TM-specific variability could be more related to differences in TMs bioavailability.
The normalized TM concentrations also significantly differed among sites in trapped sediment and *D. magna* while they were similar in surficial sediment. This result suggests that, despite a similar global contamination within the fringe of littoral zone studied (i.e. surficial sediment), contaminants mobility and uptake could differ among sites (i.e. short-spatial scale). In trapped sediment, that supported the deposited contamination after the mobilization, the shallower site clearly had lower TM normalized concentrations than the two other sites. Quite unexpectedly, the contamination of *D. magna* did not follow the contamination pattern of trapped sediment as *D. magna* were more contaminated at the shallower and the deepest site compared to the intermediate. Clear processes implicated in the differences in site contamination among the three matrices remain difficult to address due to the large array of possible variables and their complex interactions (e.g. temperature and ORP associated fluctuations). Nonetheless, the important environmental variability among the three sites could support the differences observed among sites for the three matrices (Eggleton and Thomas, 2004).
The effect of WLF (i.e. steps) was clearly significant on TM normalized concentrations for two of the three matrices (i.e. surficial and trapped sediment) and was almost significant for *D.*

magna. In contrast to our initial hypothesis, the normalized concentrations did not tend to increase during the lowest water-level period (i.e. step 2). Specifically, the normalized concentrations were lower after than before the WLF for surficial and trapped sediment and they started to decrease as soon as the water-level was low for surficial sediment. Different processes could be involved to explain these results with possible implications of environmental (e.g. enhancement of the TM solubilization) or hydrodynamic (e.g. transfer of the TM from the littoral to the pelagic zone) variability. Altogether, the results highlighted that WLF could affect contaminant distribution both within mineral (i.e. surficial and trapped sediment) and biological (i.e. *D. magna*) matrices.

Conclusion

This study revealed important environmental variability in the littoral zone of Lake Bourget at both short spatial and time scales that still remain seldom estimated although it can have consequences for the contaminant mobility, spread and uptake within the foodweb. The WLF have been shown to modulate the influence of external forcings on proxies for contaminant mobility and spread (i.e. turbidity and water velocity) that may be implicated in the contaminants variability among sites and WLF steps. Consequently, the implications of such management action, not only of ecological compartments but also regarding contaminant fate, should meet specific attention. The development of mechanistic models coupling environmental and hydrodynamic variables to forecast contaminant behavior during WLF is likely to be a fruitful perspective to better manage and conserve littoral areas of large lakes.

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Supplementary data

Table S1. TM concentrations (mg kg^{-1} DM) in surface sediment, trap sediment and encaged D. magna *from the 3 steps of WLF and the 3 study sites ($S_{0.5}$, $S_{1.5}$ and $S_{2.5}$).*

			Concentration (mg kg^{-1} DM)					
Site	Matrice	Step	Cd	Cr	Cu	Ni	Pb	Zn
S2.5	surface sediment	1	0.10	38.77	9.61	11.38	6.92	63.73
S2.5	surface sediment	1	0.09	38.64	7.60	10.23	5.87	58.37
S2.5	surface sediment	1	0.11	38.05	8.75	9.82	7.50	61.58
S1.5	surface sediment	1	0.10	37.86	8.37	9.20	6.30	59.11
S1.5	surface sediment	1	0.12	39.80	9.39	10.05	7.52	68.97
S1.5	surface sediment	1	0.17	71.34	9.49	10.30	20.96	71.29
S0.5	surface sediment	1	0.15	64.24	10.85	11.02	7.13	56.37
S0.5	surface sediment	1	0.15	51.94	8.11	11.40	7.76	53.92
S0.5	surface sediment	1	0.14	59.40	8.93	11.70	7.79	56.59
S2.5	surface sediment	2	0.14	29.84	5.32	11.95	5.27	56.26
S2.5	surface sediment	2	0.13	29.54	6.44	12.82	5.06	53.97
S2.5	surface sediment	2	0.16	38.59	5.49	13.29	5.37	57.04
S1.5	surface sediment	2	0.15	30.04	5.53	13.96	6.02	75.91
S1.5	surface sediment	2	0.16	30.59	6.14	15.09	6.82	76.28
S1.5	surface sediment	2	0.15	30.75	6.65	13.15	5.54	56.76
S0.5	surface sediment	2	0.11	47.14	4.44	14.00	4.67	44.33
S0.5	surface sediment	2	0.12	48.96	4.38	13.87	5.71	47.26
S0.5	surface sediment	2	0.12	50.37	3.79	12.68	5.26	41.54
S2.5	surface sediment	3	0.14	40.51	9.49	12.99	6.98	54.51
S2.5	surface sediment	3	0.12	40.09	6.37	13.97	7.35	59.29
S2.5	surface sediment	3	0.13	44.60	6.63	14.96	8.11	61.94
S1.5	surface sediment	3	0.11	39.83	5.14	11.48	6.62	59.70
S1.5	surface sediment	3	0.11	42.25	6.14	12.96	7.15	61.70
S1.5	surface sediment	3	0.11	42.95	5.38	13.37	7.33	59.58
S0.5	surface sediment	3	0.08	83.86	2.45	11.83	4.85	34.76
S0.5	surface sediment	3	0.09	83.82	2.13	11.96	6.63	37.17
S0.5	surface sediment	3	0.08	89.33	2.38	13.19	5.18	37.39
S2.5	trap sediment	1	0.13	38.42	15.44	10.88	8.63	103.96
S2.5	trap sediment	1	0.14	39.63	17.05	12.43	10.25	107.18
S2.5	trap sediment	1	0.15	41.91	17.54	11.27	9.31	147.93
S1.5	trap sediment	1	0.17	40.59	20.85	11.28	10.56	127.45
S1.5	trap sediment	1	0.17	43.76	22.35	12.23	11.63	139.17
S1.5	trap sediment	1	0.18	42.96	24.25	13.10	12.94	140.78
S0.5	trap sediment	1	0.13	43.71	10.89	10.28	8.08	92.32
S0.5	trap sediment	1	0.17	43.04	9.25	10.04	6.16	91.95
S0.5	trap sediment	1	0.14	38.11	10.52	10.29	7.21	77.52
S2.5	trap sediment	2	0.17	30.60	14.75	13.27	8.90	118.34
S2.5	trap sediment	2	0.17	30.39	13.65	13.72	8.72	115.65
S2.5	trap sediment	2	0.17	30.95	13.72	12.95	8.22	116.57
S1.5	trap sediment	2	0.18	34.14	16.61	14.52	12.30	119.88
S1.5	trap sediment	2	0.19	36.30	17.06	14.89	13.89	120.33
S1.5	trap sediment	2	0.18	33.12	15.35	13.97	10.11	105.19

Table S1. Continued.

			Concentration (mg kg^{-1} DM)					
Site	Matrice	Step	Cd	Cr	Cu	Ni	Pb	Zn
S0.5	trap sediment	2	NA	NA	NA	NA	NA	NA
S0.5	trap sediment	2	NA	NA	NA	NA	NA	NA
S0.5	trap sediment	2	NA	NA	NA	NA	NA	NA
S2.5	trap sediment	3	0.14	35.12	11.73	12.71	8.96	94.72
S2.5	trap sediment	3	0.13	39.27	13.11	13.57	9.32	96.63
S2.5	trap sediment	3	0.14	41.35	13.61	14.51	10.29	99.11
S1.5	trap sediment	3	0.14	39.89	12.65	13.30	10.54	112.86
S1.5	trap sediment	3	0.13	43.47	13.60	13.12	10.78	115.31
S1.5	trap sediment	3	0.13	39.84	12.81	13.84	10.76	114.19
S0.5	trap sediment	3	0.07	43.39	2.01	10.08	3.49	39.60
S0.5	trap sediment	3	0.06	37.67	2.60	10.92	4.27	39.14
S0.5	trap sediment	3	0.06	35.58	1.81	9.59	3.26	32.21
S2.5	*D. magna*	1	0.0003	0.0030	0.0108	0.0012	0.0015	0.0346
S2.5	*D. magna*	1	0.0003	0.0030	0.0107	0.0012	0.0014	0.0302
S2.5	*D. magna*	1	0.0002	0.0030	0.0109	0.0012	0.0015	0.0346
S1.5	*D. magna*	1	0.0002	0.0035	0.0126	0.0016	0.0022	0.0716
S1.5	*D. magna*	1	0.0002	0.0035	0.0125	0.0016	0.0022	0.0698
S1.5	*D. magna*	1	0.0003	0.0033	0.0125	0.0016	0.0020	0.0680
S0.5	*D. magna*	1	0.0021	0.0631	0.1889	0.0261	0.0219	ND
S0.5	*D. magna*	1	0.0021	0.0639	0.1886	0.0313	0.0227	ND
S0.5	*D. magna*	1	0.0020	0.0603	0.1891	0.0287	0.0222	ND
S2.5	*D. magna*	2	ND	0.0204	0.0546	0.0168	0.0102	0.1200
S2.5	*D. magna*	2	ND	0.0201	0.0558	0.0162	0.0108	0.1200
S2.5	*D. magna*	2	ND	0.0192	0.0570	0.0159	0.0096	0.1260
S1.5	*D. magna*	2	ND	0.0053	0.0258	0.0022	0.0036	ND
S1.5	*D. magna*	2	ND	0.0053	0.0263	0.0023	0.0032	ND
S1.5	*D. magna*	2	ND	0.0049	0.0259	0.0018	0.0036	ND
S0.5	*D. magna*	2	NA	NA	NA	NA	NA	NA
S0.5	*D. magna*	2	NA	NA	NA	NA	NA	NA
S0.5	*D. magna*	2	NA	NA	NA	NA	NA	NA
S2.5	*D. magna*	3	0.0022	0.0197	0.0651	0.0091	0.0107	ND
S2.5	*D. magna*	3	0.0022	0.0196	0.0648	0.0090	0.0107	ND
S2.5	*D. magna*	3	0.0016	0.0198	0.0538	0.0090	0.0101	ND
S1.5	*D. magna*	3	0.0005	0.0036	0.0141	0.0015	0.0021	0.1135
S1.5	*D. magna*	3	0.0005	0.0038	0.0141	0.0016	0.0021	0.1309
S1.5	*D. magna*	3	0.0005	0.0038	0.0159	0.0018	0.0023	0.1963
S0.5	*D. magna*	3	0.0007	0.0065	0.0155	0.0027	0.0036	ND
S0.5	*D. magna*	3	0.0007	0.0061	0.0155	0.0027	0.0036	ND
S0.5	*D. magna*	3	0.0006	0.0055	0.0209	0.0029	0.0029	ND

« NA » = Non available values

« ND » = Non detected values

3. Synthèse

Les facteurs influençant l'exposition aux contaminants sédimentaires sous l'effet du marnage sont nombreux (Figure 20) (Arenas-Sánchez et al., 2016). A cela s'ajoute l'intensité de leurs fluctuations temporelles et spatiales à court terme en zone littorale, ce qui tend à complexifier la compréhension des mécanismes régissant la mobilité et la biodisponibilité des ETM sédimentaires. Notre étude montre que l'abaissement de la colonne d'eau accentue les phénomènes de remise en suspension sédimentaire provoqués par les forçages météorologiques tels que les précipitations et la vitesse du vent. Néanmoins, les résultats de cette étude semblent indiquer un impact écotoxique négligeable du marnage dans ce cas précis, tout du moins au regard des teneurs en contaminants du sédiment de surface, des particules en suspension et du biote pélagique exposé. Cependant, dans chacun de ces compartiments d'étude les comportements de mobilité ont significativement varié entre les ETM, montrant une nouvelle fois que les facteurs d'influence de la mobilité et de la biodisponibilité agissent différemment selon l'élément.

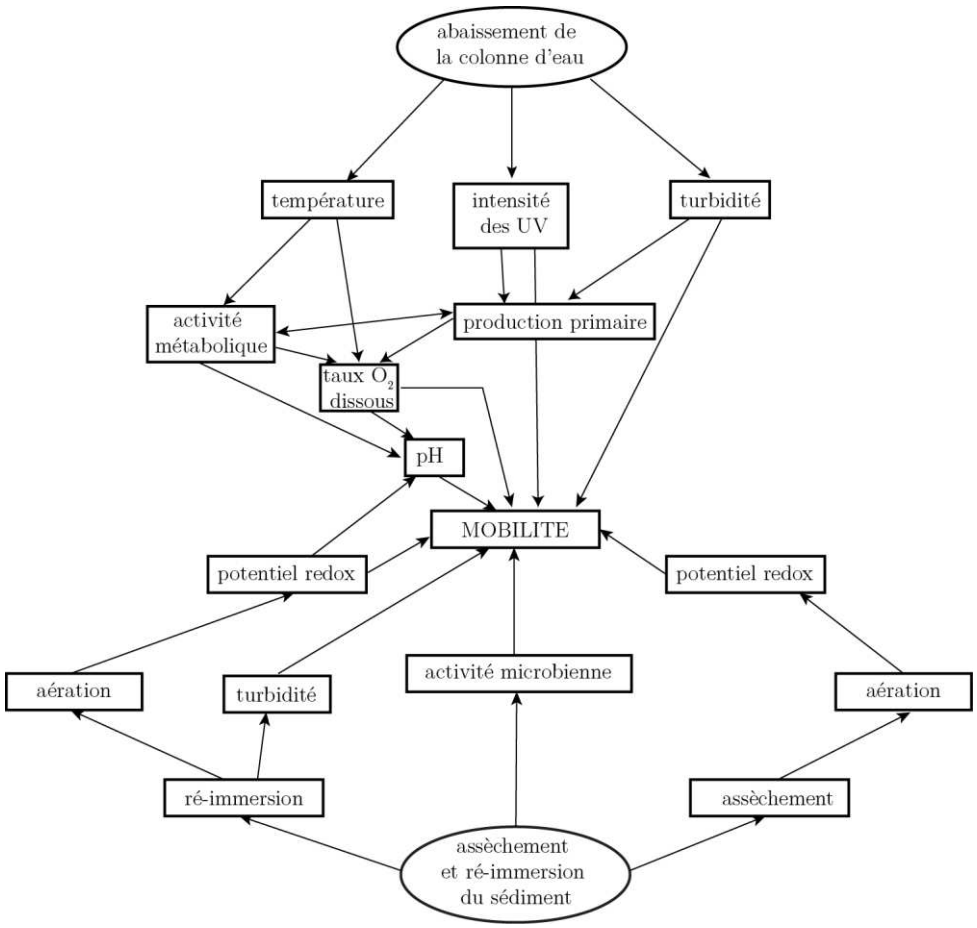

Figure 20. Exemples de facteurs d'influence de la mobilité des ETM sédimentaires liés au marnage en zone littorale lacustre (adapté de Arenas-Sánchez et al. (2016)).

Discussion et Perspectives

Nos travaux portent sur l'étude de la contamination des sédiments lacustres littoraux et de l'écotoxicité associée. Cette étude se justifie par le besoin (1) d'accroître les connaissances sur la variabilité spatiale de la contamination et du risque écotoxicologique à l'échelle de la zone littorale des grands lacs et (2) d'améliorer la compréhension des facteurs de modulation de cette écotoxicité (Figure 21).

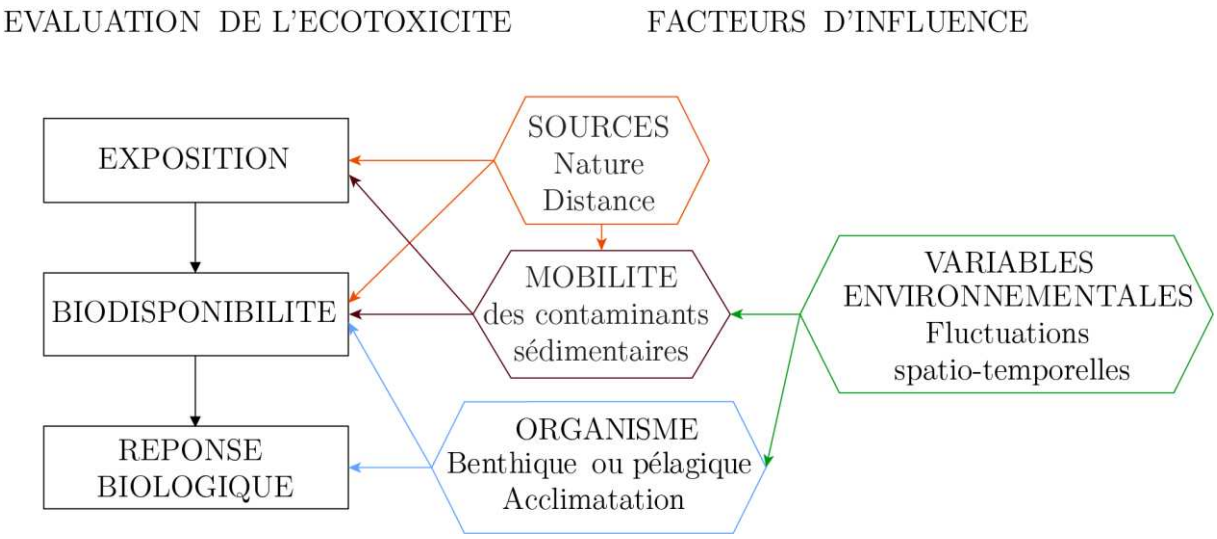

Figure 21. Facteurs d'influence de l'écotoxicité des sédiments de la zone littorale lacustre abordés dans nos travaux et messages clés.

I. Facteurs d'influence de l'écotoxicité des sédiments littoraux lacustres (Figure 1)

I.1. Sources de contamination

La nature des sources de contamination du lac (e.g. ports, sites industriels) et la distance qui les sépare au sédiment littoral récepteur conditionnent en partie la composition et l'intensité de la multi-contamination du sédiment de la ZL.

D'un côté, les fortes concentrations du sédiment dans la partie sud par rapport à la zone septentrionale du lac du Bourget semblent liées à la proximité des aires urbaines d'Aix-les-Bains et de Chambéry *(Chapitres 1 et 2)*. De plus, l'hétérogénéité spatiale de la contamination sédimentaire des ZL des lacs du Bourget et d'Annecy met en évidence des sites littoraux touchés par des sources ponctuelles locales (e.g. stations d'épuration des eaux usées pour le lac du Bourget, route en bordure pour le lac d'Annecy) *(Chapitres 2 et 3)*. Ces variations de concentrations sédimentaires sur le littoral tendent à moduler l'exposition du biote littoral.

D'un autre côté, la composition de la multi-contamination (i.e. profils) du sédiment littoral influence la mobilité et la biodisponibilité des contaminants. A titre d'exemple, le *Chapitre 3* a montré que les HAP légers, et plus particulièrement le fluorène, étaient davantage bioconcentrés

par les Corbicules de la ZL du lac d'Annecy que les HAP lourds, probablement en raison de leur mobilité accrue vers l'eau interstitielle et la colonne d'eau, augmentant ainsi leur biodisponibilité (Lee et al., 2014; Noh et al., 2018).

I.2. Variables environnementales

La mobilité vers l'eau interstitielle et la colonne d'eau est également favorisée par les fluctuations temporelles et spatiales des variables environnementales abiotiques en ZL.
Les fluctuations des paramètres physico-chimiques susceptibles d'influencer l'écotoxicité peuvent être abordées à plusieurs échelles temporelles ; de la saison (Wu et al., 2014) à l'heure (Chapitre 6 et Grabas et Rokitnicki-Wojcik (2015)). Le suivi en continu sur plusieurs mois des paramètres abiotiques de la colonne d'eau dans le *Chapitre 6* a en effet mis en évidence des fluctuations horaires de la température, l'oxygène dissous ou la conductivité en zone littorale susceptibles d'impacter rapidement la mobilité chimique des contaminants sédimentaires. De plus, la rapidité de réponse de la turbidité aux forçages extérieurs (e.g. vents, précipitations), de l'ordre de l'heure également, montre à quel point l'exposition et la biodisponibilité des contaminants du sédiment en suspension sont susceptibles de fluctuer rapidement.
Le marnage lacustre, en ZL, semble en outre augmenter l'amplitude de ces fluctuations temporelles. Ce constat, réalisé en ZL lacustre, est similaire aux observations de Lake (2011) vis-à-vis des écosystèmes lentiques temporaires (Figure 22).

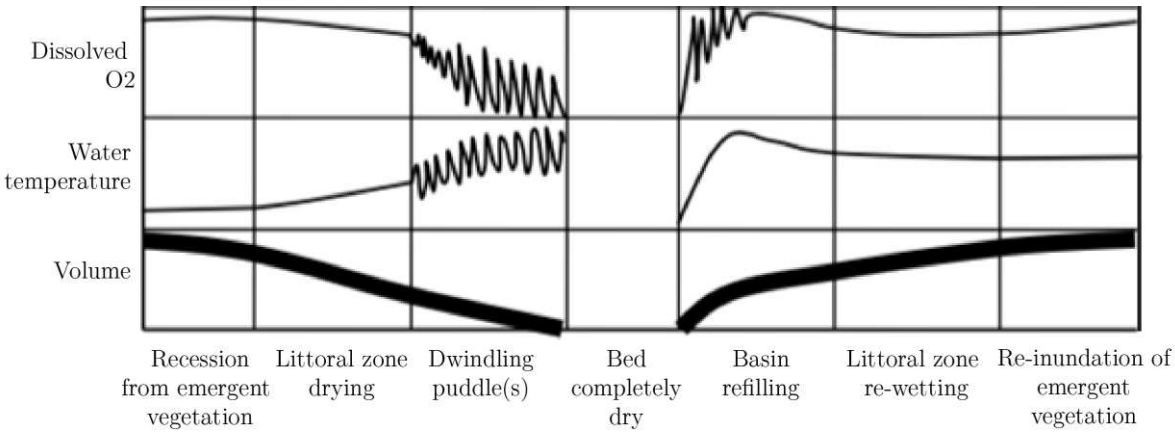

Figure 22. Schématisation des changements de la teneurs en oxygène dissous et de la température de la colonne d'eau sous l'effet de l'assèchement et remise en eau de systèmes lentiques temporaires selon Lake (2011).

Ces fluctuations environnementales temporelles dépendent également de leur localisation, en fonction de la profondeur d'eau relative à la distance à la berge. Dans le cas du marnage observé en ZL du Bourget *(Chapitre 6)*, l'amplitude des fluctuations des variables abiotiques variait en fonction de la profondeur et était plus importante à 0,5 m de profondeur qu'à 3,5 m. Pour les sédiments les plus proches de la berge, l'assèchement provoque des changements abiotiques

drastiques qui dans nos travaux en laboratoire ont conduit à la réduction de la fraction échangeable des ETM sédimentaires *(Chapitre 5)*.
Les fluctuations spatiales des variables abiotiques opèrent également à l'échelle de l'ensemble de la ZL. Nos travaux soulignent par exemple la variabilité spatiale de la granulométrie et du taux de matière organique du sédiment, de la pente, de l'énergie des vagues *(Chapitres 1 à 3)*. Ces variables influencent la mobilité et de la biodisponibilité des contaminants sédimentaires de la ZL. Le *Chapitre 1* par exemple discute du rôle de ces variables abiotiques fluctuantes le long du littoral du lac du Bourget dans l'absence de lien significatif entre la réponse des biomarqueurs enzymatiques des organismes autochtones et la multi-contamination des sédiments. Le *Chapitre 3*, quant à lui, met en évidence les liens significatifs entre les concentrations internes en HAP et ETM des Corbicules et la pente et la MO du sédiment.

I.3. Organismes

Nos travaux ont montré que l'espèce, la guilde trophique, le stade de vie et la capacité d'acclimatation des organismes exposés influencent l'exposition, l'internalisation et la régulation de la contamination sédimentaire littorale. En effet, le *Chapitre 1* met en évidence une sensibilité (activités enzymatiques) plus forte à la contamination sédimentaire de la ZL du lac du Bourget des Daphnies de laboratoire par rapport aux organismes benthiques autochtones. Ces résultats peuvent s'expliquer par une exposition élevée à la contamination sédimentaire des organismes pélagiques, comme l'a montré le *Chapitre 4*, mais surtout par une acclimatation des organismes autochtones contrairement aux organismes de laboratoire. Des mécanismes de régulation de l'internalisation de la contamination ont été suggérés dans nos travaux d'après les relations négatives obtenues entre le facteur de bioconcentration et la contamination du sédiment (Adams et al., 2011; McGeer et al., 2003) lors d'exposition d'organismes benthiques et pélagiques en bioessais de laboratoire dans le Chapitre 4. De telles relations négatives ont également été observées sur les *C. fluminea* de la ZL du lac du Bourget vis-à-vis de la contamination en ETM du sédiment (Figure 23, données issues de l'Annexe II) et du lac d'Annecy, vis-à-vis de la contamination en ETM (Figure 24, données issues de l'Article 3) et HAP (Figure 25, données issues de l'Article 3).

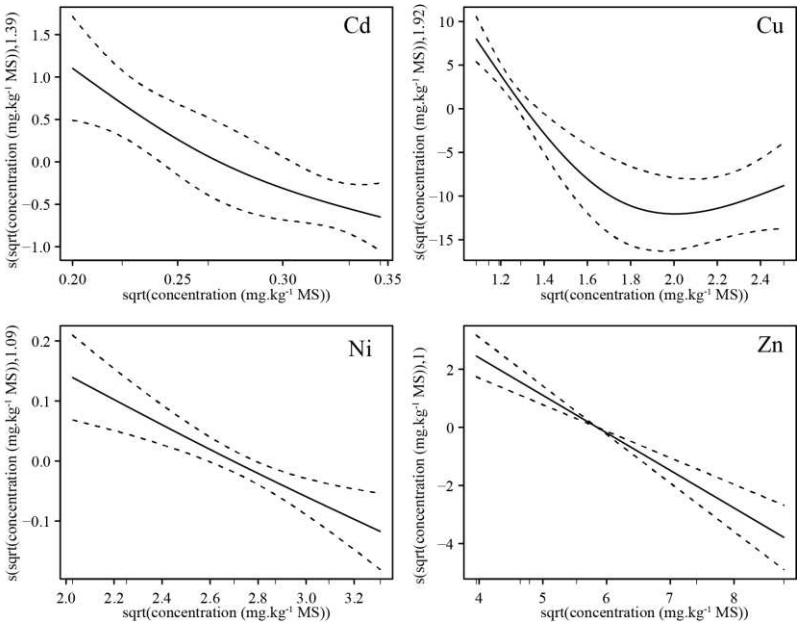

Figure 23. Représentation graphique des fonctions lissées entre la concentration en ETM du sédiment (en abscisses) exprimée en √(concentration en mg kg^{-1}) et le BCF des C. fluminea *prélevés en zone littorale du lac du Bourget (données supplémentaires). Les lignes en pointillées représentent les intervalles de confiance à 95 %. Les graduations sur l'axe des abscisses indiquent les valeurs réelles mesurées. Les nombres entre parenthèses dans la légende des ordonnées correspondent aux degrés de liberté pour chaque fonction lissée.*

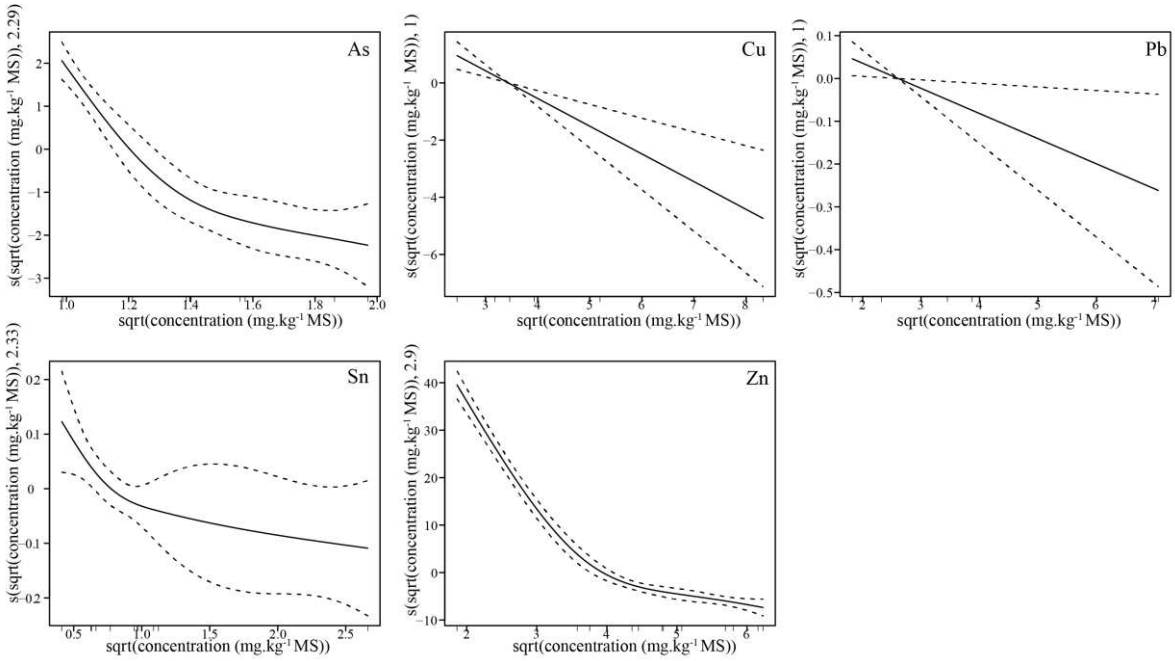

Figure 24. Représentation graphique des fonctions lissées entre la concentration en ETM du sédiment (en abscisses) exprimée en √(concentration en mg kg^{-1}) et le BCF des C. fluminea *prélevés en zone littorale du lac d'Annecy (cf Article 3). Les lignes en pointillées représentent les intervalles de confiance à 95 %. Les graduations sur l'axe des abscisses indiquent les valeurs réelles mesurées. Les nombres entre parenthèses dans la légende des ordonnées correspondent aux degrés de liberté pour chaque fonction lissée.*

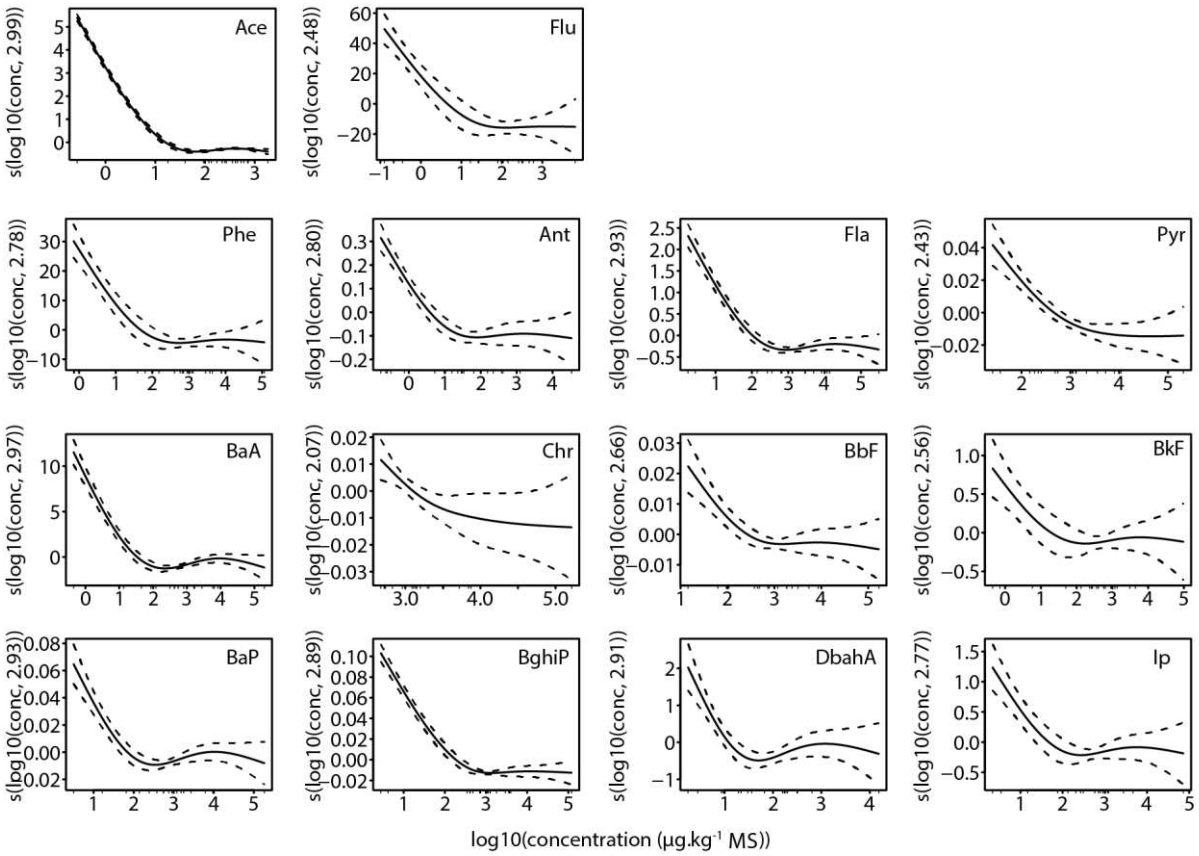

Figure 25. Représentation graphique des fonctions lissées entre la concentration en HAP du sédiment (en abscisses) exprimée en log_{10}(concentration µg kg^{-1} MS) et le BCF des C. fluminea *prélevés en zone littorale du lac d'Annecy (cf Article 3). Les lignes en pointillées représentent les intervalles de confiance à 95 %. Les graduations sur l'axe des abscisses indiquent les valeurs réelles mesurées. Les nombres entre parenthèses dans la légende des ordonnées correspondent aux degrés de liberté pour chaque fonction lissée.*

Les différences de contamination en ETM des Corbicules en fonction de leur taille, et donc également de leur âge (Annexe II), laissent envisager que ces mécanismes de régulation sont dépendants du stade de vie des organismes.

II. L'évaluation des risques écotoxicologiques comme aide à la gestion écologique des zones littorales

Nos travaux ont montré que l'évaluation de la contamination de la zone littorale permettait d'améliorer les connaissances sur la contribution des sources de pollution lacustre. L'analyse de la variabilité spatiale de la contamination des sédiments et du biote de la ZL des lacs du Bourget

et Annecy a renseigné sur l'influence locale (i.e. bassin-versant) de sources de pollution au lac, qu'elles soient ponctuelles (Chapitre 3) ou diffuses (Chapitre 2 et Brazner et al. (2007)). Nos travaux ont montré que le ruissellement est une voie d'entrée majoritaire des familles de contaminants étudiées (i.e. ETM, HAP et PCB) aux lacs du Bourget et d'Annecy. De plus, la contamination littorale du lac du Bourget nous a également renseigné sur l'implication des tributaires dans l'apport de contaminants au lac sans mettre en jeu des analyses chimiques coûteuses et chronophages de la contamination des tributaires (Chapitre 2). Dans le cas du Bourget, les sous-bassins-versants à l'amont du lac présentent la densité urbaine la plus élevée et les tributaires en cette zone contribuent majoritairement à l'apport d'une multi-contamination en polluants organiques au lac. D'autres études ont également montré l'implication forte des tributaires dans la contamination lacustre et notamment en polluants émergents (Thomas et al., 2017).

De plus, l'évaluation des risques écotoxicologiques en zone littorale lacustre renseigne sur les impacts de la pollution chimique dans la zone du lac abritant la plus grande proportion de la biodiversité lacustre (Vadeboncoeur et al., 2011). Dans certains cas, l'écotoxicité est telle qu'elle conduit à la sélection d'espèces résistantes (Bustos-Baez et Frid, 2003). Altérer cette biodiversité peut ainsi conduire à la disparition d'espèces à forte valeur patrimoniale, mais aussi perturber le bon fonctionnement des écosystèmes par l'altération des réseaux trophiques pouvant induire des changements dans les cycles biogéochimiques (e.g. dégradation de la MO). La mise en évidence des sites littoraux à risque permet de cibler les actions de réduction des risques écotoxicologiques et de restauration écologique.

Les *Chapitre 5* et *6* mettent en évidence des impacts sur la mobilité des ETM sédimentaires sous l'effet du marnage en ZL. Ces changements de mobilité peuvent accentuer le risque écotoxicologique de la contamination sédimentaire en ZL. La mise en évidence de ces phénomènes est importante pour l'aide à la décision des gestionnaires dans les projets de restauration basés sur un marnage accentué par exemple. De plus, la fréquence des événements extrêmes (i.e. sécheresse et fortes précipitations) est supposée s'accroître dans un contexte de changement climatique (Milly et al., 2005). A titre d'exemple, la fréquence actuelle des fortes précipitations à l'origine d'inondations dans les Alpes est supposée quadrupler dans la perspective d'un réchauffement climatique de 1,5 °C (Jacob et al., 2018). Ces changements dans la balance hydrique des bassins-versants des grands lacs péri-alpins laissent entrevoir des fluctuations de niveau d'eau à la fréquence et l'intensité croissantes, soulignant la pertinence d'étudier d'ores et déjà les impacts de ces phénomènes sur la contamination littorale. Le déficit hydrique observé sur le lac d'Annecy, qui correspondait à une baisse de 60 cm de la cote du lac, à l'automne 2018[7] (Figure 26), illustre bien un phénomène qui tendra à se renouveler dans les prochaines décennies.

[7] http://www.haute-savoie.gouv.fr/Politiques-publiques/Environnement-risques-naturels-et-technologiques/Lacs-et-cours-d-eau/Baisse-historique-du-niveau-du-lac-d-Annecy

Figure 26. Photographie depuis la berge de la zone littorale Nord du lac d'Annecy asséchée sous l'effet de la baisse de 60 cm de la cote, prise le 6 Octobre 2018. © Nathalie Lécrivain.

Ces résultats montrent la pertinence d'étudier la zone littorale plutôt qu'un point central profond et unique pour juger de l'état écotoxicologique d'un lac et appuyer des initiatives d'aménagement du territoire autour des grands lacs péri-alpins.

III. Approche intégrée d'évaluation des risques écotoxicologiques

Dans nos travaux, l'analyse chimique du sédiment, les essais d'exposition en laboratoire et les observations *in situ* menés en parallèle s'apparentent aux démarches de type Triade (Chapman, 1990; Burton et Nedrich, 2018) et visent à convenablement attribuer aux contaminants les effets observés sur le biote. Cette approche intégrée s'avère pertinente dans un contexte de faible multi-contamination et de multi-stress, comme c'est souvent le cas en zone littorale lacustre (Figure 3) (Allan et al., 2013; Smith et al., 2015; Sterner et al., 2017) pour discerner l'impact des substances toxiques de celui exercé par d'autres pressions sur le biote littoral.

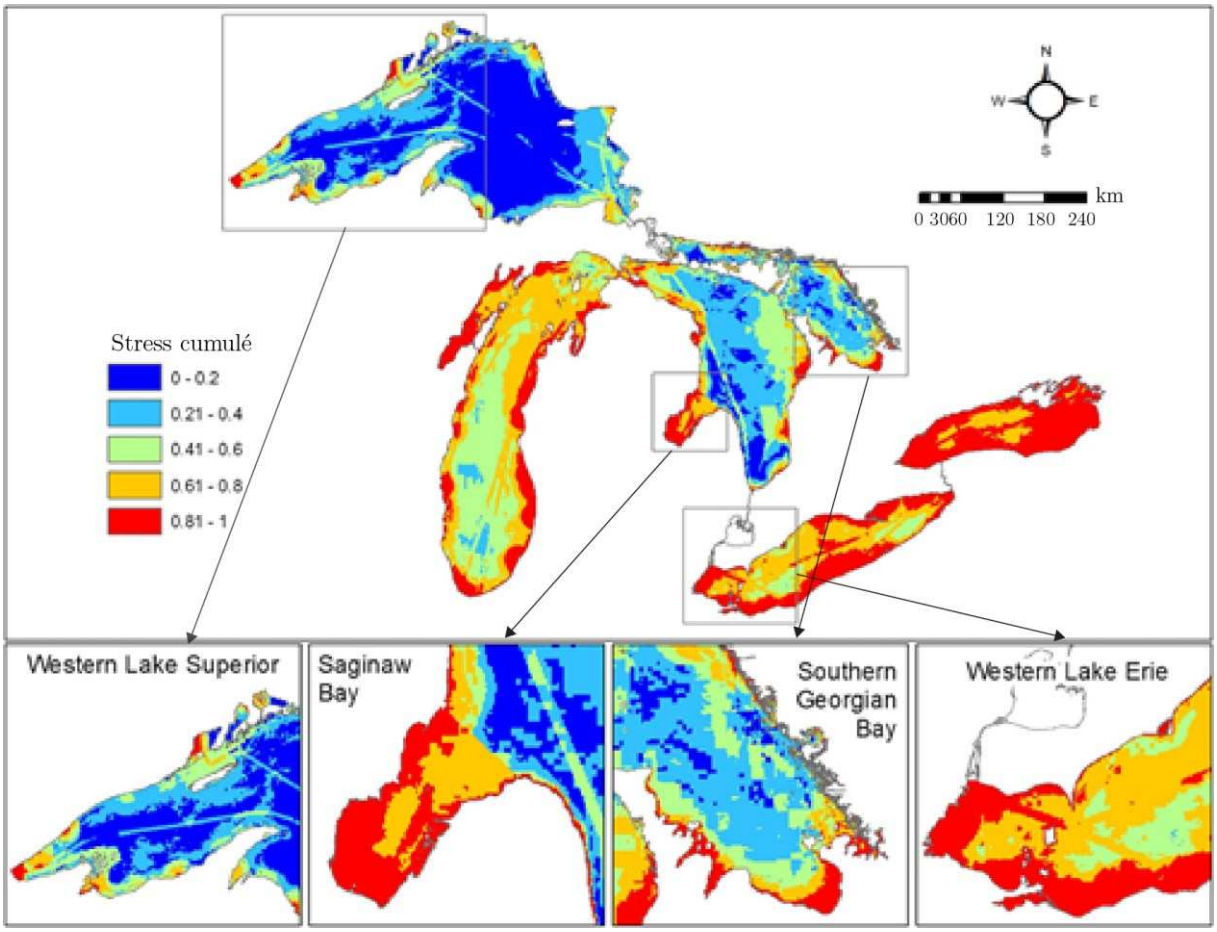

Figure 3. Variations spatiales du stress cumulé de 34 facteurs de stress anthropiques sur les Grands Lacs d'Amérique du Nord. Le stress cumulé a été calculé d'après les intensités de chaque facteur de stress pondéré par leur impact (déterminé par un jugement d'experts). Les stress cumulés sont représentés sur une échelle relative (percentile), groupé par quintile ; les pixels en rouge représentent les 20 % de stress cumulés les plus haut et les pixels bleus représentent les 20 % les moins élevés (modifié d'après Allan et al. (2013)).

A titre d'exemple, la multi-contamination des sédiments littoraux du lac du Bourget n'engendrait pas nécessairement des altérations au niveau des traits d'histoire de vie (e.g. taux de survie) dans nos travaux. Des effets ont néanmoins été observés à des niveaux biologiques inférieurs comme la capacité de bioconcentration de la contamination ou les réponses de biomarqueurs enzymatiques. Nos essais en laboratoire ont également montré l'importance d'étudier la réponse des organismes pélagiques dans l'évaluation de l'écotoxicité des sédiments littoraux, y compris dans un contexte de faible contamination *(Chapitre 4)*. Enfin, les fluctuations des paramètres abiotiques en zone littorale détaillées dans le Chapitre 6 et susceptibles d'impacter la mobilité et la biodisponibilité des contaminants sédimentaires montrent à quel point les observations *in situ* sont importantes dans l'évaluation du risque écotoxicologique des sédiments de la ZL. Les approches croisées permettent ainsi de réduire les incertitudes liées aux facteurs modulant l'écotoxicité dans l'évaluation de l'état écotoxicologique de la ZL lacustre.

IV. Limites et Perspectives de nos travaux

IV.1. Comprendre les mécanismes

Dans nos travaux, nous avons mesuré des changements de mobilité chimique des contaminants du sédiment en ZL par des tests d'extractions (lixiviation et extractions séquentielles). Nous avons également supposé l'activation de mécanismes de régulation de la contamination internalisée par le biote suite aux relations négatives obtenues entre les BCF des organismes et la contamination du sédiment. Néanmoins, les mécanismes régissant ces mobilités chimiques et biologiques n'ont pas été mis en évidence. Il serait donc intéressant, en perspective à ce travail, d'évaluer :

(1) les formes de liaison des contaminants métalliques avec le sédiment par la mesure des sulfures acides volatils et des hydroxydes de Fe et Mn pour mieux comprendre les mécanismes de mobilité chimique des ETM sous l'effet du marnage (i.e. assèchement / ré-immersion et abaissement de la colonne d'eau) (Nedrich and Burton, 2017),

(2) les mécanismes moléculaires en jeu dans la détoxication tels que l'activation des métallothionéines chez les invertébrés utilisés dans nos essais pour mettre en évidence les processus biologiques impliqués dans ces mécanismes de défense (Amiard et al., 2006).

Ces axes d'étude permettraient de mieux comprendre le comportement intrinsèque à chaque ETM puisque nos résultats ont montré des mobilités chimiques et biologiques très variables selon l'élément considéré.

Un des travaux de cette thèse a consisté en la comparaison des profils en PCB et HAP des sédiments littoraux du lac du Bourget avec un profil sédimentaire référence de source urbaine locale (i.e. sur le bassin-versant) pour évaluer l'impact des sources locales dans la contamination littorale du lac (Chapitre 2). Il était également question de sélectionner un profil référence de sédiment d'un lac reculé (i.e. intact de contamination locale). La recherche de ce profil de référence a conduit au constat que les profils sédimentaires étaient à échelle planétaire davantage similaires entre eux, qu'ils proviennent de lacs urbains ou reculés, que ne l'étaient les profils de contamination dans l'atmosphère ou l'hydrosphère (Supplementary data du Chapitre 2). En effet, si le phénomène dit de « sauterelles » (« grass-hopper ») s'observe à l'échelle des profils atmosphériques (Fernández et Grimalt, 2003; Gouin et al., 2004), de telles tendances au niveau des sédiments lacustres n'ont pas été observées dans nos travaux. Ces résultats nous incitent à comprendre les mécanismes de transport des polluants organiques aux interfaces air-eau-sédiment et les modifications que ce transport engendre dans la composition de la contamination depuis la source vers le compartiment sédimentaire final.

IV.2. Améliorer la prise en compte des mélanges de contaminants

Dans nos travaux, la considération de l'impact écotoxique des mélanges de contaminants a été abordée au travers du calcul des quotients de PEC moyens. Ces derniers ont montré leur limite dans la non prise en compte des effets additifs, synergiques et antagonistes qui résultent des interactions entre contaminants au niveau des cibles biologiques, et qui peuvent par conséquent influencer l'écotoxicité des sédiments (Chapitre 1 et Burton, 2018). Le fait de moyenner les quotients de PEC est en effet susceptible de minimiser le risque écotoxicologique lorsqu'il est question d'additivité, comme c'est souvent le cas (Rodea-Palomares et al., 2015), ou de synergie, et cette limite peut donc présenter un problème dans le cadre d'application simple de ces seuils, sans approche croisée. Dans nos travaux, nous sommes consciente que les relations entre concentrations sédimentaires pour un élément chimique donné et réponse du biote (e.g. régression linéaire simple) présentent un biais lié à la non prise en compte des potentiels effets liés au mélange des contaminants puisque nous nous situons dans un contexte de sédiment naturel multi-contaminé. L'analyse par régression linéaire multiple intégrant simultanément les teneurs en différents contaminants du sédiment comme variables explicatives de la réponse du biote (Gopalapillai and Hale, 2016) peut être une approche à explorer pour la prise en compte d'effets additifs des mélanges de contaminants en perspective de ce travail.

IV.3. Prendre en compte les fluctuations spatio-temporelles des variables environnementales

La complexité structurale et fonctionnelle de la ZL lacustre se caractérise notamment par des fluctuations temporelles à courte échelle (i.e. échelle horaire) des variables environnementales susceptibles d'influencer la mobilité et la biodisponibilité des contaminants sédimentaires *(Chapitre 6)*. L'étude conjointe de la contamination devrait par conséquent s'opérer à la même échelle. Nos résultats du Chapitre 6 relatant des concentrations en ETM mesurées ponctuellement (sédiment de surface et des trappes) ou sur une durée d'exposition d'une semaine de Daphnies ne permettent pas par conséquent d'enregistrer ces fluctuations de mobilité de la contamination. L'enregistrement en continu de proxies de la mobilité des contaminants, comme la turbidité dans nos travaux, pourrait permettre d'évaluer au plus près ces fluctuations temporelles de mobilité. Une perspective à nos travaux serait donc la calibration des liens entre les fluctuations des variables environnementales proxies et les fluctuations des contaminants d'étude *in situ* pour une compréhension fine du comportement des polluants en ZL sous l'influence de changements d'amplitude des fluctuations environnementales, comme lors d'un marnage. Ce travail devrait être complété par une analyse des relations entre ces conditions variables d'exposition aux

contaminants et les effets associés sur les organismes exposés, question rarement étudiée dans les bioessais de laboratoire où l'on s'efforce de fixer au maximum les concentrations en toxiques.

IV.4. Réponses des populations et communautés

Dans nos travaux, nous nous sommes concentrée sur la réponse biologique aux échelles de l'organisme. Les mécanismes de régulation de la contamination interne évoqués dans nos résultats sont susceptibles d'engendrer des compromis et, par exemple l'allocation d'énergie à la reproduction pourrait être impactée (Levins, 1968; Yu et al., 2016). Il serait intéressant d'observer d'éventuelles réponses à l'échelle des populations compte tenu de ce constat.
De plus, nous nous sommes cantonnée à l'étude de producteurs et consommateurs primaires et détritivores dans cette thèse. Nos expériences se sont opérées dans un contexte de faibles doses de contamination entrainant peu d'impact sur les taux de survie des organismes exposés. Une perspective à nos travaux serait d'étudier le transfert de contamination dans les réseaux trophiques denses de la zone littorale (i.e. bioamplification) et l'influence des fluctuations abiotiques que peut provoquer un phénomène comme le marnage sur l'impact de ce transfert de contamination. Dans un premier temps, il serait intéressant d'étudier ce transfert de contamination en essais multi-espèces en laboratoire.

IV.5. Vers une harmonisation des suivis écotoxicologiques ?

Devant l'enjeu de protection écologique des masses d'eau continentales et particulièrement des systèmes lacustres, des réseaux d'observation et étude scientifiques se sont développés autour des grands lacs à l'échelle planétaire. A titre d'exemple, plus de 220 lacs et plus de 500 chercheurs du monde entier sont réunis dans le Global Lake Ecological Observatory Network (GLEON ; www.gleon.org) (Hanson et al., 2018) et, à une échelle régionale, l'Observatoire des LAcs (SOERE OLA ; https://www6.inra.fr/soere-ola/) regroupe des projets scientifiques sur l'étude des processus qui sous-tendent le fonctionnement écologique des lacs par le suivi de 10 lacs français dont le lac du Bourget et d'Annecy. Les bases de données alimentées par ces consortiums scientifiques sont précieuses pour avancer vers une évaluation uniforme des états écologiques des grands lacs (e.g. eutrophisation). Néanmoins, ces bases sont encore peu fournies en données propres à la ZL et les suivis en contamination sédimentaire et biologique sont sporadiques. Compte tenu de l'intérêt que présente l'étude de la contamination et l'écotoxicité de ZL lacustre dans l'évaluation des pressions anthropiques sur les lacs, il serait intéressant d'alimenter ces bases en données propres à l'écotoxicité des ZL, comme les concentrations internes d'organismes benthiques et les profils de contaminations sédimentaires afin d'intégrer un suivi harmonisé de l'état écotoxicologique des ZL dans le suivi écologique. Cette mise en commun permettrait notamment des comparaisons inter-lacs des pressions anthropiques (Ostendorp, 2004; Reyjol et al., 2014) et ainsi de hiérarchiser les mesures de mitigation et restauration écologiques (Brazner et al., 2007; Smith et al., 2015).

V. Littérature

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Annexes

Annexe 1 – Situer la contamination en ETM, HAP et PCB des sédiments des lacs du Bourget et d'Annecy dans la contamination mondiale

1. Démarche

Les articles ont été sélectionnés dans les résultats du moteur de recherche BibCNRS (https://bib.cnrs.fr/) durant l'année 2015-2016 selon les mots clés suivants :

- « lake » AND « sediment » AND « trace metals » OR « heavy metals » pour les ETM,
- « lake » AND « sediment » AND « polycyclic aromatic hydrocarbons » OR « PAH » pour les HAP,
- « lake » AND « sediment » AND « polychlorinated biphenyls » OR « PCB » pour les PCB.

La sélection a été restreinte aux articles académiques et revues intégraux relus par un comité de lecture, écris en anglais et publiés entre 1997 et 2017. Les articles qui faisaient référence à des études pertinentes pour cette revue de la littérature et qui rentraient dans les critères précédemment évoqués ont été retenus.

Les valeurs de contamination concernent des sédiments de surface (i.e. 0-10 cm de profondeur maximale). Ont été retenues les valeurs moyennes de contamination sur l'ensemble des échantillons sédimentaires disponibles pour chaque lac.

Les graphes de densité ont été effectués sous R (R Core Team, 2015) avec le package network (Butts, 2008).

2. Tableaux des résultats de la recherche

Tableau 4. Résultats des concentrations sédimentaires lacustres moyennes en ETM (mg kg^{-1} MS) (N=31).

Lake	Country	Land use	As	Cd	Cr	Cu	Ni	Pb	Zn	Reference
Lake Ohrid	Albania	agriculture industry urban	NA	NA	NA	4.2	NA	NA	19.5	Malaj et al. (2011)
Jacarepagua lagoon	Brazil	agriculture industry urban	NA	NA	86.0	75.0	50.0	3.7	320.0	Fernandes (1997)
lakes of the Yangtze River catchment of Wuhan	China	agriculture industry urban	NA	0.4	91.0	41.0	42.0	44.0	121.0	Yang et al. (2009)
Dongjiang Harbor	China	agriculture industry urban	17.1	0.06	NA	19.4	NA	4.3	88.4	Guo et al. (2010)
Lake Baiyangdian	China	agriculture industry urban	12.3	0.3	74.9	31.6	NA	28.3	79.4	Zhang and Liu (2014)
Taihu Lake	China	agriculture industry urban	9.8	0.1	68.1	34.1	36.2	33.6	105.6	Fu et al. (2013)
Yilong Lake	China	agriculture industry urban	15.5	0.8	86.7	31.4	36.0	53.2	86.8	Bai et al. (2011)
Lake Dongting	China	agriculture industry urban	29.7	4.7	88.3	47.5	NA	61.0	185.3	Li et al. (2013)
Poyang Lake	China	agriculture industry urban	10.7	0.6	70.8	27.7	NA	48.7	65.8	Yuan et al. (2011)
Longgan lake	China	agriculture industry urban	NA	NA	97.4	39.5	43.7	41.8	95.5	Bing et al. (2012)
Manwan reservoir	China	agriculture industry urban	40.6	1.4	54.7	38.9	NA	47.1	156.7	Wang et al. (2012)
Lake Bourget	**France**	**agriculture industry urban**	**8.1**	**0.1**	**29.9**	**19.2**	**17.6**	**10.4**	**77.5**	**Agence de l'Eau Rhône Méditerranée Corse, (2017a)**
Lake Annecy	**France**	**agriculture industry urban**	**8.5**	**0.3**	**37.5**	**24.2**	**26.4**	**12.8**	**53.7**	**Agence de l'Eau Rhône Méditerranée Corse, (2017b)**
Lake Kerkini	Greece	protected (RAMSAR)	NA	NA	28.0	0.2	24	3.7	120.0	Pertsemli et Voutsa (2007)
Lake Doirani	Greece	agriculture	NA	NA	19.6	0.2	21	2.9	70	Fytianos et Lourantou (2004)
Lake Koronia	Greece	agriculture industry	NA	1.0	32.2	16.8	NA	20.4	85.9	Fytianos et Lourantou (2004)
Lake Volvi	Greece	agriculture industry	NA	0.9	21.8	14.2	NA	13.0	61.4	Özmen et al. (2004)
lake Vegoritis	Greece	agriculture industry urban	11.8	NA	266.0	36.6	215.8	25.8	88.1	Skoulikidis et al. (2008)
Veeranam lake	India	agriculture industry urban	NA	0.8	88.2	94.1	63.6	30.1	180.1	Suresh et al. (2012)
Kolleru lake	India	agriculture industry urban	NA	0.2	52.3	410.0	1.1	4.1	533.6	Chandra Sekhar et al. (2004)
Lake Nainital	India	agriculture industry urban	NA	NA	NA	NA	45.0	44.0	150.0	Ali et al. (1999)
Vembanad lake	India	agriculture industry urban	NA	5.0	NA	27.0	64.0	NA	253.0	Priju et Narayana (2007)
Masan Bay	Korea	agriculture industry urban	NA	1.3	41.0	73.0	NA	78.0	334.0	Kwon et Lee (1998)
Lake Nicaragua	Nicaragua	agriculture industry urban	4.1	0.1	23.1	5955	14.0	3.7	58.7	Scheibye et al. (2014)

Tableau 4 – suite et fin.

Lake	Country	Land use	As	Cd	Cr	Cu	Ni	Pb	Zn	Reference
Manchar Lake	Pakistan	agriculture industry urban	14.3	6.8	20.0	20.2	20.8	16.6	96.6	Arain et al. (2008)
Esmoriz-Paramos lagoon	Portugal	agriculture industry	NA	NA	46.5	83.2	NA	87.0	241.3	Fernandes et al. (2008)
Lake Geneva	Switzerland	agriculture industry urban	12.3	0.4	97.3	50.6	78.8	32.1	136.7	Agence de l'Eau Rhône Méditerranée Corse, (2017c)
Lake Victoria	Tanzania	agriculture industry urban	NA	2.5	11.0	21.6	NA	29.6	36.4	Kishe et Machiwa (2003)
Hazar Lake	Turkey	agriculture	NA	NA	17.0	10.0	45.0	NA	46.0	Nguyen et al. (2005)
Sapanca lake	Turkey	agriculture industry urban	NA	0.3	19.1	26.7	NA	15.2	62.0	Duman et al. (2006)
Lake Uluabat	Turkey	agriculture industry urban	2.4	1.3	32.9	NA	55.2	8.3	NA	Katip et al. (2011)
Lake Texoma	USA	agriculture industry urban	11.0	2.0	30.0	38.0	17.0	10.0	89.0	An et Kampbell (2003)
Lake Hough Park	USA	urban	NA	0.3	28.8	15.6	22.9	11.1	43.1	Ikem et Adisa (2011)

Tableau 5. Résultats des concentrations sédimentaires lacustres moyennes en HAP (µg kg^{-1} MS) (N=34).

Lake	Country	Land use	Ace	Flu	Phe	Ant	Fla	Pyr	BaA	Chr	BbF	BkF	BaP	BghiP	DbahA	IP	Reference
10W	Canada	remote	NA	5.6	10.2	NA	4.8	3.8	NA	2.8	6.2	NA	NA	NA	NA	0.9	Ahad et al. (2015)
13C	Canada	remote	NA	8.1	14.2	NA	13.0	15.8	NA	3.5	9.0	NA	NA	NA	3.7	2.7	Ahad et al. (2015)
8D	Canada	remote	NA	9.8	7.7	1.0	3.4	6.5	NA	3.5	8.0	NA	NA	NA	NA	8.2	Ahad et al. (2015)
10G	Canada	remote	NA	6.0	8.4	0.5	9.1	11.1	NA	1.8	NA	NA	NA	NA	0.6	NA	Ahad et al. (2015)
Lake Baiyangdian	China	industry	4.3	55.6	140.0	137.0	34.6	88.9	3.5	3.4	1.2	2.7	1.3	NA	NA	NA	Guo et al. (2011)
Lake Nansi	China	NA	6.8	34.0	53.1	7.5	19.7	31.0	14.5	15.2	18.1	22.4	14.5	16.1	3.2	14.0	Zhang et al. (2015)
Lake Laja	Chile	industry	NA	0.1	0.2	0.1	NA	0.0	NA	NA	NA	NA	NA	0.0	NA	0.0	Quiroz et al. (2005)
Lake Poyang	China	agriculture urban	1.1	7.4	32.6	3.3	15.2	13.7	3.5	6.3	18.4	4.6	7.5	7.2	3.8	6.3	Lu et al. (2012)
Lake Maryut	Egypt	NA	84.7	152.5	167.1	126.8	231.9	413.8	268.8	290.3	NA	NA	278.3	272.1	48.8	273.1	Barakat et al. (2011)
Lake Manzala	Egypt	NA	7.9	11.0	28.1	16.4	71.5	73.9	33.5	30.0	NA	NA	43.0	12.6	5.3	17.0	Barakat et al. (2013)
Lake Ziway	Ethiopia	NA	NA	17.2	22.4	29.8	6.1	5.4	NA	0.5	4.9	1.9	2.4	5.4	NA	2.9	Mekonnen et al. (2015)

Tableau 5. Suite.

Lake	Country	Land use	Ace	Flu	Phe	Ant	Fla	Pyr	BaA	Chr	BbF	BkF	BaP	BghiP	DbahA	IP	Reference
Lake Awassa	Ethiopia	NA	4.8	11.6	34.8	17.6	20.4	20.0	NA	45.5	5.0	1.9	1.8	4.1	NA	5.5	Mekonnen et al. (2015)
Lake Peipsi	Estony	NA	NA	NA	17.0	NA	26.3	52.5	11.3	30.0	84.4	NA	30.0	58.1	11.3	61.9	Punning et al. (2008)
Lake Bourget	**France**	**agriculture industry urban**	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**	**19**	**15**	**41**	**14**	**19**	**NA**	**NA**	**18**	**Agence de l'Eau Rhône Méditerranée Corse, (2017a)**
Lake Annecy	**France**	**agriculture industry urban**	**NA**	**NA**	**NA**	**NA**	**43**	**NA**	**23**	**16**	**49**	**15**	**20**	**NA**	**NA**	**23**	**Agence de l'Eau Rhône Méditerranée Corse, (2017b)**
Lake Piediluco	Italia	industry urban	2.9	8.5	3.3	28.0	NA	8.7	2.8	5.8	9.3	4.0	4.3	9.2	4.8	11.0	Di Veroli et al. (2010)
Lake Biwa	Japan	industry urban	NA	19.2	103.9	24.8	154.4	196.2	45.1	129.4	142.8	55.6	46.5	106.6	21.1	97.4	Itoh et al. (2010)
Lake Victoria	Kenya	NA	2.5	0.7	3.9	5.8	0.8	3.8	2.8	1.2	0.4	0.4	1.1	1.4	13.5	2.7	Kwach et al. (2009)
El Tule lake	Mexico	NA	NA	12.6	67.9	11.5	31.1	50.7	9.1	20.0	NA	NA	2.5	3.1	NA	NA	Ruiz-Fernández et al. (2014)
Lake Santa Elena	Mexico	NA	21.8	12.0	82.6	14.5	65.3	105.2	20.2	25.2	NA	NA	6.3	9.8	NA	NA	Ruiz-Fernández et al. (2014)
Lake Nicaragua	Nicaragua	NA	15.0	10.0	30.0	5.5	4.0	21.0	11.0	15.0	35.0	35.0	21.0	85.0	20.0	56.0	Scheibye et al. (2014)
Lake Deest Oost 3B	Netherlands	industry urban	NA	NA	15.5	4.5	26.0	22.0	14.5	13.0	15.5	6.5	14.0	9.5	2.0	12.0	De Lange et al. (2009)
Spitzberg	Norway	remote	11.0	27.0	139.0	18.0	90.0	45.0	NA	45.0	51.0	41.0	54.0	49.0	NA	39.0	Jiao et al. (2009)
Spitzberg	Norway	agriculture	9.3	5.0	9.3	0.8	2.9	2.0	NA	2.4	1.5	1.0	0.7	1.3	NA	1.0	Jiao et al. (2009)
Spitzberg	Norway	remote	6.7	6.6	9.6	1.0	2.6	1.8	NA	2.6	2.3	0.9	1.9	2.7	NA	2.0	Jiao et al. (2009)
Spitzberg	Norway	agriculture	1.5	1.8	3.0	0.2	1.2	0.7	NA	1.0	1.4	1.0	0.7	1.9	NA	1.4	Jiao et al. (2009)
Spitzberg	Norway	agriculture	29.0	50.0	150.0	18.0	40.0	19.0	NA	27.0	24.0	34.0	10.0	12.0	NA	14.0	Jiao et al. (2009)
Spitzberg	Norway	remote	5.6	8.8	35.0	2.1	7.3	4.2	NA	6.4	4.6	2.8	3.2	7.4	NA	3.2	Jiao et al. (2009)
Lake Male Lille	Norway	NA	64.0	97.0	450.0	190.0	1100.0	940.0	540.0	560.0	870.0	410.0	680.0	880.0	180.0	660.0	Andersson et al. (2014)
Lake Chini	Malaysia	industry urban	NA	16.2	45.2	25.5	NA	40.8	0.7	3.9	NA	273.0	17.3	NA	NA	NA	Bakhtiari et al. (2009)

Tableau 5. Suite et fin.

Lake	Country	Land use	Ace	Flu	Phe	Ant	Fla	Pyr	BaA	Chr	BbF	BkF	BaP	BghiP	DbahA	IP	Reference
27 alpine lakes	Poland	remote	NA	0.0	0.1	0.0	0.2	0.1	0.0	0.1	0.2	NA	0.0	0.1	0.0	0.1	Van Drooge et al. (2010)
Lake Ludas	Serbia	NA	2.2	9.3	8.4	1.9	16.2	24.1	3.3	3.8	18.6	4.1	3.4	3.7	25.0	4.2	Grba et al. (2017)
48 Lakes	Spain	Agriculture	1.7	3.1	16.6	1.4	21.5	16.9	10.5	12.9	26.5	70.7	266.0	167.0	34.0	219.0	Hijosa-Valsero et al. (2016)
Lake Bolgoda	Sri Lanka	NA	NA	NA	NA	NA	67.4	70.7	NA	NA	40.8	NA	12.3	NA	NA	NA	Ratnayake et al. (2017)
Lake Iznik	Turkey	NA	NA	21.9	30.3	9.6	NA	18.5	10.8	18.3	NA	NA	15.0	NA	NA	NA	Ünlü et al. (2010)
Lake Michigan	USA	NA	NA	0.2	70.4	9.1	134.1	110.3	55.8	75.9	28.5	22.5	2.7	6.7	18.2	18.2	Huang et al. (2014)

Tableau 6. Résultats des concentrations sédimentaires lacustres moyennes en PCB (µg kg^{-1} MS) (N=62).

Lake	Country	PCB28	PCB52	PCB101	PCB118	PCB138	PCB153	PCB180	Reference
La Peregrina Lake	Argentina	NA	0.400	0.100	NA	0.100	NA	NA	Barni et al. (2016)
Lake Nanyang	China	0.054	0.032	0.025	0.031	0.031	0.026	0.025	Pan et al. (2010)
Lake Weishan	China	0.050	0.022	0.025	0.025	0.045	0.041	0.045	Pan et al. (2010)
Lake Chaohu	China	0.360	2.040	NA	NA	0.210	0.050	0.040	Wang et al. (2012)
Lake Dianchi	China	0.530	0.430	0.180	NA	0.080	0.100	0.140	Wan et al. (2011)
Lake Baiyangdian	China	0.800	0.400	0.730	0.950	0.400	0.460	0.490	Dai et al. (2011)
Lake Nansihu	China	2.220	0.030	0.450	NA	NA	0.720	NA	Zheng et al. (2016)
East lake	China	8.000	0.700	1.900	1.300	NA	NA	2.050	Yun et al. (2015)
Lake Ma	Congo	0.001	0.001	0.001	0.001	0.001	0.001	0.001	Mwanamoki et al. (2014)
Lake Chon	England	0.300	0.300	0.400	1.700	0.900	0.800	0.500	Rippey et al. (2008)
Lake Agden	England	0.500	0.300	0.500	1.500	0.700	0.600	0.400	Rippey et al. (2008)
Lake Scoat Tarn	England	0.400	0.300	0.500	2.000	1.100	0.900	0.700	Rippey et al. (2008)
Lake Llyn Llagi	England	0.400	0.300	0.600	1.900	1.200	1.000	0.600	Rippey et al. (2008)
Lake Lochnagar	England	0.300	0.300	0.600	2.200	1.400	1.000	0.800	Rippey et al. (2008)
Coire Fionnaraich Lake	England	0.050	0.050	0.050	0.400	0.300	0.200	0.050	Rippey et al. (2008)

Tableau 6. Suite

Lake	Country	PCB28	PCB52	PCB101	PCB118	PCB138	PCB153	PCB180	Reference
Lake Burnmoor Tarn	England	0.050	0.050	0.050	0.300	0.200	0.050	0.050	Rippey et al. (2008)
Lake Doilet	England	0.100	0.300	0.100	0.500	0.300	0.300	0.050	Rippey et al. (2008)
Lake Tooting Common	England	0.900	0.700	1.200	4.200	1.500	1.300	0.600	Rippey et al. (2008)
Llyn Cwm Mynach Lake	England	0.400	0.300	0.500	1.400	0.700	0.700	0.300	Rippey et al. (2008)
Lake Burullus	Egypt	27.920	1.270	11.200	1.650	35.940	34.190	9.040	Said et al. (2008)
Lake Bourget	**France**	**2.948**	**1.706**	**5.145**	**1.635**	**14.486**	**25.846**	**16.584**	**Agence de l'Eau Rhône Méditerranée Corse, (2017a)**
Lake Annecy	**France**	**0.18**	**0.034**	**0.013**	**3.92**	**0.014**	**0.026**	**NA**	**Agence de l'Eau Rhône Méditerranée Corse, (2017b)**
Plan Vianney	France	NA	NA	0.001	0.000	0.004	0.002	0.006	Nellier et al. (2015)
Lake Muzelle	France	NA	0.014	0.002	0.005	0.003	0.003	0.027	Nellier et al. (2015)
Lake Miemalanselkä	Finland	0.220	0.250	0.080	0.060	0.040	0.030	0.010	Mäenpää et al. (2015)
Lake Kernaalanjarvi	Finland	2.050	4.720	2.000	1.320	0.650	0.510	0.050	Mäenpää et al. (2015)
Lake Vesijarvi	Finland	2.000	3.000	9.600	4.000	19.800	14.500	14.500	Honkonen et Rantalainen (2013)
Lake Maggiore	Italia	NA	NA	NA	0.174	NA	NA	NA	Castro-Jiménez et al. (2008)
Lake Superior	Italia	11.650	5.840	5.840	7.550	4.230	8.850	5.140	Guzzella et al. (2016)
Lake Mahoma	Kenya	2.370	0.870	3.870	2.550	0.954	0.273	1.090	Arinaitwe et al. (2016)
Lake Victoria	Kenya	NA	0.120	0.010	0.260	0.370	0.050	0.080	Kwach et al. (2009)
Lake Bujuku	Kenya	2.780	0.380	0.020	0.820	0.080	2.660	0.040	Arinaitwe et al. (2016)
Lake Matas	Mexico	6.100	1.000	0.500	0.300	0.100	0.200	NA	Ruiz-Fernández et al. (2014)
Lake Espejo de los Lirios	Mexico	32.900	9.460	1.540	0.310	1.990	0.460	0.570	Piazza et al. (2009)
Lake Kalapattar 6	Nepal	NA	NA	2.390	2.830	3.900	2.270	NA	Guzzella et al. (2016)
Lake Kalapattar 5	Nepal	NA	0.300	NA	NA	NA	NA	NA	Guzzella et al. (2016)
Lake nb53	Nepal	2.020	0.430	NA	0.810	NA	NA	NA	Guzzella et al. (2016)
Lake nb31	Nepal	NA	0.490	1.220	1.710	NA	NA	NA	Guzzella et al. (2016)
Lake Inferior	Nepal	2.650	NA	1.500	0.270	NA	NA	NA	Guzzella et al. (2016)
Lake nb161	Nepal	2.060	1.420	1.180	1.710	0.480	NA	NA	Guzzella et al. (2016)
Lake nb24	Nepal	NA	0.650	1.530	5.020	NA	NA	NA	Guzzella et al. (2016)
Lake Eleyele reservoir	Nigeria	14.000	10.000	14.000	NA	10.000	12.000	NA	Adeogun et al. (2016)
Lake Ellasjoen	Norway	1.440	0.720	0.480	4.320	10.100	12.000	5.280	Evenset et al. (2007)
Lake Oyangen	Norway	NA	NA	NA	0.540	1.860	1.260	0.440	Gewurtz et al. (2009)
Lake Shihwa	South Korea	NA	NA	NA	0.540	NA	NA	NA	Moon et al. (2012)

Tableau 6. Suite et fin.

Lake	Country	PCB28	PCB52	PCB101	PCB118	PCB138	PCB153	PCB180	Reference
Lake Stein	Switzerland	0.035	0.112	0.111	NA	0.071	0.146	0.041	Schmid et al. (2011)
Lake Silvretta S2	Switzerland	0.050	0.110	0.170	NA	0.160	0.165	0.065	Pavlova et al. (2016)
Lake Thun	Switzerland	0.090	0.101	0.200	NA	0.150	0.170	0.160	Bogdal et al. (2010)
Lake Greifensee	Switzerland	0.250	0.460	1.010	0.089	2.130	2.150	1.320	Zennegg et al. (2007)
Lake Engstlen	Switzerland	0.103	0.515	0.515	NA	0.299	0.350	0.154	Schmid et al. (2011)
Lake Bret	Switzerland	NA	NA	NA	NA	0.970	1.220	NA	Thevenon et al. (2013)
Lake Eymir	Turkey	1.180	1.180	1.000	0.590	1.730	2.000	1.140	Karakas et al. (2017)
Island lake 10B	USA	NA	0.003	NA	NA	NA	NA	0.002	Vecchiato et al. (2015)
Lake Tarn Flat	USA	0.008	0.003	0.012	0.001	NA	0.002	0.000	Vecchiato et al. (2015)
Lake Edmonson point 15A	USA	0.009	0.002	0.021	0.055	0.076	0.143	0.068	Vecchiato et al. (2015)
Lake Carezza	USA	0.008	0.008	0.009	0.006	0.006	0.010	0.002	Vecchiato et al. (2015)
Lake Gondwana	USA	0.008	0.002	0.008	0.008	0.011	0.019	0.008	Vecchiato et al. (2015)
Lake Edmonson Point 14	USA	0.005	0.007	0.013	0.028	0.037	0.065	0.032	Vecchiato et al. (2015)
Lake Superior	USA	0.083	0.385	NA	NA	NA	0.500	0.520	Li et al. (2009)
Lake Huron	USA	1.080	0.517	NA	NA	NA	1.100	0.500	Li et al. (2009)
Lake Michigan	USA	1.320	0.510	0.460	0.610	NA	NA	0.250	Robinson et al. (2008)
Lake Erie	USA	2.200	3.200	4.000	4.700	6.300	5.000	3.000	Hu et al. (2011)
Lake Ontario	USA	9.900	16.500	23.650	34.100	33.000	22.550	14.300	Hu et al. (2011)
Lake Yen So	Vietnam	NA	5.750	6.470	7.520	5.780	6.110	2.370	Hoai et al. (2010)

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Annexe II - Evaluation de la contamination en ETM des *C. fluminea* de la zone littorale du lac du Bourget

1. Démarche et objectifs

Des Corbicules ont été collectées en 6 sites littoraux du lac du Bourget (S1, S3, S4, S8, S9 et S10) au cours de l'été 2016 à la benne Ekman à des profondeurs comprises entre 1,5 et 2,5 m sous eau. Les organismes échantillonnés ont été mesurés et divisés en 3 sous-groupes par site en fonction de leur largeur de coquille ;

- Groupe 1 : taille $<$ 16 mm,
- Groupe 2 : 16 $\leq$ taille $\leq$ 20 mm,
- Groupe 3 : taille $>$ 20 mm.

Les sous-échantillons ont été minéralisés ; 3 mL HNO_3, 1 mL de HCL, 1 ml H_2O_2, micro-onde CEM/MARS Xpress, puissance 1200 W, température 180 °C, rampe = 15 min et palier = 15 min, dilution eau ultra-pure. Les ETM (Cd, Cr, Cu, Ni, Pb et Zn) ont été dosés par spectromètrie d'absorption atomique (Perkin Elmer, modèle PinAAcle 900 T ; limites de détection : Cd = 0.1 µg.L^{-1}, Cr = 0.040 µg.L^{-1}, Cu = 0.014 µg.L^{-1}, Ni = 0.07 µg.L^{-1}, Pb = 0.05 µg.L^{-1}, Zn = 0.02 µg.L^{-1}).
Les concentrations internes obtenues (Tableau 7) ont été normalisées par la concetration maximale pour chaque ETM afin de pouvoir comparer le comportement des ETM en s'affranchissant des différences de concentrations inhérentes aux éléments.

Les objectifs étaient :

- d'évaluer la variabilité spatiale de la contamination en ETM des *C. fluminea* le long du littoral du lac,
- d'évaluer les différences de concentrations internes selon différents groupes de tailles afin d'aboutir à d'éventuelles préconisations quant au prélèvement de ces organismes en vue d'en étudier leur contamination et la biodisponibilité des ETM du sédiment auxquels ils sont exposés.

Une première hypothèse était que la contamination en ETM des *C. fluminea* variait selon leur localisation au sud (plus fortement contaminées) ou au nord (plus faiblement contaminées), d'après les résultats de contamination du sédiment en ETM du littoral du lac (cf Chapitre 2).
La seconde hypothèse était que les concentrations internes globales (i.e. tous ETM confondus) des *C. fluminea* diminuaient avec l'augmentation de la taille des organismes par l'activation de mécanisme de régulation de la concnetration interne en ETM (Bilos et al., 2009).

Tableau 7. Concentrations internes (mg kg^{-1} MS) des C. fluminea de 6 sites littoraux (S1, S3, S4, S8, S9 et S10) du lac du Bourget réparties en 3 groupes de tailles.

		Concentration (mg. kg^{-1} MS)					
Site	Groupe de taille	Cd	Cr	Cu	Ni	Pb	Zn
S1	1	0,12	2,69	18,23	1,69	0,14	178,65
	2	0,09	1,61	22,30	1,14	0,06	156,45
	3	0,22	3,07	26,85	2,82	0,19	184,60
S3	1	0,11	1,40	23,00	1,02	0,09	158,19
	2	0,10	1,49	27,05	0,88	0,09	135,14
	3	0,11	1,42	30,10	0,84	0,12	113,72
S4	1	0,30	2,58	33,62	1,94	1,26	178,96
	2	0,15	2,57	41,00	2,18	0,26	184,39
	3	0,16	2,07	37,83	1,90	0,19	170,31
S8	1	0,17	4,86	32,84	2,02	0,12	279,10
	2	0,12	5,35	22,30	1,21	0,05	207,36
	3	0,16	2,01	27,57	2,08	0,51	175,40
S9	1	0,15	2,95	47,43	1,74	1,17	252,94
	2	0,13	2,19	44,57	1,05	0,41	254,83
	3	0,18	2,98	58,58	1,16	0,50	232,26
S10	1	0,14	3,05	20,31	1,88	0,44	220,09
	2	0,10	1,93	22,73	1,42	0,35	234,33
	3	0,17	3,07	25,56	1,46	0,23	230,59

2. Résultats et discussions

Les organismes, toutes tailles confondues, ont présenté une contamination significativement plus faible au nord (e.g. S3) qu'au sud du lac (Figure 28-A, S4, S8, S9 et S10), plus urbanisé et aux concentrations en ETM du sédiment significativement plus élevées (Chapitre 1 et 2).

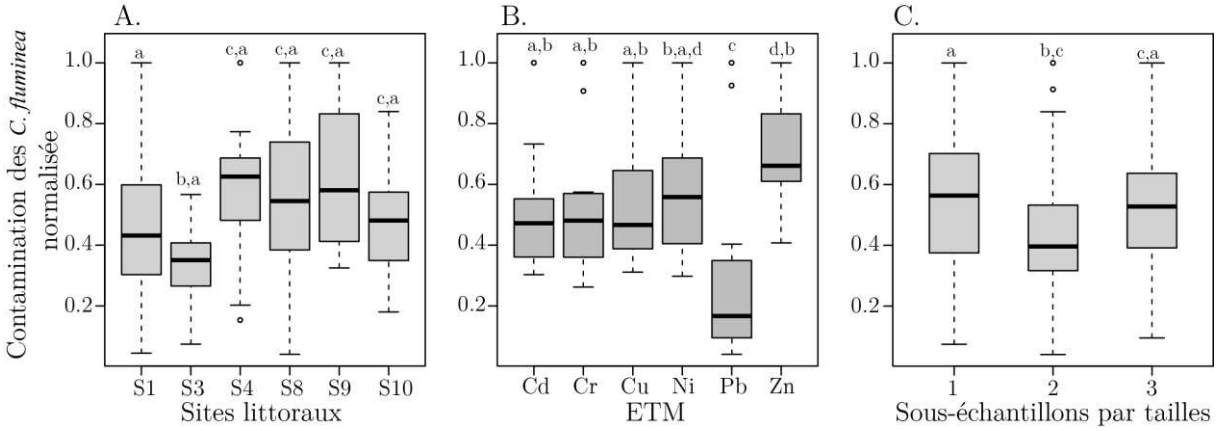

Figure 28. Boites à moustaches des concetrations en ETM normalisées pour 6 sites littoraux du lac du Bourget (A), en distinguant les différents ETM (B) et par groupe de tailles de Corbicules (groupe 1 =

taille < 16 mm, groupe 2 = 16 ≤ taille ≤ 20 mm, groupe 3 = > 20 mm) es lettres repreésentent fes différences significatives entre groupes d'après les analyses de variances (ANOVA) effectuées.

Les fluctuations de contamination des organismes ne semblent pas similaires antre les ETM ; le Cd, Cr et Pb présentent des fluctuations restreintes le long du littoral à l'exception de quelques mesures extrêmes, alors que les concentrations internes aux organismes en Cu, Ni et Zn semblent être plus variables selon les sites (Figure 28-B). La capacité de stockage des ETM est susceptible d'être modulée par l'âge, le sexe de l'organisme par exemple (Eggleton and Thomas, 2004). Le dosage en ETM sur les 3 groupes de tailles montre que le groupe intermédiaire présente des teneurs tous ETM confondus significativement plus faibles que le premier groupe de taille (Figure 28-C). Ce groupe intermédiaire met potentiellement en jeu des mécanismes plus performants pour limiter l'internalisation (Redmond et al., 2017) ou éliminer la contamination intégrée (Richir and Gobert, 2016). Néanmoins, l'hypothèse selon laquelle plus la taille de l'organisme augmente, plus la concentration diminue n'est pas vérifiée ici puisqu'il n'y a pas de différence significative entre les contaminations des groupes 1 et 3. Ces résultats indiquent que les dosages en ETM sur *C. fluminea* et l'interprétation au regard des fractions bioaccumulées de la contamination ambiante doivent se faire avec précaution sur un échantillon de taille uniforme.

3. Littérature

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Annexe III - Les différentes fonctions créées au cours de la thèse

1. Fonctions

```
source("tox_proxy.R")
```

Data example

```
PAH<-c(124,679,31.283,109.788,1965.735,575.459,5280.299,3526.032,3361.911,
2781.375,
       2859.396,1641.107,3131.570,1243.068,2050.682)
names(PAH)<-c("Nap","Ace","Flu","Phe","Ant","Fla","Pyr","BaA","Chr","BbjF"
,"BkF","BaP","Ip","BghiP","DbahA")

TME<-   c(1.06,10.12,60.79,14.05,49.81,38.86)
names(TME)<-c("Cd","Cr","Cu","Ni","Pb","Zn")

PCB<-c(121,324,87,154,79,54,61)
names(PCB)<-c("PCB28","PCB52","PCB101","PCB118","PCB138","PCB153","PCB180"
)

data_contam_example<-list(PAH=PAH,PCB=PCB,TME=TME)
```

The function “PAHfun”

The function considers a series of 15 PAH typically present in aquatic sediment accounted in the priority list of the USEPA and computes

[1] The sum of the 15 ratios TEC and PEC for the different PAHs (SUM_TEC and SUM_PEC)
and the mean of the 15 ratios TEC and PEC or the different PAHs (MQ_TEC and MQ_PEC)

[2] TOT_PAH_TEC and TOT_PAH_PEC: the ratio between the sum of the PAH concentrations
and the total TEC/PEC values
TEC and PEC values originate from MacDonald et al. (2000)

[3] Miscellaneous PAH ratios proposed by Abdel-shafy et al. (2016), Akyuz et al. (2010), Giao et al. (2006), Ravindra et al. (2008), Tobiszewski (2012), Unker et al. (2002) and Zhang et al.(2008)

According to the literature, the ratios can be interpreted as follows:
Flu_Ant_Phe_Fla/PAH: value towards 1 –> predominance of petrogenic PAHs
Ip/Ip_BghiP: < 0.20 petrogenic, 0.20-0.50 burning fuel, >0.50 wood and coal combustion
Fla_Phe_Pyr/PAH: value towards 1 –> predominance of petrogenic PAHs
BaP/BghiP: <0.6 non-traffic emissions, >0.6 traffic emissions

Fla_Pyr_BaA_Chr_BkF_BbjF_BaP_Ip_BghiP/PAH: < 0.3 petrogenic, > 0.7 pyrogenic, = 1 combustion
Flu/Flu_Pyr: <0.5 petrol emissions, >0.5 diesel emissions
Fla/Pyr: <<1 petrogenic, >=1 pyrogenic
BaA/BaA_Chr: <0.20 petrogenic, 0.20-0.35 coal combustion, >0.35 vehicle emissions or combustion
Phe/Ant: >5 petrogenic, <5 pyrogenic
BaA/Chr: decreases from urban to rural sites
BbjF/BkF: 0.92-2.67 wood and coal combustion, 2.5-2.9 aluminium melting BbjF/c178: <0.10 petroleum, >0.10 combustion
Fla/Fla_Pyr: <0.4 petrogenic, 0.4-0.5 combustion, >0.5 pyrogenic
Nap_Ace_Flu_Phe_Ant/Fla_Pyr_BaA_Chr_BbjF_BkF_BaP: <1 pyrogenic, >1petrogenic
The function returns:
[1] SUM_TEC and SUM_PEC / MQ_TEC and MQ_PEC / TOT_PAH_TEC and TOT_PAH_PEC
[2] TEC and PEC ratios for each PAH
[3] PAH ratios

If available the Total Organic Carbon (TOC) can be used in the function to normalize sediment-borne PAH concentrations to 1% TOC

Arguments are :
PAH = numerical vector of 15 PAH named by their official abbreviations
and expressed in micrograms per kilogram of dry mass of sediment (see example)
TOC = the total organic carbon measured in the sediment, if not TOC = NA

```
PAHfun=function(PAH,TOC){

  if(is.na(TOC)){

    TEC_PAH<-c(176,6.7,77.4,176,57.2,423,195,108,166,240,240,150,170,33,20
0)
    names(TEC_PAH)<-c("Nap","Ace","Flu","Phe","Ant","Fla","Pyr","BaA","Chr
","BbjF","BkF","BaP","Ip","BghiP","DbahA")

    TEC<-data.frame(round(PAH/TEC_PAH,4));names(TEC)<-c("TEC")
    SUM_TEC<-sum(TEC)
    MQ_TEC<-colMeans(TEC)

    PEC_PAH<-c(561,128,536,561,845,2230,1520,1050,1290,13400,13400,1450,32
00,135,3200)
    names(PEC_PAH)<-c("Nap","Ace","Flu","Phe","Ant","Fla","Pyr","BaA","Chr
","BbjF","BkF","BaP","Ip","BghiP","DbahA")

    PEC<-data.frame(round(PAH/PEC_PAH,4));names(PEC)<-c("PEC")
    SUM_PEC<-sum(PEC)
    MQ_PEC<-colMeans(PEC)

    TOT_PAH<-c(1610,22800)
    TOT<-round(sum(PAH)/TOT_PAH,4)
```

```
    Flu_Ant_Phe_Fla_d_PAH<-round(sum(PAH[c("Flu","Ant","Phe","Fla")])/sum(
PAH),3)
    Ip_d_Ip_BghiP<-round(sum(PAH["Ip"])/sum(PAH[c("Ip","BghiP")]),3)
    Fla_Phe_Pyr_d_PAH<-round(sum(PAH[c("Fla","Phe","Pyr")])/sum(PAH),3)
    BaP_d_BghiP<-round(sum(PAH["BaP"])/sum(PAH["BghiP"]),3)
    Fla_Pyr_BaA_Chr_BkF_BbjF_BaP_Ip_BghiP_d_PAH<-round(sum(PAH[c("Fla","Py
r","BaA","Chr","BkF","BbjF","BaP","Ip","BghiP")])/sum(PAH),3)
    Flu_d_Flu_Pyr<-round(sum(PAH["Flu"])/sum(PAH[c("Flu","Pyr")]),3)
    Fla_d_Pyr<-round(sum(PAH["Fla"])/sum(PAH["Pyr"]),3)
    BaA_d_BaA_Chr<-round(sum(PAH["BaA"])/sum(PAH[c("BaA","Chr")]),3)
    Phe_d_Ant<-round(sum(PAH["Phe"])/sum(PAH["Ant"]),3)
    BaA_d_Chr<-round(sum(PAH["BaA"])/sum(PAH["Chr"]),3)
    BbjF_d_BkF<-round(sum(PAH["BbjF"])/sum(PAH["BkF"]),3)
    BbjF_d_m178<-round(sum(PAH["BbjF"])/178,3)
    Fla_d_Fla_Pyr<-round(sum(PAH["Fla"])/sum(PAH[c("Fla","Pyr")]),3)
    Nap_Ace_Flu_Phe_Ant_d_Fla_Pyr_BaA_Chr_BbjF_BkF_BaP<-round(sum(PAH[c("N
ap","Ace","Flu","Phe","Ant")])/sum(PAH[c("Fla","Pyr","BaA","Chr","BbjF","B
kF","BaP")]),3)

    ratios<-data.frame(c(Flu_Ant_Phe_Fla_d_PAH=Flu_Ant_Phe_Fla_d_PAH,Ip_d_
Ip_BghiP=Ip_d_Ip_BghiP,Fla_Phe_Pyr_d_PAH=Fla_Phe_Pyr_d_PAH,BaP_d_BghiP=BaP
_d_BghiP,
                         Fla_Pyr_BaA_Chr_BkF_BbjF_BaP_Ip_BghiP_d_PAH=Fla_P
yr_BaA_Chr_BkF_BbjF_BaP_Ip_BghiP_d_PAH,Flu_d_Flu_Pyr=Flu_d_Flu_Pyr,
                         Fla_d_Pyr=Fla_d_Pyr,BaA_d_BaA_Chr=BaA_d_BaA_Chr,P
he_d_Ant=Phe_d_Ant,BaA_d_Chr=BaA_d_Chr,BbjF_d_BkF=BbjF_d_BkF,BbjF_d_m178=B
bjF_d_m178,
                         Fla_d_Fla_Pyr=Fla_d_Fla_Pyr,Nap_Ace_Flu_Phe_Ant_d
_Fla_Pyr_BaA_Chr_BbjF_BkF_BaP=Nap_Ace_Flu_Phe_Ant_d_Fla_Pyr_BaA_Chr_BbjF_B
kF_BaP));names(ratios)<-"Value"
  }
  else
    {
      PAH2<-PAH/TOC

      TEC_PAH<-c(176,6.7,77.4,176,57.2,423,195,108,166,240,240,150,170,33,
200)
      names(TEC_PAH)<-c("Nap","Ace","Flu","Phe","Ant","Fla","Pyr","BaA","C
hr","BbjF","BkF","BaP","Ip","BghiP","DbahA")

      TEC<-data.frame(round(PAH2/TEC_PAH,4));names(TEC)<-c("TEC")
      SUM_TEC<-sum(TEC)
      MQ_TEC<-colMeans(TEC)

      PEC_PAH<-c(561,128,536,561,845,2230,1520,1050,1290,13400,13400,1450,
3200,135,3200)
      names(PEC_PAH)<-c("Nap","Ace","Flu","Phe","Ant","Fla","Pyr","BaA","C
hr","BbjF","BkF","BaP","Ip","BghiP","DbahA")

      PEC<-data.frame(round(PAH2/PEC_PAH,4));names(PEC)<-c("PEC")
      SUM_PEC<-sum(PEC)
      MQ_PEC<-colMeans(PEC)
```

```
      TOT_PAH<-c(1610,22800)
      TOT<-round(sum(PAH2)/TOT_PAH,4)

      Flu_Ant_Phe_Fla_d_PAH<-round(sum(PAH2[c("Flu","Ant","Phe","Fla")])/s
um(PAH2),3)
      Ip_d_Ip_BghiP<-round(sum(PAH2["Ip"])/sum(PAH2[c("Ip","BghiP")]),3)
      Fla_Phe_Pyr_d_PAH<-round(sum(PAH2[c("Fla","Phe","Pyr")])/sum(PAH2),3
)
      BaP_d_BghiP<-round(sum(PAH2["BaP"])/sum(PAH2["BghiP"]),3)
      Fla_Pyr_BaA_Chr_BkF_BbjF_BaP_Ip_BghiP_d_PAH<-round(sum(PAH2[c("Fla",
"Pyr","BaA","Chr","BkF","BbjF","BaP","Ip","BghiP")])/sum(PAH2),3)
      Flu_d_Flu_Pyr<-round(sum(PAH2["Flu"])/sum(PAH2[c("Flu","Pyr")]),3)
      Fla_d_Pyr<-round(sum(PAH2["Fla"])/sum(PAH2["Pyr"]),3)
      BaA_d_BaA_Chr<-round(sum(PAH2["BaA"])/sum(PAH2[c("BaA","Chr")]),3)
      Phe_d_Ant<-round(sum(PAH2["Phe"])/sum(PAH2["Ant"]),3)
      BaA_d_Chr<-round(sum(PAH2["BaA"])/sum(PAH2["Chr"]),3)
      BbjF_d_BkF<-round(sum(PAH2["BbjF"])/sum(PAH2["BkF"]),3)
      BbjF_d_m178<-round(sum(PAH2["BbjF"])/178,3)
      Fla_d_Fla_Pyr<-round(sum(PAH2["Fla"])/sum(PAH2[c("Fla","Pyr")]),3)
      Nap_Ace_Flu_Phe_Ant_d_Fla_Pyr_BaA_Chr_BbjF_BkF_BaP<-round(sum(PAH2[c
("Nap","Ace","Flu","Phe","Ant")])/sum(PAH2[c("Fla","Pyr","BaA","Chr","BbjF
","BkF","BaP")]),3)

      ratios<-data.frame(c(Flu_Ant_Phe_Fla_d_PAH=Flu_Ant_Phe_Fla_d_PAH,Ip_
d_Ip_BghiP=Ip_d_Ip_BghiP,Fla_Phe_Pyr_d_PAH=Fla_Phe_Pyr_d_PAH,BaP_d_BghiP=B
aP_d_BghiP,
                           Fla_Pyr_BaA_Chr_BkF_BbjF_BaP_Ip_BghiP_d_PAH=Fla
_Pyr_BaA_Chr_BkF_BbjF_BaP_Ip_BghiP_d_PAH,Flu_d_Flu_Pyr=Flu_d_Flu_Pyr,
                           Fla_d_Pyr=Fla_d_Pyr,BaA_d_BaA_Chr=BaA_d_BaA_Chr
,Phe_d_Ant=Phe_d_Ant,BaA_d_Chr=BaA_d_Chr,BbjF_d_BkF=BbjF_d_BkF,BbjF_d_m178
=BbjF_d_m178,
                           Fla_d_Fla_Pyr=Fla_d_Fla_Pyr,Nap_Ace_Flu_Phe_Ant
_d_Fla_Pyr_BaA_Chr_BbjF_BkF_BaP=Nap_Ace_Flu_Phe_Ant_d_Fla_Pyr_BaA_Chr_BbjF
_BkF_BaP));names(ratios)<-"Values"
    }

  results<-round(c(SUM_TEC,MQ_TEC,SUM_PEC,MQ_PEC,TOT),4);names(results)<-c
("SUM_TEC","MQ_TEC","SUM_PEC","MQ_PEC","TOT_PAH_TEC","TOT_PAH_PEC")

  list(Risk_eco=data.frame(results=results),onePAH=data.frame(TEC_PAH,PEC_
PAH),Ratios=data.frame(ratios))
}
```

The function “PCBfun”

The function considers 7 PCBs to compute
[1] 2 ratios between the PCB-borne sediment concentrations and
both 1) Treshold Effect Concentration (TEC) and 2) Probable Effect Concentration (PEC)

TEC and PEC values originate from MacDonald et al. (2000)

[2] 2 ratios regarding the possible origin of PCBs according to Naffrechoux et al. (2015) Ratio 1: the sum of the light over the total PCB excluding PCB 101 and 118
Ratio2: the sum of the light over the total PCB

PCBs must by names by their official abbreviations and expressed
in micrograms per kilogram of dry mass of sediment (see example)

The sum of the 7 PCBs can be multiplied by 2 to estimate the total PCB contamination according to Afssa - Saisine n° 2002-SA-0149

If available the Total Organic Carbon (TOC) can be used in the function to normalize sediment-borne PCB concentrations to 1% TOC
Arguments are :
PCB = numerical vector of 7 TME (see example) named by their official abbreviations and expressed in micrograms per kilogram of dry mass of sediment
TOC = the total organic carbon measured in the sediment, if not TOC = NA
consider_all_PCB = a logical value (TRUE or FALSE) indicating wether the sum of actual PCBs must be multiplied by 2 as a surrogate of total PCBs

```
PCBfun=function(PCB, TOC,consider_all_PCB){

if(consider_all_PCB==TRUE){

  PCB2<-PCB*2

  if(is.na(TOC)){
    #total PCB TEC and PEC
    TOT_PCB<-c(59.8,676)
    results<-c(round(c(sum(PCB2),sum(PCB2)/TOT_PCB),3),
    round(sum(PCB2[c("PCB28","PCB52")])/sum(PCB2[c("PCB28","PCB52","PCB138
","PCB153","PCB180")]),3),round(sum(PCB[c("PCB28","PCB52")])/sum(PCB),3))
    names(results)<-c("TOT_PCB","TOT_PCB_TEC","TOT_PCB_PEC","LH_excl_101_1
18","LH")

  }else
    {
    PCB3<-PCB2/TOC
    TOT_PCB<-c(59.8,676)
    results<-c(round(c(sum(PCB3),sum(PCB3)/TOT_PCB),3),
               round(sum(PCB3[c("PCB28","PCB52")])/sum(PCB3[c("PCB28","PCB
52","PCB138","PCB153","PCB180")]),3),round(sum(PCB[c("PCB28","PCB52")])/su
m(PCB),3))
    names(results)<-c("TOT_PCB","TOT_PCB_TEC","TOT_PCB_PEC","LH_excl_101_1
18","LH")

     }

}else
  {

  if(is.na(TOC)){
    TOT_PCB<-c(59.8,676)
```

```
    results<-c(round(c(sum(PCB),sum(PCB)/TOT_PCB),3),
                round(sum(PCB[c("PCB28","PCB52")])/sum(PCB[c("PCB28","PCB52
","PCB138","PCB153","PCB180")]),3),round(sum(PCB[c("PCB28","PCB52")])/sum(
PCB),3))
    names(results)<-c("TOT_PCB","TOT_PCB_TEC","TOT_PCB_PEC","LH_excl_101_1
18","LH")

  }else
    {
      PCB4<-PCB/TOC
      TOT_PCB<-c(59.8,676)
      results<-c(round(c(sum(PCB4),sum(PCB4)/TOT_PCB),3),
                  round(sum(PCB4[c("PCB28","PCB52")])/sum(PCB4[c("PCB28","P
CB52","PCB138","PCB153","PCB180")]),3),round(sum(PCB[c("PCB28","PCB52")])/
sum(PCB),3))
      names(results)<-c("TOT_PCB","TOT_PCB_TEC","TOT_PCB_PEC","LH_excl_101
_118","LH")

  }
  }
  return(data.frame(results=results))
}
```

The function “TMEfun”

The functionconsiders a series of 6 trace metal elements (TME) typically
present in aquatic sediment and computes
the sum of the 6 ratios TEC and PEC for the different TME (SUM_TEC and SUM_PEC)
and the mean of the 6 ratios TEC and PEC or the different TME (MQ_TEC and MQ_PEC)

TEC and PEC values originate from MacDonald et al. (2000)

If available the Total Organic Carbon (TOC) can be used in the function to normalize
sediment-borne TME concentrations to 1% TOC

The function returns:
[1] SUM_TEC and SUM_PEC / MQ_TEC and MQ_PEC
[2] TEC and PEC ratios for each TME

Arguments are :
TME = numerical vector of 6 TME (see example) named by their official abbreviations
and expressed in milligrams per kilogram of dry mass of sediment
TOC = the total organic carbon measured in the sediment, if not TOC = NA

```
TMEfun=function(TME,TOC){

  if(is.na(TOC)){
TEC_TME<-c(0.99,43.4,31.6,22.7,35.8,121);names(TEC_TME)<-c("Cd","Cr","Cu",
"Ni","Pb","Zn")
TEC<-data.frame(round(TME/TEC_TME,3));names(TEC)<-c("TEC")
SUM_TEC<-round(sum(TEC),3)
MQ_TEC<-round(colMeans(TEC),3)
```

```
PEC_TME<-c(4.98,111,149,48.6,128,459);names(PEC_TME)<-c("Cd","Cr","Cu","Ni
","Pb","Zn")
PEC<-data.frame(round(TME/PEC_TME,3));names(PEC)<-c("PEC")
SUM_PEC<-round(sum(PEC),3)
MQ_PEC<-round(colMeans(PEC),3)

  }else{

    TME2<-TME/TOC

    TEC_TME<-c(0.99,43.4,31.6,22.7,35.8,121);names(TEC_TME)<-c("Cd","Cr","
Cu","Ni","Pb","Zn")
    TEC<-data.frame(round(TME2/TEC_TME,3));names(TEC)<-c("TEC")
    SUM_TEC<-round(sum(TEC),3)
    MQ_TEC<-round(colMeans(TEC),3)

    PEC_TME<-c(4.98,111,149,48.6,128,459);names(PEC_TME)<-c("Cd","Cr","Cu"
,"Ni","Pb","Zn")
    PEC<-data.frame(round(TME2/PEC_TME,3));names(PEC)<-c("PEC")
    SUM_PEC<-round(sum(PEC),3)
    MQ_PEC<-round(colMeans(PEC),3)

  }


  list(Risk_eco=data.frame(SUM_TEC=SUM_TEC,MQ_TEC=MQ_TEC,SUM_PEC=SUM_PEC,M
Q_PEC=MQ_PEC),
       oneTME=data.frame(data.frame(TEC,PEC)))
}
```

The function "bioacc"

The function computes 3 bio-accumulation metrics:

[1] BCF = bioconcentration factor according to Fan et al. (2017),
Mendoza-Carranza et al. (2016), Mountouris et al. (2002)

[2] BAF = bioaccumulation factor according to La Guardia et al. (2012)
[3] BSAF = biota-Sediment Accumulation Factor according to La Guardia et al. (2012)

The lipid content (%) of organism is estimated according to Post et al. (2007)
based on CN ratio

LOI of the organism is estimated from TOC of the organism according to Dean (1974)

Arguments are:
contam_sed = contaminant concentration in the sediment
contam_orga = contaminant concentration in the organism
TOC = total organic carbon concentration of the organism
CN = Carbon to Nitrogen ratio of the organism
Kp = Equilibrium constant

Koc = Soil Organic Carbon-Water Partitioning coefficient
TME = logical value (True or FALSE) to indicate if the contaminant is a TME or not

if TOC, Koc, Kp, and/or CN are missing, hese arguments must be labelled as “NA”

```
bioacc=function(contam_sed,contam_orga,TOC,Koc,Kp,CN,TME){

  BCF<-contam_orga/contam_sed

  LOI<-2.13*TOC


  lipid_percent<-20.54+7.24*CN

  if(TME==TRUE){

     BAF<-(contam_orga/lipid_percent*Kp)/contam_sed
     BSAF<-(contam_orga/lipid_percent*LOI)/contam_sed
  }else{
    BAF<-(contam_orga/lipid_percent*LOI*Koc)/contam_sed
    BSAF<-(contam_orga/lipid_percent*LOI)/contam_sed
  }

  return(data.frame(BCF=BCF,BAF=BAF,BSAF=BSAF))
}
```

Contaminant metrics

Diverse metrics characterizing different contaminants :
15 PAHs, 6 TMEs and 7 PCBs
that are :
Kp = Equilibrium constant
Koc = Soil Organic Carbon-Water Partitioning coefficient
Kow = Octanol-Water partition coefficient
H = Henry constant

References
Sander, R. Atmos. Chem. Phys. April 30, 2015
Hawker, D. W. & Connell, D. W. Environ. Sci. Technol. 1988
Shoeib, M., and Harner, T. Environ. Sci. Technol. 2002
Seth, D Mackay, J Muncke - Environmental Science & Technology, 1999

```
H<-c(34.49,26.46,33.39,39.93,25.58,23.31,17.92,36.5,14.8,6.5,2.9,3.3,0.7,1
.1,0.8,0.1,0.1,0.7,1.2,0.4,0.2,0.8)
logKow<-c(5.67,5.84,6.38,6.74,6.83,6.92,7.36,3.37,3.92,4.18,4.57,4.54,5.22
,5.18,5.91,5.86,5.9,5.9,6.04,6.5,6.5,6.75)
logKoa<-c(8.03893088020134,8.35133907483222,9.10821892818792,9.86433348993
289,10.0426034375839,9.81681751510067,10.5864777036913,4.8,5.7,6.3,6.7,6.7
,7.5,7.4,8.6,8.6,9.4,9.5,9.2,10.1,9.8,10.6)
logKoc<-c(1.9845,2.044,2.233,2.359,2.3905,2.422,2.576,1.1795,1.372,1.463,1
.5995,1.589,1.827,1.813,2.0685,2.051,2.065,2.065,2.114,2.275,2.275,2.3625)
```

```
metrics<-rbind(H,logKow,logKoa,logKoc)
colnames(metrics)<-c("PCB28","PCB52","PCB101","PCB118","PCB138","PCB153","
PCB180","Nap","Ace","Flu","Phe","Ant","Fla","Pyr","BaA","Chr","BbjF","BkF"
,"BaP","Ip","BghiP","DbahA")

Kp_TME<-c(130,290,50,8,640,110);names(Kp_TME)<-c("Cd","Cr","Cu","Ni","Pb",
"Zn")
Koc_PCB<-c(192239,284343,2258613,985920,2778701,3418549,9415466);names(Koc
_PCB)<-c("PCB28","PCB52","PCB101","PCB118","PCB138","PCB153","PCB180")
Koc_PAH<-c(1991,1472,13709,31189,28642,99541,69024,377572,413048,1445440,1
527566,1006932,4055085,2494595,3971915)
names(Koc_PAH)<-c("Nap","Ace","Flu","Phe","Ant","Fla","Pyr","BaA","Chr","B
bjF","BkF","BaP","Ip","BghiP","DbahA")


contaminant_metrics<-list(metrics=metrics,Kp_TME=Kp_TME,Koc_PCB=Koc_PCB,Ko
c_PAH=Koc_PAH)
```

The function “distrib”

The function fit a normal and a logormal distribution to the data and assess the best fit using AIC
data must be a vector with or without NA or not

```
distrib=function(data){
  library(fitdistrplus)
  if(which.min(c(fitdist(as.numeric(na.omit(data)),"norm",method="mle")$ai
c,
                 fitdist(as.numeric(na.omit(data)),"lnorm",method="mle")$a
ic))==1){result<-"normal"}
  else{result<-"lognormal"}
  return(result)
}
```

Function “NDsolve”

The function aims at estimating values of a dataset which are below the quantification limit (LQ) using two possible distributions (i.e. normal or lognormal) estimated from the actual dataset.
Two options to retrieve the estimated values are possible:
the surrogate data are sampled over a range from the minimal value of the surrogate distribution to LQ either randomly along the range (opt1) or regularly (opt2)
Arguments are :
data = a vector of numerical values with the presence of NA
LQ = the quantification limit
method = the distribution to be considered either “normal” or “lognormal” reg = logical value indicating either surrogate points must be sampled randomly (FALSE) or regularly (TRUE)

```
NDsolve=function(data,LQ, method,reg){
  library(MASS)

  if(reg==FALSE){
    if(method=="normal")
    {
      est<- fitdistr(as.numeric(na.omit(data)),method)
      res<-rnorm(10000, mean=est$estimate[1], sd=est$estimate[2])
      for (i in 1:length(data)){
        if(is.na(data[i])){data[i]<-sample(res[which(res<LQ & res>0)],1)}
      }
    }
    if(method=="lognormal")
    {
      est<- fitdistr(as.numeric(na.omit(data)),method)
      res<-rlnorm(10000, meanlog=est$estimate[1], sdlog=est$estimate[2])
      for (i in 1:length(data)){
        if(is.na(data[i])){data[i]<-sample(res[which(res<LQ & res>0)],1)}
      }
    }
  }

  if(reg==TRUE){
    if(method=="normal")
    {
      est<- fitdistr(as.numeric(na.omit(data)),method)
      res<-rnorm(10000, mean=est$estimate[1], sd=est$estimate[2])
      Lna<-length(which(is.na(data)))
      LLQest<-length(res[which(res<LQ & res>0)])
      estimpoints<-round(seq(from=1,to=LLQest,by=LLQest/Lna),0)
      data[c(which(is.na(data)))]<- sort(res[which(res<LQ & res>0)],decrea
sing=T)[estimpoints]

    }
    if(method=="lognormal")
    {
      est<- fitdistr(as.numeric(na.omit(data)),method)
      res<-rlnorm(10000, meanlog=est$estimate[1], sdlog=est$estimate[2])
      Lna<-length(which(is.na(data)))
      LLQest<-length(res[which(res<LQ & res>0)])
      estimpoints<-round(seq(from=1,to=LLQest,by=LLQest/Lna),0)
      data[c(which(is.na(data)))]<- sort(res[which(res<LQ & res>0)],decrea
sing=T)[estimpoints]
    }
  }
  return(data.frame(data=data))
}
```

Function “NDsolveCorr”

The function aims at estimating values of a dataset which are below the quantification limit (LQ) using two possible distributions (i.e. normal or lognormal) estimated from the actual dataset.

Two options to retrieve the estimated values are possible:
the surrogate data are sampled over a range from the minimal value of the surrogate
distribution to LQ either randomly along the range (opt1) or regularly (opt2)
The function also account for constant biais
of the “fitdistr” (MASS package) when inferring “mean” and “sd” parameters
for the surrogate distributions, a specific correction is then applied for each of the parameter
of the two distributions

Arguments are :
data = a vector of numerical values with the presence of NA
LQ = the quantification limit
method = the distribution to be considered either “normal” or “lognormal”
reg = logical value indicating either surrogate points must be sampled randomly (FALSE) or
regularly (TRUE)

```
NDsolveCorr=function(data,LQ, method,reg){
  library(MASS)

  if(reg==FALSE){
    if(method=="normal")
    {
      est<- fitdistr(as.numeric(na.omit(data)),method)
      res<-rnorm(10000, mean=est$estimate[1]*0.95, sd=est$estimate[2]*1.24
9)
      for (i in 1:length(data)){
        if(is.na(data[i])){data[i]<-sample(res[which(res<LQ & res>0)],1)}
      }
    }
    if(method=="lognormal")
    {
      est<- fitdistr(as.numeric(na.omit(data)),method)
      res<-rlnorm(10000, meanlog=log(exp(est$estimate[1])*0.89), sdlog=log
(exp(est$estimate[2])*1.272))
      for (i in 1:length(data)){
        if(is.na(data[i])){data[i]<-sample(res[which(res<LQ & res>0)],1)}
      }
    }
  }

  if(reg==TRUE){
    if(method=="normal")
    {
      est<- fitdistr(as.numeric(na.omit(data)),method)
      res<-rnorm(10000, mean=est$estimate[1]*0.95, sd=est$estimate[2]*1.24
9)
      Lna<-length(which(is.na(data)))
      LLQest<-length(res[which(res<LQ & res>0)])
      estimpoints<-round(seq(from=1,to=LLQest,by=LLQest/Lna),0)
      data[c(which(is.na(data)))]<- sort(res[which(res<LQ & res>0)],decrea
sing=T)[estimpoints]
    }
    if(method=="lognormal")
```

```
    {
      est<- fitdistr(as.numeric(na.omit(data)),method)
      res<-rlnorm(10000, meanlog=log(exp(est$estimate[1])*0.89), sdlog=log
(exp(est$estimate[2])*1.272))
      Lna<-length(which(is.na(data)))
      LLQest<-length(res[which(res<LQ & res>0)])
      estimpoints<-round(seq(from=1,to=LLQest,by=LLQest/Lna),0)
      data[c(which(is.na(data)))]<- sort(res[which(res<LQ & res>0)],decrea
sing=T)[estimpoints]
    }
  }
  return(data.frame(data=data))
}
```

2. Utilisation des fonctions

```
source("tox_proxy.R")
```

Data available for example for three families of contaminants

```
data_contam_example

## $PAH
##      Nap      Ace      Flu      Phe      Ant      Fla      Pyr      BaA

##  124.000  679.000   31.283  109.788 1965.735  575.459 5280.299 3526.032

##      Chr     BbjF      BkF      BaP       Ip    BghiP    DbahA
## 3361.911 2781.375 2859.396 1641.107 3131.570 1243.068 2050.682
##
## $PCB
##  PCB28  PCB52 PCB101 PCB118 PCB138 PCB153 PCB180
##    121    324     87    154     79     54     61
##
## $TME
##    Cd    Cr    Cu    Ni    Pb    Zn
##  1.06 10.12 60.79 14.05 49.81 38.86
```

Functions for PAH, PCB and TME

```
PAHfun(PAH=data_contam_example$PAH,TOC=2)

## $Risk_eco
##              results
## SUM_TEC     159.7843
## MQ_TEC       10.6523
## SUM_PEC      15.0913
## MQ_PEC        1.0061
## TOT_PAH_TEC   9.1182
## TOT_PAH_PEC   0.6439
##
## $onePAH
```

```
##       TEC_PAH PEC_PAH
## Nap     176.0     561
## Ace       6.7     128
## Flu      77.4     536
## Phe     176.0     561
## Ant      57.2     845
## Fla     423.0    2230
## Pyr     195.0    1520
## BaA     108.0    1050
## Chr     166.0    1290
## BbjF    240.0   13400
## BkF     240.0   13400
## BaP     150.0    1450
## Ip      170.0    3200
## BghiP    33.0     135
## DbahA   200.0    3200
##
## $Ratios
##                                                    Values
## Flu_Ant_Phe_Fla_d_PAH                               0.091
## Ip_d_Ip_BghiP                                       0.716
## Fla_Phe_Pyr_d_PAH                                   0.203
## BaP_d_BghiP                                         1.320
## Fla_Pyr_BaA_Chr_BkF_BbjF_BaP_Ip_BghiP_d_PAH         0.831
## Flu_d_Flu_Pyr                                       0.006
## Fla_d_Pyr                                           0.109
## BaA_d_BaA_Chr                                       0.512
## Phe_d_Ant                                           0.056
## BaA_d_Chr                                           1.049
## BbjF_d_BkF                                          0.973
## BbjF_d_m178                                         7.813
## Fla_d_Fla_Pyr                                       0.098
## Nap_Ace_Flu_Phe_Ant_d_Fla_Pyr_BaA_Chr_BbjF_BkF_BaP  0.145
```

```
PAHfun(PAH=data_contam_example$PAH,TOC=NA)
```

```
## $Risk_eco
##              results
## SUM_TEC     319.5687
## MQ_TEC       21.3046
## SUM_PEC      30.1824
## MQ_PEC        2.0122
## TOT_PAH_TEC  18.2365
## TOT_PAH_PEC   1.2878
##
## $onePAH
##       TEC_PAH PEC_PAH
## Nap     176.0     561
## Ace       6.7     128
## Flu      77.4     536
## Phe     176.0     561
## Ant      57.2     845
## Fla     423.0    2230
## Pyr     195.0    1520
```

```
## BaA     108.0    1050
## Chr     166.0    1290
## BbjF    240.0   13400
## BkF     240.0   13400
## BaP     150.0    1450
## Ip      170.0    3200
## BghiP    33.0     135
## DbahA   200.0    3200
##
## $Ratios
##                                                    Value
## Flu_Ant_Phe_Fla_d_PAH                              0.091
## Ip_d_Ip_BghiP                                      0.716
## Fla_Phe_Pyr_d_PAH                                  0.203
## BaP_d_BghiP                                        1.320
## Fla_Pyr_BaA_Chr_BkF_BbjF_BaP_Ip_BghiP_d_PAH        0.831
## Flu_d_Flu_Pyr                                      0.006
## Fla_d_Pyr                                          0.109
## BaA_d_BaA_Chr                                      0.512
## Phe_d_Ant                                          0.056
## BaA_d_Chr                                          1.049
## BbjF_d_BkF                                         0.973
## BbjF_d_m178                                       15.626
## Fla_d_Fla_Pyr                                      0.098
## Nap_Ace_Flu_Phe_Ant_d_Fla_Pyr_BaA_Chr_BbjF_BkF_BaP 0.145

PCBfun(PCB=data_contam_example$PCB, TOC=2,consider_all_PCB=TRUE)

##                 results
## TOT_PCB         880.000
## TOT_PCB_TEC      14.716
## TOT_PCB_PEC       1.302
## LH_excl_101_118   0.696
## LH                0.506

PCBfun(PCB=data_contam_example$PCB, TOC=NA,consider_all_PCB=TRUE)

##                  results
## TOT_PCB         1760.000
## TOT_PCB_TEC       29.431
## TOT_PCB_PEC        2.604
## LH_excl_101_118    0.696
## LH                 0.506

PCBfun(PCB=data_contam_example$PCB,TOC=NA,consider_all_PCB=FALSE)

##                 results
## TOT_PCB         880.000
## TOT_PCB_TEC      14.716
## TOT_PCB_PEC       1.302
## LH_excl_101_118   0.696
## LH                0.506

TMEfun(TME=data_contam_example$TME,TOC=NA)
```

```
## $Risk_eco
##     SUM_TEC MQ_TEC SUM_PEC MQ_PEC
## TEC   5.559  0.926   1.475  0.246
##
## $oneTME
##      TEC   PEC
## Cd 1.071 0.213
## Cr 0.233 0.091
## Cu 1.924 0.408
## Ni 0.619 0.289
## Pb 1.391 0.389
## Zn 0.321 0.085
```

Functions to estimate different factors of bioaccumulation

```
bioacc(contam_sed=10,contam_orga=20,TOC=2,Koc=6,Kp=3,CN=5,TME=TRUE)
```

```
##   BCF       BAF      BSAF
## 1   2 0.1057455 0.1501586
```

```
bioacc(contam_sed=10,contam_orga=20,TOC=2,Koc=6,Kp=3,CN=5,TME=FALSE)
```

```
##   BCF       BAF      BSAF
## 1   2 0.9009517 0.1501586
```

```
bioacc(contam_sed=10,contam_orga=20,TOC=NA,Koc=6,Kp=NA,CN=5,TME=FALSE)
```

```
##   BCF BAF BSAF
## 1   2  NA   NA
```

```
bioacc(contam_sed=10,contam_orga=20,TOC=10,Koc=6,Kp=NA,CN=10,TME=FALSE)
```

```
##   BCF      BAF      BSAF
## 1   2 2.750161 0.4583602
```

Functions to estimates values below quantification limits

```
# Simulating contamination
simLN<-rlnorm(500,meanlog=log(10),sdlog=log(1.7))
LQ<-10 # Quantification limit

hist(simLN)
abline(v=LQ,col="red")

#Introduce NA for data below LQ
simLQLN<-simLN
simLQLN[which(simLQLN<LQ)]<-NA
simLQLN
```

```
##   [1]       NA 12.57694 11.38187       NA       NA 10.14636 10.75975
##   [8] 13.78229 12.80683 14.00674 11.89884       NA 10.47802 14.93692
##  [15]       NA 18.27329 11.80405 17.56145       NA 19.63245 32.45857
##  [22]       NA 14.82246 15.47967       NA 20.43778       NA 25.81012
##  [29] 13.91795       NA       NA 14.57534 19.48989 14.23302 19.18332
##  [36] 17.85220       NA       NA       NA       NA 12.58156       NA
##  [43]       NA       NA 13.81996       NA       NA 27.03115 10.15617
##  [50] 21.17233 11.99605       NA       NA 12.64694       NA       NA
```

```
##  [57] 14.76030       NA       NA       NA 10.47694 10.43419       NA
##  [64]       NA       NA       NA 15.17362 12.55249       NA       NA
##  [71]       NA       NA       NA 13.39237 15.39454       NA 26.05602
##  [78]       NA       NA 82.50342       NA       NA 11.70108 23.05078
##  [85] 17.02738 11.36847       NA 11.04359 20.91439       NA       NA
##  [92] 15.45721 16.41014       NA 24.47189 15.51369       NA 23.16738
##  [99] 14.21648 11.37924       NA       NA       NA 10.09080       NA
## [106] 27.49912 27.74498       NA       NA       NA 16.94362       NA
## [113] 17.45452 10.36640       NA 33.95449       NA       NA 41.04353
## [120]       NA 14.38871 10.71151 14.01437 11.56536       NA 14.12743
## [127]       NA       NA       NA 13.67967 10.69005       NA       NA
## [134]       NA 10.73822 10.16859 31.28368       NA       NA 14.00560
## [141]       NA       NA 10.69980 10.73493 21.93612       NA 14.54292
## [148]       NA 11.46197       NA 17.30615       NA 13.08989       NA
## [155]       NA 11.50576 11.09855 26.34569       NA       NA 11.50641
## [162] 15.11480 43.90070       NA 11.38287 14.52470       NA 12.67832
## [169]       NA       NA 13.42045 16.24026 21.61578 17.25475 29.51618
## [176] 15.83805       NA       NA       NA 11.52557 10.86067 11.94456
## [183]       NA 14.55315       NA       NA 11.72421       NA 18.48922
## [190] 16.12730 13.96677       NA 13.72809       NA 15.36780       NA
## [197] 23.01772 10.22624       NA       NA 17.52487       NA 13.77417
## [204]       NA 16.79210 15.14919       NA       NA       NA 13.37699
## [211]       NA 10.13074       NA       NA 17.78745       NA       NA
## [218]       NA       NA       NA       NA       NA       NA       NA
## [225] 11.22770 10.59502 11.97554       NA       NA       NA       NA
## [232]       NA       NA 11.41991 15.65695 11.15563       NA 17.00018
## [239]       NA 27.81126 15.70542       NA       NA       NA       NA
## [246]       NA 29.48264 36.21688 13.03415       NA       NA 16.73899
## [253]       NA 14.44490       NA       NA       NA       NA 14.15295
## [260]       NA       NA       NA 17.49673 22.32355       NA 22.26296
## [267]       NA 32.09285 13.43036 31.10170 22.61785       NA       NA
## [274] 23.86441       NA       NA       NA 20.92274       NA 15.61600
## [281] 14.69539       NA       NA 51.94313       NA 13.72469       NA
## [288] 24.67641       NA       NA 12.81578       NA       NA 20.51253
## [295]       NA       NA 15.14055       NA 10.29324       NA       NA
## [302] 15.04972       NA       NA 14.83984       NA 11.95592       NA
## [309]       NA       NA 10.12833 10.28127       NA 36.07589       NA
## [316] 13.76202 12.75488 15.05640       NA 24.95201 31.82730 20.17490
## [323]       NA 11.53477 21.28920       NA       NA 10.34094 14.60613
## [330]       NA       NA       NA       NA 18.56260       NA       NA
## [337] 12.75717       NA 36.25692 10.52076       NA       NA 19.18586
## [344] 18.15602       NA 23.64462 10.96602       NA 14.93237 12.58566
## [351] 10.88377 11.94815 17.14115       NA       NA       NA       NA
## [358] 15.45654 13.79104 11.88804       NA 12.76730       NA 12.01074
## [365] 15.94636       NA 25.33176 11.88432 12.45039       NA 14.40494
## [372]       NA 29.95729       NA 11.94359 10.91223 11.11793 25.06443
## [379] 19.00882       NA 12.62685 11.54402       NA 10.51017 15.21281
## [386] 16.43652 39.75141       NA       NA       NA 15.79083 28.85267
## [393]       NA       NA       NA 10.84118 14.78229 20.14403       NA
## [400]       NA       NA       NA 10.98244       NA       NA       NA
## [407] 18.60627 11.52319       NA 17.51868 11.66105       NA 13.89180
## [414] 24.64788       NA 16.85296       NA 11.03057 10.84953       NA
## [421] 20.53742       NA 14.36429 16.79082       NA       NA 15.37801
## [428] 12.61494 10.72233       NA       NA       NA 13.37736 20.24153
```

```
## [435]       NA 35.51394       NA       NA       NA 13.13334 12.74592
## [442] 12.07687       NA 21.77642       NA 10.91083       NA       NA
## [449] 18.86435 12.43030       NA 14.41380 11.36852 10.66128 12.64971
## [456]       NA       NA       NA 10.29622 15.23795 10.40065 13.70575
## [463] 10.02450 31.56408       NA 10.06530       NA 40.27694       NA
## [470]       NA       NA       NA       NA       NA       NA 14.82127
## [477] 34.74281       NA 20.88387       NA 14.05370       NA       NA
## [484] 18.05085 12.77793 15.25932       NA 11.64008       NA       NA
## [491] 23.67998 11.76954       NA 16.36597 16.44499       NA       NA
## [498]       NA       NA       NA
```

```
# Estimate the distribution of the data
distrib(simLQLN)
```

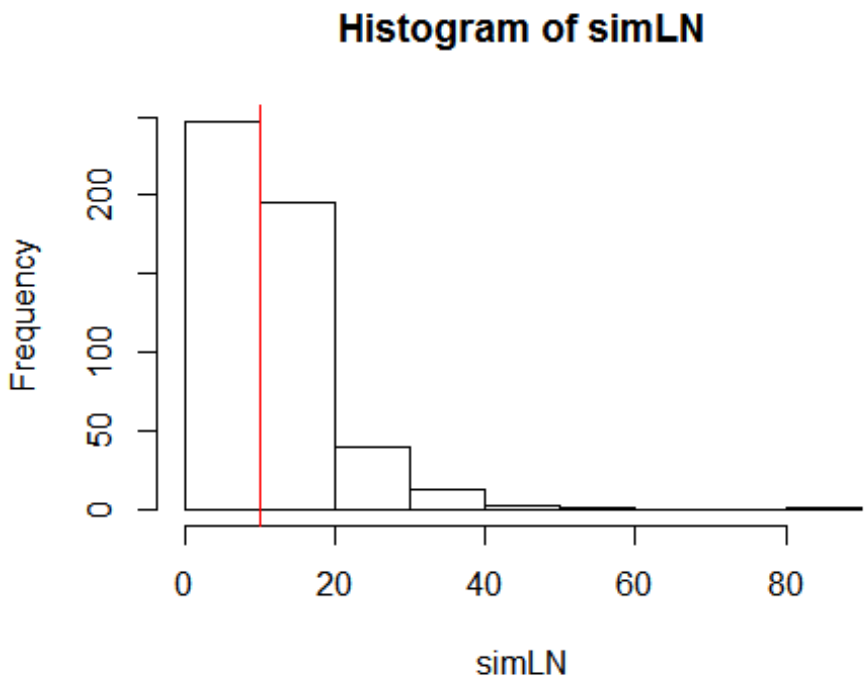
```
## Warning: package 'fitdistrplus' was built under R version 3.5.1
```

```
## Loading required package: MASS
```

```
## Loading required package: survival
```

```
## Loading required package: npsurv
```

```
## Loading required package: lsei
```



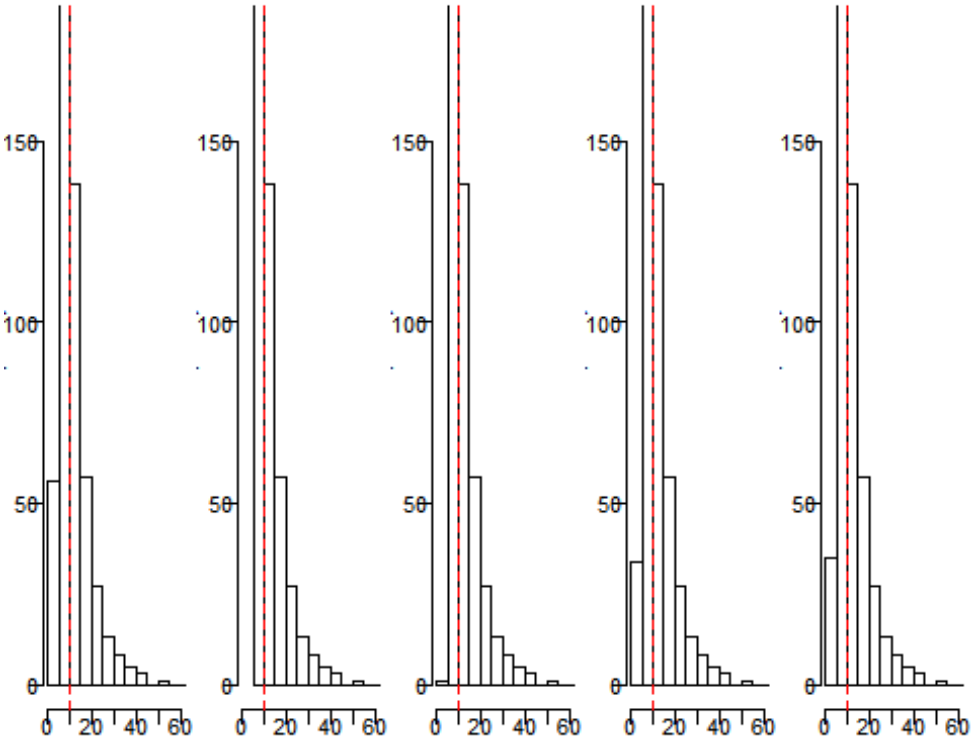

```
## [1] "lognormal"
```

Use the functions “NDsolve” and “NDsolveCorr” to estimate values below LQ

```
ex1<-NDsolve(simLQLN,LQ=LQ,method="lognormal",reg=FALSE)
ex2<-NDsolve(simLQLN,LQ=LQ,method="lognormal",reg=TRUE)
ex3<-NDsolveCorr(simLQLN,LQ=LQ,method="lognormal",reg=FALSE)
ex4<-NDsolveCorr(simLQLN,LQ=LQ,method="lognormal",reg=TRUE)
```

```
op <- par(mfrow=c(1,5),mar = c(1,1,0.8,0) + 0.5,mgp = c(1.5, 0.1, 0))

hist(simLN,xlim=c(0,60),20,ylim=c(0,180),las=1,main="")
abline(v=LQ,col="red",lwd=1,lty=2)
hist(ex1$data,xlim=c(0,60),20,ylim=c(0,180),las=1,main="")
abline(v=LQ,col="red",lwd=1,lty=2)
hist(ex2$data,xlim=c(0,60),20,ylim=c(0,180),las=1,main="")
abline(v=LQ,col="red",lwd=1,lty=2)
hist(ex3$data,xlim=c(0,60),20,ylim=c(0,180),las=1,main="")
abline(v=LQ,col="red",lwd=1,lty=2)
hist(ex4$data,xlim=c(0,60),20,ylim=c(0,180),las=1,main="")
abline(v=LQ,col="red",lwd=1,lty=2)
```

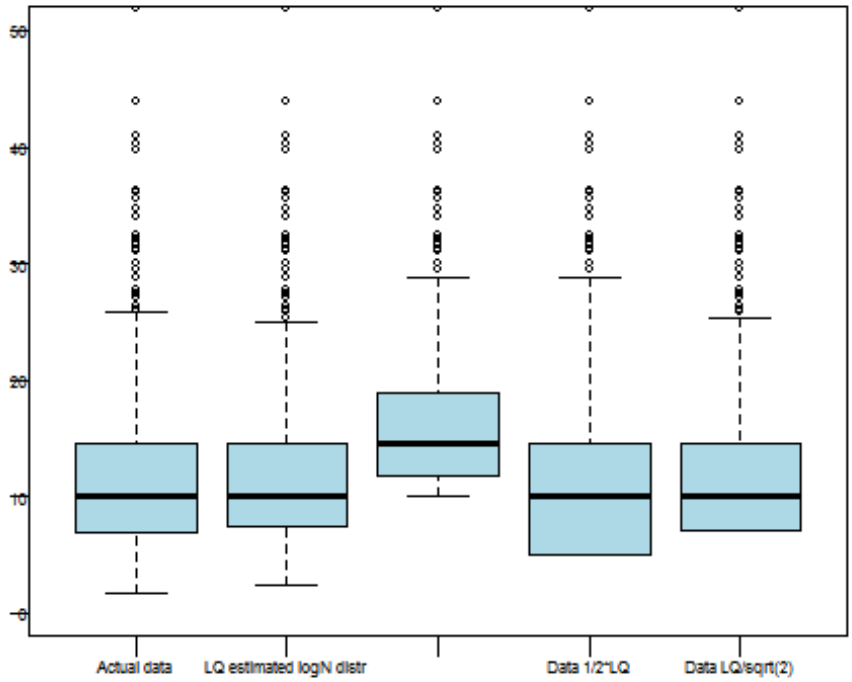



```
# Replace values below LQ by 1/2LQ or sqrt(2)*LQ
simLN_0.5LQ<-simLQLN
simLN_0.5LQ[which(is.na(simLN_0.5LQ))]<-LQ/2

simLN_sqrt2LQ<-simLQLN
simLN_sqrt2LQ[which(is.na(simLN_sqrt2LQ))]<-LQ/sqrt(2)

res<-data.frame(c(simLN,ex4$data,simLQLN,simLN_0.5LQ,simLN_sqrt2LQ),rep(c(
"Actual data","LQ estimated logN distr","Data without below LQ","Data 1/2*
LQ","Data LQ/sqrt(2)"),each=500))

op <- par(mfrow=c(1,1),mar = c(2,2,0.8,1) + 0.5,mgp = c(1.5, 0.1, 0))
boxplot(simLN,ex4$data,simLQLN,simLN_0.5LQ,simLN_sqrt2LQ,col="lightblue",c
ex.axis=.5,ylim=c(0,50),cex=.5,las=1,
        names=c("Actual data","LQ estimated logN distr","Data without belo
w LQ","Data 1/2*LQ","Data LQ/sqrt(2)"))
```




```
# Assess possible significant differences among the different datasets
library(pgirmess)
kruskalmc(res[,1]~res[,2])

## Multiple comparison test after Kruskal-Wallis
## p.value: 0.05
## Comparisons
##                                                 obs.dif critical.dif
## Actual data-Data 1/2*LQ                         160.832     115.4900
## Actual data-Data LQ/sqrt(2)                      36.274     115.4900
## Actual data-Data without below LQ               533.732     140.8857
## Actual data-LQ estimated logN distr              33.522     115.4900
## Data 1/2*LQ-Data LQ/sqrt(2)                     197.106     115.4900
## Data 1/2*LQ-Data without below LQ               694.564     140.8857
## Data 1/2*LQ-LQ estimated logN distr             194.354     115.4900
## Data LQ/sqrt(2)-Data without below LQ           497.458     140.8857
## Data LQ/sqrt(2)-LQ estimated logN distr           2.752     115.4900
## Data without below LQ-LQ estimated logN distr 500.210     140.8857
##                                                 difference
## Actual data-Data 1/2*LQ                               TRUE
## Actual data-Data LQ/sqrt(2)                          FALSE
## Actual data-Data without below LQ                     TRUE
## Actual data-LQ estimated logN distr                  FALSE
## Data 1/2*LQ-Data LQ/sqrt(2)                           TRUE
## Data 1/2*LQ-Data without below LQ                     TRUE
## Data 1/2*LQ-LQ estimated logN distr                   TRUE
## Data LQ/sqrt(2)-Data without below LQ                 TRUE
## Data LQ/sqrt(2)-LQ estimated logN distr              FALSE
## Data without below LQ-LQ estimated logN distr         TRUE
```

```
# Estimate distribution parameters for the different datasets
tapply(res[,1],res[,2],mean,na.rm=T)

##             Actual data             Data 1/2*LQ         Data LQ/sqrt(2)

##                11.97899                11.08475                12.10786

##   Data without below LQ LQ estimated logN distr
##                17.02520                12.15386

tapply(res[,1],res[,2],sd,na.rm=T)

##             Actual data             Data 1/2*LQ         Data LQ/sqrt(2)

##                7.873410                8.377483                7.666870

##   Data without below LQ LQ estimated logN distr
##                8.200819                7.745191
```