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**The role of environmental factors on
trace-metal concentrations in urban lakes - Lake
Pampulha, Lake Créteil and 49 lakes in the Ile-de-France
region**

Viet Tran Khac

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by

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The role of environmental factors on trace-metal concentrations in urban lakes

Lake Pampulha, Lake Créteil and 49 lakes in the Ile-de-France region

This thesis was conducted at École Nationale des Ponts et Chaussées (France) and Universidade Federal de Minas Gerais (UFMG) and defended on **19-12-2016** in front of the thesis committee composed of:

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Le rôle des facteurs environnementaux sur la concentration des métaux-traces dans les lacs urbains

Lac de Pampulha, Lac de Créteil et 49 lacs péri-urbains d'Ile de France

Thèse soutenue le **19/12/2016** devant le jury composé de :

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concentration des métaux-traces
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Thèse présentée au Programa de Pós-graduação em Saneamento, Meio Ambiente e Recursos Hídricos de l'Universidade Federal de Minas Gerais et à l'Ecole Doctorale Sciences, Ingénierie et Environnement de l' Université Paris-Est, comme exigence partielle à l'obtention du Doctorat en Assainissement, Environnement et Ressources Hydriques (UFMG) et Sciences et Techniques de l'Environnement (UPE).

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Abstract

Lakes have a particular influence on the water cycle in urban catchments. Thermal stratification and a longer residence time of the water within the lake can boost the phytoplankton production. Most metals are naturally found in the environment in trace amounts due to erosion and physicochemical or biological alteration processes. Trace metals are essential to growth and reproduction of organisms. However, some are also well known for their toxic effects on animals and humans. Total metal concentration only reflects the quantity of metals in the medium. Their ecotoxicity depends on metal properties and their speciation (particulate, dissolved: labile or bioavailable and inert fractions). Trace metals can be adsorbed to various components in aquatic systems including inorganic and organic ligands. The ability of metal binding to dissolved organic matter (DOM), in particular humic substances, has been largely studied. In urban lakes, various factors can enhance the phytoplankton development, which can produce autochthonous DOM, non humic substances, that can have the ability of metal binding as well. But there are few studies about trace metal speciation in lake water column until now.

The main objectives of this thesis are (1) to obtain a consistent database of trace metal concentrations in the water column of representative urban lakes; (2) to access their bioavailability through an adapted speciation technique; (3) to analyze the seasonal and spatial evolution of the metals and their speciation; (4) to study the potential impact of environmental variables, particularly of autochthonous dissolved organic matter related to phytoplankton production on metal bioavailability in these lakes and (5) to link the metal concentrations to the land use in the lake watershed.

Our methodology is based on a dense field survey of the water bodies in addition to specific laboratory analysis. The research has been conducted on three study sites: Lake Créteil in France, Lake Pampulha in Brazil and a panel of 49 peri-urban lakes in the Ile de France region. Lake Créteil is an urban lake relatively less impacted by anthropogenic pollution. It benefits of a large number of monitoring equipment, which allowed us to collect a part of the data set. In Lake Pampulha catchment, the anthropogenic pressure is higher. Lake Pampulha has to face with many pollution point and non-point sources. The climate and limnological characteristics of the lakes are also very different. The panel of 49 lakes of Ile de France was sampled once during three successive summers (2011-2013); they provided us with a synoptic, representative data set of the regional metal contamination in a densely anthropized region.

In order to explain the role of the environmental variables on the metal concentrations, we applied the Random Forest model on the Lake Pampulha dataset and on the 49 urban lake dataset with two specific objectives: (1) in Lake Pampulha, understanding the role of environmental variables on the trace metal labile concentration, which is considered as potentially bioavailable and (2) in the 49 lakes, understanding the relationship of the environmental variables, more particularly the watershed variables, on the dissolved metal concentrations. The analysis of the relationships between the trace metal speciation and the environmental variables provided the following key results of this thesis.

In Lake Pampulha, around 80% of the variance of the labile cobalt is explained by the some limnological variables: Chlorophyll a, oxygen concentration, pH, and total phosphorus. For the other metals, the RF model did not succeed in explaining more than 50% of the relationships between the metals and the limnological variables.

In the 49 urban lakes in Ile de France region, the RF model gave a good result for Co (66% of explained variance) and very satisfying result for Ni (86% of explained variance). For Ni, the best explanatory variables are landuse variables such as “activities” (facilities for water, sanitation and energy, logistical warehouses, shops, office...) and “landfill”. This result fits with Lake Creteil where dissolved Ni concentration is particularly high and where the “activities” and “landfill” landuse categories are the highest in the buffer zone.

Keywords Urban lakes; trace metal; speciation; bioavailability, land use, Random Forest model

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General introduction

Urban lakes present specific characteristics: they are generally highly artificial, small and shallow water bodies and they constitute specific elements of storm water drainage networks. These water bodies, such as ponds and grave-pits lakes, are common in an urban and peri-urban landscape. Urban lakes play a key role in recreation and storing rainwater (Stephen Birch, 1999). According to Downing et al. (2006), 99.2% of water bodies in the world have an area of 10ha or less. These aquatic ecosystems are highly impacted by urbanization in their watershed and by urban activities such as industry, traffic and drainage systems (Friese et al., 2010). Moreover, they are also very sensitive to a large variety of planetary environmental changes (PECs) such as increased CO₂, increased air temperature and atmospheric pollution. Despite the abundance and the usefulness of these water bodies for the society, there is a lack of research on these urban lakes in comparison with large and deep lakes (Jeppesen 1998, Moss 2010, Davies et al. 2008).

Because urban lakes are often small and shallow, they should respond rapidly and strongly to climatic fluctuations (Whitehead et al. 2007). Regarding their thermal regime, urban lakes are frequently polymictic and their water quality may be particularly impacted by changes in the water temperature and the mixing patterns caused by climatic extremes (Wagner & Adrian 2009). Climate change could increase wet period duration and intensity during rainy seasons and increase drought duration and intensity during dry season. Consequently, water residence time would be modified (Bates et al. 2008). During extreme climatic events, high runoff volume leads to a decline of bacteriological and chemical water quality and thus impacts the sanitary state and the functioning of aquatic ecosystems (Characklis et al. 2005, Patz et al. 2005, Allan & Castilla 2007). Heat wave events can enhance phytoplankton production rates (Nöges 2009, Moijj et al. 2005). All these environmental and anthropogenic disturbances can modify both hydrodynamic and physical-chemical conditions of urban lakes, which can favor phytoplankton development or even reinforce eutrophication due to higher nutrient internal cycling and more intense light climate (Nöges 2009, Bertolo et al. 1999).

Regarding trace-metals, two types of sources exist in aquatic environment: natural sources and anthropogenic sources. Trace metals are naturally present in the environment due to erosion and physical-chemical or biological alteration processes. Trace metals also enter urban water bodies via several pathways such as atmospheric deposition, industrial and domestic wastewater discharge, agricultural activities or storm water runoff (Thévenot et al, 2009).

Trace metals are essential components for living organisms (Buffle, 1988; Tessier et Turner, 1995). A lack of metals can be a limiting factor for the development of the organisms, for example, a lack of iron can limit phytoplankton growth (Martin et Fitzwater, 1988; Martin et al., 1991). However, a high concentration of metals can be extremely toxic. Indeed, trace metal toxicity for aquatic organisms is considered as a serious threat for human and animal health (Bryan and Langston, 1992).

Trace metals have been largely studied in marine (estuarine and coastal) and freshwater (river and lake) systems. With an increasing economic development, which entails industrial activities in large scale and rapid urbanization, trace metal pollution captures rising public concerns even though it is considered as a “traditional” environmental problem. With the aim of understanding and quantifying trace metal in ecosystems, many investigations have been carried out on different topics: bioaccumulation of metals by terrestrial and aquatic organisms (Goodyear et al., 1999, Heikens et al., 2001), metal biogeochemistry in marine, estuarine and lacustrine systems (Demina et al., 2013, Luengen et al., 2007, Emmenegger et al., 2001), metal quantification and speciation (Audry et al., 2004, Friese et al., 2010) etc. Fewer studies focused on trace metal in lake systems. Moreover, the trace metals in lakes are largely studied in sediments that are considered as their ultimate destiny. As a result, we have an uncomplete image of behaviors of trace metals and their fate in the water column.

Ecotoxicity and bioavailability of trace metals are not directly related to total metal concentrations but depend on the form and the nature of chemical species (Florence, 1986, Scoullou and Pavlidou, 1997, Lores and Pennock, 1998). In aquatic systems, trace metals can exist in many different chemical forms, which determine bioavailability and toxicity to aquatic organisms (Hirose, 2006, Morel et al., 2003). Trace metals can be particulate or dissolved (free or complexed to organic and inorganic ligands). Under different physical-chemical conditions (pH, salinity, hardness of water, organic carbon content...), trace metal forms can change (Forstner and Wittmann 1979). In the dissolved metal fraction, metals can be labile (free or weakly linked to organic or inorganic ligand) or inert (no interaction with surrounding environment). Labile metal is defined as free metal or weakly linked to mineral ions (hydroxyl, carbonate) or to organic molecules (Thevenot et al. 2002). Labile metal is also defined as “easily modifiable, exchangeable by easy and rapid interaction with surrounding water” (Tusseu-Vuillemin 2005). In other words, labile metal is constituted of cationic free form or weakly associated to mineral ions (Thevenot et al. 2002). Because of their mobility in aquatic systems, this fraction is directly related to bioavailability of metals. The labile metal fraction, which can be easily linked to aquatic organisms, is a good indicator of toxicity. Therefore, it is important to study this fraction of trace metal in aquatic systems.

The speciation of trace metals in the aquatic systems depends on environmental variables, pH, oxygen, suspended solids, dissolved organic matter. Dissolved organic matter (DOM) plays a key role in the trace metal speciation in aquatic systems.

DOM can be divided into two categories: the humic substances and the non-humic substances. According to Thurman (1985), humic substances predominate in non-urban areas, up to 70% of DOM in comparison with non-humic substances (~ 25%). Humic and fulvic acids are the most studied because they play a key role on complexing free metal ions in most of the aquatic systems. However, in urban areas, the non-humic, mainly hydrophilic DOM, can constitute a significant fraction as a result of treated or untreated wastewater discharge (Pernet-Coudrier et al., 2011). The binding ability of wastewater organic matter has been highlighted during an acute toxicity test of copper with *Daphnia magna* (Pernet-Coudrier et al., 2008).

In lentic water bodies, non-humic DOM can also be produced by biological activity, mainly phytoplankton and bacteria. The complexing ability of trace-metals of this natural aquagenic DOM, called extracellular polymeric substances (EPS) is still unclear. One type of EPS is constituted by Transparent Exopolymer Particles (TEP), which are defined as particles formed from acid polysaccharides. During phytoplankton blooms in freshwater and marine systems, phytoplankton and bacteria abundantly exude TEPs. Diatoms are especially known for producing TEPs during their growth (Passow, 2002). TEPs can play a role in the trace metal speciation because of the large affinity of trace metals to surface-active exopolymers (Tye et al., 1996). Between 40-90% of trace elements can be adsorbed by the TEPs in the marine system (Passow, 2002). However, until now, the TEPs have been more widely studied in marine systems than in freshwaters. Moreover, very few results exist about the TEP characteristics in urban lakes. Most of the scientific studies about TEP were conducted by experiment in the laboratory with simulated environmental conditions.

In this context, the key objectives of this thesis are as follows:

- (1) to analyze the seasonal and spatial evolution of the trace-metal concentrations and their speciation in the water column of representative urban lakes;
- (2) to study the potential impact of environmental variables, particularly of autochthonous dissolved organic matter related to phytoplankton production on metal bioavailability in these lakes;
- (3) to link the metal concentrations to the land use in the lake watershed.

To achieve these uppermost objectives, two prior tasks had to be performed:

- (1) to obtain reliable measurements of trace metal concentrations in the water column of the lakes;
- (2) to access their bioavailability through an adapted speciation technique.

As study sites, two urban lakes were selected, one in France, Lake Créteil, and the other one in Brazil, Lake Pampulha. A panel of 49 urban and peri-urban lakes in the Ile-de-France region was also studied. Two main reasons guided the selection of these lakes: (1) they are study sites of major research projects in France and in Brazil and (2) they are very different regarding their urban and climate contexts. This Ph.D. research is embedded within research projects of LEESU-ENPC (France) and EHR-UFGM (Brazil), PULSE (Peri-Urban Lakes, Society and Environment) supported by ANR (National Research Agency) for Lake Créteil and the research project MAPLU, funded by the Brazilian Agency for Funding Study and Projects – FINEP) for Lake Pampulha.

This report is divided in two parts. The first part includes two chapters, “State of the art” and “Materials and Methods”. It is structured as follows:

- The chapter “State of the art” is dedicated to the presentation of the main trace metals which will be considered, their natural and anthropogenic sources, their different pathways entering the aquatic systems. Then trace metal speciation and the impact of environmental conditions are introduced. We focus on the role of a non-humic DOM, the extracellular polymeric substances (EPS), especially the transparent exopolymeric substances (TEP) on the trace metals speciation. The regulatory context on trace metal environmental standards will be briefly presented. This first chapter will be concluded by the presentation of the general and specific objectives of the thesis
- The chapter “Materials and Methods” is dedicated to the description of the materials and methods we used. The monthly monitoring in Lake Créteil (France) and Lake Pampulha (Brazil) are presented as well as the annual survey of 49 lakes of the Ile de France region. A complementary field study, Savigny retention pond, is described in Annex 8.3. All the analytical methods are described. Finally, the statistical methods are presented.

The second part includes the presentation and discussion of the results for Lake Pampulha, Lake Créteil and the Ile-de-France lakes.

- For each study site, are presented the results of the environmental monitoring program which has been conducted: monthly campaigns, monitoring of the tributaries, raining campaigns and other specific campaigns. The monitoring results of Lake Créteil and Lake Pampulha show the seasonal evolution of trace metal concentrations in the water column, the impact of raining events on the metal speciation. The results on trace metals in 49 lakes in region Ile de France highlight at a regional scale, the impact of land use in the watershed on trace metals in peri-urban lakes.
- The final chapter is dedicated to conclusion and perspectives.

-

PART 1

1. State of the art

Heavy metals are defined as elements with a density greater than $5\text{g}\cdot\text{cm}^{-3}$. Most of the transition metals have a density in this range. In environmental science, the term “trace metal” tend to replace the one “heavy metals”. The notion of “trace” refers to an extremely low concentration in the earth’s crust which is inferior to 0.1% by weight.

Trace metal contamination represents a significant risk to the environment and public health, because of their toxicity, non-biodegradability and accumulation in the biosphere. In aquatic systems, the range of trace metal concentrations generally varies from ng/L to $\mu\text{g/L}$. They are considered as conservative pollutants that are not biodegradable or other degradation processes and are permanent additions to the environment systems (El-Nady et al., 1996). Trace metals are classified as essential or non-essential. They can be essential for a normal metabolic functioning with an optimal concentration such as Cobalt, Copper, Iron, Manganese, Molybdenum, Nickel, Vanadium and Zinc. Others are non-essential and are toxic for organisms even at very low concentrations, such as Cadmium, Mercury and Lead (Campbell et al., 2006; Pawlik-Skowronska and Skowronski; Rand et al., 1995; Geffard, 2001). According to Mason et Jenkins (1995) we can distinguish:

- Metals found in high quantities in organisms (superior to 1mmol/kg of wet weight) such as Na, K, Ca and Mg.
- Metals found in trace concentrations (between 0.001 and 1mmol/kg) such as Ag, Cd, Cr, Co, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Se, Si, Sn, V et Zn.

In aquatic systems, trace metals can come from both natural sources such as geochemical background, volcanoes and anthropogenic sources such as industrial activity, road network, traffic, housing, energy plants and waste. Transport and transformation of trace metals are driven by many factors, including biogeochemistry of these elements, the influence of environmental factors and fluvial inputs. In natural waters, the distribution of trace metals depends on water chemistry such as redox conditions, hardness, pH, alkalinity, specific ion concentrations, complexing agents and dissolved organic matter (DOM) (Templeton et al. 2000). Trace metals can be found in many different forms such as hydrated ions, complexes with inorganic or organic ligands, adsorbed onto colloids, particles or microorganisms. In order to estimate the impact of trace metals in the environment, it is essential to know their quantity and especially their speciation. It is generally assumed that total concentration is not a good predictor of metal bioavailability and ecotoxicity (Buffle, 1988; Tessier and Turner, 1995).

1.1. Sources of trace metals in aquatic systems

Trace metals come from both natural and anthropogenic sources. In this research, we will most particularly focus on 7 trace metals specific of urban areas, Cd, Co, Cr, Cu, Ni, Pb, Zn.

1.1.1.1. Natural sources

Trace metals are naturally found in the Earth’s crust where they can be weathered (dissolved) and eroded (particulate). They are mainly concentrated in rocks and generally included in crystalline structure of mineral in soil (oxides, carbonates, silicates, sulfurs). The natural concentration of trace metals in soils depends on the soil type. Soil geochemical background is defined as natural concentration of a substance in soil resulting from geological and pedological evolution, excluding any anthropogenic contributions (Baize, 1997). The natural emissions of six metals, Pb, Zn, Cd, Cr, Cu and Ni, are respectively 12,000 tons per year (Pb); 45,000 (Zn); 1,400 (Cd); 43,000 (Cr); 28,000 (Cu); and 29,000 (Ni) (Nriagu 1990b). Other source of trace metal emission is injection into the Earth’s atmosphere by volcanic activity. These two sources account for 80% of all the natural sources. Forest fires and biogenic sources, account for 20% (Callender, 2003).

1.1.1.2. Anthropogenic sources and pathways

Because of their physical and chemical properties such as ductility, malleability, high electrical and thermal conductivity and high density, metals are materials most widely used in industrial and domestic work. Metals enter into the environment through numerous anthropogenic emissions. The major source of these metals is from mining and smelting. Mining releases metals into aquatic systems directly or indirectly as discharge and runoff and into atmosphere as metal-enriched dust. Smelting releases metals into atmosphere as result of high temperature refining processes. These metals will enter into aquatic systems by atmospheric deposition. During the 1970s and 1980s, metal production remained relatively constant for Pb, Zn, Cd, Cu and Ni whereas Cr production was doubled between the two decades due to technological advances (Table 1). Other sources of metal to the environment are listed as fossil fuel combustion, alloy industry, wood industry, waste incineration, fabrication of fertilizer (Phosphate), road traffic etc (Bisson et al., 2003, 2005a,b,c, 2006, 2011). Important sources of metals to the aquatic environment include sewage sludge, use of commercial fertilizer and pesticide, animal waste and waste water discharge (Nriagu and Pacyna 1988).

Table 1 Global production and emissions of six metals during the 1970s and the 1980s.

Metal	Metal production		Emissions to air		Emissions to soil	Emissions to water	
	1970s	1980s	1970s	1980s	1980s	1980s	
Pb	3,400	3,100	449	332		796	138
Zn	5,500	5,200	314	132		1,372	226
Cd	17	15	7.3	7.6		22	9.4
Cr	6,000	11,250	24	30		896	142
Cu	6,000	7,700	56	35		954	112
Ni	630	700	47	56		325	113

Source: Nriagu (1980a), Pacyna (1986), and Nriagu and Pacyna (1988).

All values are thousand metric tons per year.

Titanium (Ti) is a very conservative element that is associated with crystal rock. Normalization with Ti allows us to see more clearly metal enrichment due to anthropogenic emissions. Table 2 shows average pre-industrial and recent concentration of six trace metals in aquatic systems. The mean concentration of trace metals between pre-industrial baseline and recent lacustrine sediment point out that there is a progressive anthropogenic metal enrichment. It is true for all metals presented in the table, except Ni that is not especially enriched.

Table 2 Average concentration of six trace metals in aquatic systems

Material	Pb (ppm)	Zn (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Ni (ppm)	Ti (wt. %)	Reference
Pre-industrial, baseline, lacustrine, sediment	22(69)	97(303)	0.3(0.55)	48(150)	34(106)	40(125)	0.32	(1)
Recent lacustrine sediment	102(316)	207(640)	2.2(6.8)	63(195)	60(186)	39(121)	0.32	(2)
River particulate matter	68(120)	250(446)	1.2(2.1)	100(178)	100(178)	90(161)	0.56	(3)
Estuarine sediment	54(108)	136(272)	1.2(2.4)	94(188)	52(104)	35(70)	0.5	(4)

Values in brackets are Ti-normalized.

- (1) Shafer and Armstrong (1991); Forstner (1981); Heit et al. (1984); Mudroch et al. (1988); Eisenreich (1980); Kemp et al. (1976, 1978); Wren et al. (1983); Wahlen and Thompson (1980)
- (2) Above references plus: Dominik et al. (1984); Rowell (1996); Mccray et al. (2001)
- (3) Martin and Windom (1991); Martin and Whitfield (1981)
- (4) Alexander et al. (1993); Coakley and Poulton (1993); Anikiyev et al. (1994); Hanson (1997)

1.1.2. Atmospheric deposition

The release of metals into the atmosphere by human activities has dramatically increased since the industrialization. Natural sources such as volcanic eruption, sea sprays and forest fires do not dominate over anthropogenic sources. Atmospheric deposition includes dry deposition that is dominant when close to sources, wet deposition that is prevailing in rural locations and gas exchange across the air-water interface. (Mason et al., 2013) (Figure 1).

- Dry deposition is defined as the process by which aerosol particles accumulate on solid surfaces. The rate of deposition depends on many factors including wind speed, atmospheric turbulence or the particle diameter. It is shown that anthropogenic sources emit finer particles than natural sources (Poster and Lindberg 1997). Dry deposition includes also the uptake of gaseous species by vegetation, for example the Hg uptake process of vegetation (Berg and Steinnes 2005).
- Wet deposition refers to the removal of species from the atmosphere in precipitation including rainfall, snowfall, fog and other intermediate forms. Wet deposition is an important source of trace metal. It is the result of the scavenging of gaseous or particles materials from the atmosphere by raindrops and other physical processes and chemical reactions occurring before or during the cloud formation. Chemical reaction can have an impact on the solubility of trace metal, thus on their bioavailability and their fate upon deposition. For instance, iron can be soluble as Fe(II) and insoluble as Fe(III); both Cu(I) and Cu(II) oxidation state can exist in the atmosphere and mercury can be soluble as Hg(II) and dissolved gas as Hg⁰. Sources of metal in wet deposition can come from industrial emissions, domestic emissions and traffic emissions (Pacyna and Graedel, 1995). According to Mason et al. (2013) collection of wet deposition in Chesapeake Bay, USA showed a metal enrichment in urban areas comparing to rural areas. Similar relationship has been found for other locations.

Since the growth of environmental awareness and technological advances in pollution control, metal emissions have been significantly reduced by 5 to 10 fold from 1990 to now. The case of lead can illustrate this evolution. Lead has been used in the production of gasoline, ceramic, paints, metal alloys. In the 1990s, automotive sources were the main contributor of lead emissions to the atmosphere. Due to the removal of lead from fuel, lead emissions by traffic almost disappeared or at least reduced by 50-fold between the 1990s and 2010. Now the main source of lead is the industry. A similar evolution is observed for zinc with a reduction factor until 12 fold in 20 years. Other metals emissions are stable since 1990 except copper due to rail transport (catenary wear) and road (pads wear) (CITEPA, 2011).

For aquatic systems, atmospheric deposition can be a direct source of trace metals or an indirect source of trace metals (accumulation on surface and transport to water by wash off). Depending on location, this source can be dominant or secondary.

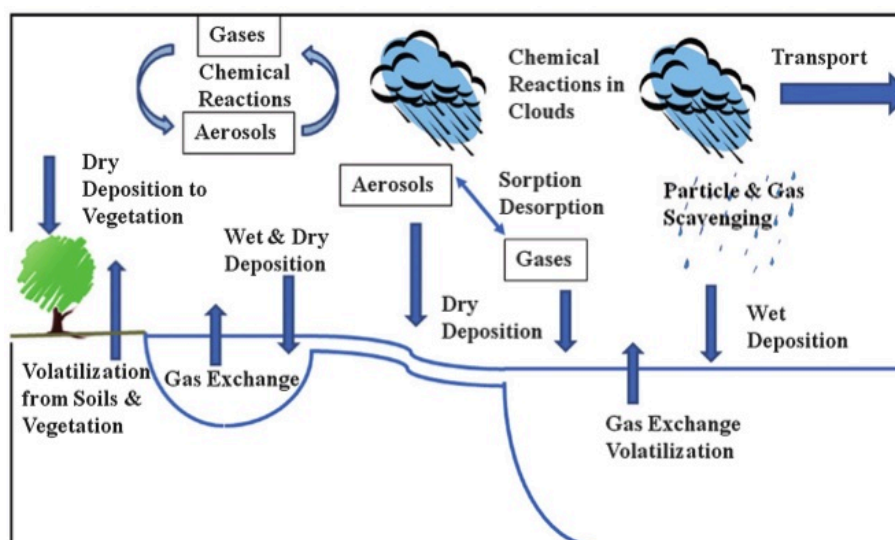


Figure 1 Atmospheric deposition processes (Mason et al., 2013)

1.1.3. Incineration plants

Incineration is the most widely used in waste treatment methods. It is defined as a fast oxidation reaction between waste and air at a high temperature in order to reduce the volume of waste to 90% (Youcai et al., 2002). Besides the composition of combustible, the waste also contains trace metals. Many studies have indicated that the major metals in waste are Zn, Cr, Cu, Pb, Ni, Hg and Cd (Min-Hao et al., 2014).

Moreover, waste incineration has implied some major secondary pollutants such as acids (HCl, HF, HS, Hbr), nitrogen oxides (NO₂, NO) and other persistent organic pollutants (dioxin, volatile organic compounds). Pacyna et al., (2001) estimated metal emissions due to incineration plants (domestic waste and sludge waste from sewage treatment) in Europe.

Table 3 Annual flow at European scale of metal emissions by incineration plants (domestic waste and sludge waste from sewage treatment) (ton.yr⁻¹) (Pacyna et al., 2001)

		Cd	Cr	Cu	Mn	Ni	Pb	Se	Sn	V	Zn
Domestic	ton.yr ⁻¹	10	18	182	47	18	250	5	26	-	520
Sludge	ton.yr ⁻¹	1	26	5	26	5	1	1	3	2	26

Copper, lead and zinc are mainly released from domestic waste incineration, around 10% in comparison to annual emissions from energy production (Table 3).

1.1.4. Industrial processes

Pacyna et al., (2001) evaluated the annual flow of metals emitted by different industrial processes (Table 4), which are classified into three classes: industry of nonferrous metals, steel industry and cement industry.

Table 4 Annual flow at European scale of metal emissions by industrial processes (ton.yr⁻¹) (Pacyna et al., 2001)

	Cd	Cr	Cu	Mn	Ni	Pb	Se	Sn	V	Zn
Nonferrous	208	-	572	2	281	3341	48	19	-	3622
Steel	26	1037	52	389	13	2255	3	-	26	778
Cement	3	273	-	-	27	55	1	-	-	547

Copper, lead and zinc are dominated from industry of nonferrous metals. Steel industry produces chromium and lead. In comparison to the two industrial processes above, the contribution

of cement industry, in term of metal emission, is inferior. However, identification and distinction of sources are truly challenging to realize in urban zones due to the density of industry (Pacyna et al., 2001).

1.1.5. Energy production

Trace metals are also emitted from fuel coal combustion. Metal emissions depend on the grade and the composition of fuel, physical chemical properties of the metal itself; combustion temperature and fuel feed mechanism. Pacyna et al., (2001) regroups the estimation of annual flow of metal emissions into atmosphere due to energy production in Europe and emission rate of 11 metals by coal and fuel combustion (Table 5).

Table 5 Annual flow at European scale of metal emissions by energy production (ton.yr⁻¹) and emission rate (g.ton⁻¹) by combustible type (Pacyna et al., 2001)

		Cd	Cr	Cu	Mn	Mo	Ni	Pb	Se	Sn	V	Zn
Energy	ton.yr ⁻¹	109	2000	1300	2000	500	2000	3000	780	815	57000	1900
Coal		0.1	1.7	1.4	1.5	0.4	2	1	0.8	0.1	1	1.5
Fuel	g.ton ⁻¹	0.05	1	0.5	1	0.3	20	2	0.3	0.8	60	1

Table 5 shows that energy production is an important source of cadmium, chromium, copper, manganese, molybdenum, nickel, plumb, selenium, vanadium and zinc in atmosphere at European scale. The emitted quantity of these elements varies from hundreds of tons per year (Cd, Mo, Se, Sn) to thousands (Cr, Cu, Ni, Pb, Zn) or 10 folds more (V). It is also shown that coals combustion emits more trace elements in case of Cd, Cr, Cu, Mn, Se, Zn; fuel combustion produces more trace elements in case of Ni, Pb, V.

1.1.6. Urban stormwater runoff

Urban stormwater runoff is recognized as a major source of pollutants, including trace metals in the aquatic systems, especially to urban receiving waters. As mentioned above, dry and wet depositions constitute an important source of trace metals in urban stormwater runoff. Other sources come from building siding and roofs; automobile and road infrastructures such as pavement wear, abrasion or erosion of brakes, tires and oil leakage (Davis et al., 2001). Urban stormwater runoff can be classified into three types: rooftop runoff, road runoff and runoff from course, square or other urban open space.

Pollution of road stormwater runoff is chronic as the result of vehicle exhaust, pavement and tire wear. Nevertheless, it can also be temporary (due to road works) or accidental that can release a number of hazardous chemicals. During winter, the use of de-icing products such as sodium chloride can enhance the corrosion of metal surfaces and promote their mobility. Metals found in urban stormwater runoff are diverse and come from road surfaces by brake and tire wear (Pb, Cu, Zn), by vehicle exhaust (Cr, Ni, Cd), by building siding release (Pb, Cu, Zn, Cd), by atmospheric deposition (main source of Cd, Cu, Pb), by corrosion of vehicle bodies (Fe, Cr, Mn, Ni) and by utilization of paints and anti-corrosive coating (Davis et al., 2001, Gunawardena et al., 2014, Abbott et al., 1995)

Rooftop runoff can have a direct impact on pollution stormwater urban due to its contribution, which can represent up to half of the runoff volume in urban zone (Förster, 1996). Metal concentrations and types depend on materiel of rooftop. Four metallic elements, which are often found in literature, are Cd, Cu, Pb, Zn (Gromaire et al., 1999). Two processes, which imply metals concentration in rooftop runoff, are: increase of pH during runoff, which favors metal adsorption on rooftop and atmospheric corrosion, which favors metal leaching (Quek et al., 1993). In case of Paris, more specifically the Marais watershed, (Gromaire et al., 1998) showed the contribution of 4 metals (Cd, Cu, Pb, Zn) from different runoff types: Rooftop runoff (64-93% for Cd, Cu, Pb and Zn), road runoff (5-9% for Cd, Pb and Zn and 32% for Cu), Course runoff (2-5% for Cd, Cu, Pb and Zn).

1.2. Trace metal characteristics

In this section, we will present the main characteristics of the selected metals, Cd, Co, Cr, Cu, Ni, Pb, Zn. It is essentially based on INERIS documents.

1.2.1. Chromium

Chromium enters into the air, water, and soil mostly in the chromium(III) and chromium(VI) forms. In water, chromium (VI) is highly soluble while chromium (III) has a low solubility. In air, chromium is present mostly as fine dust particles and can settle over land and water. In soil, chromium (VI) is widely transformed to Cr (III) under action of low pH and anaerobic condition in soil and sediment. Therefore, chromium can strongly attach to sediment and soil. A small amount is expected to dissolve in water and leach through the soil to groundwater. The concentration of chromium in different environmental compartments is indicated in Table 6

Table 6 Concentration of chromium in different environmental compartments

Environment	Concentration
Air	< 10ng/m ³ (1)
Water -fresh water (rivers, lakes, groundwater)	1-10 µg/L(1)(2)
Soil	50 mg/kg(3)
Sediment	< 100 mg/kg(1)

(1) CE (2000)

(2) OMS IPCS (1998)

(3) Worldwide average, in France concentration varies between 3 and 100mg/kg (Juste, 1995)

Bioaccumulation factor (BCF) is defined as the ratio of the concentration of a chemical in an organism to the concentration of the chemical in the surrounding environment. For example, Chromium (VI) does not accumulate in fish (BCF =1), reported by U.S. EPA (1980). Chromium (III) appears to accumulate more in fish: BCF = 260 – 800 measured on various species of fish by Giesy J.J.P. and Wiener J.G. (1977). In invertebrates, BCF varies from 125 to 200 for the Chromium (VI) and the same ratio for Chromium (III). BCF can be up to 9100 for *Mytilus edulis* chromium (VI) and up to 2 800 for chromium (III). BCF varies from 190 to 500 for four species of phytoplankton for Chrome (VI) and from 12000 to 130000 for Chrome (III) (Wang et al., 1997). BCF, measured on natural population of algae, varies from 2300 to 29000 for Chrome VI (Braunschweiler et al., 1996) while BCF estimated for the algae collected in the Rhin river is between 20 and 215.

1.2.2. Cobalt

Cobalt is relatively rare and represents only 0.002% of the Earth's crust. Cobalt is naturally found in soil, volcanic eruption, sea spray and forest fires. Anthropogenic sources include combustion of fossil fuels, metal smelting, sewage sludge, engine exhaust and processing of cobalt alloys. Due to its high affinity for other metals such as nickel, silver, lead and copper, cobalt is primarily used in production of super alloys with chromium, molybdenum and tungsten which can enhance high temperature strength. Cobalt is widely used in production of permanent magnets, pigments, paint dryer and catalysts in petroleum industry. Nitrate of cobalt is also used in pharmaceutical production of vitamin B12. In the atmosphere, cobalt is predominantly found in particulate form.

In surface water, such as rivers, lakes or estuary marine water, it generally settles to the bottom and is mainly adsorbed by sediment, in particular by carbonate and hydroxide. Depending on environmental conditions especially pH, cobalt can also be linked with humic substance. The further the environment is alkaline, the further cobalt is complexed by carbonate and other ligands. When pH is below 7, cobalt is more likely free (Collins and Kinsela, 2010). Cobalt does not appear to

significantly be linked to aquatic food chain (Gad et al., 2014). In soil, cobalt is expected to have a high affinity with soil components thus its migration ability in soil is mostly insignificant.

In term of bioaccumulation and metabolism, cobalt seems not to have a bioaccumulation in aquatic organisms. According to scientific researchs, BCF varies between 5 and 10 for *Asteria rubens* and 15 for *Mytilus edulis* (Warnau et al., 1999, Nolan and Dahlgaard (1991)). In many species of fish in marine water, BCF is lower in comparison with phytoplankton (Yamada et Takayanagi (1995)).

Cobalt is an essential nutrient at low levels (40 mg/day).

The concentration of Co in different environmental compartments is indicated in Table 7

Table 7 Concentration of cobalt in different environmental compartments

Environment	Concentration
Air	0.4 – 2 ng/m ³ ₍₁₎
Water (fresh water)	0.1-5 µg/L ₍₁₎₍₂₎
Soil	1 - 40 mg/kg ₍₂₎
Sediment	Unavailable

(1) ATSDR (2001)

(2) HSDB (2002)

1.2.3. Copper

Copper is widely distributed in nature. Natural sources of copper include volcanic eruption, vegetal decomposition, forest fires and ocean spray. Anthropogenic sources are mainly explained by its extensively use in industry because of its electric and thermic conductivity such as metal industry, wood industry, but also explained by other sources such as waste incineration, coal and fuel combustion, fabrication of fertilizer (phosphate). Copper is used in alloy metallurgy, in fabrication of electric material (dynamo, wires, transformer), in paint, in textile, as fungicide, insecticide, and catalyst and in industry.

Copper is one of the essential trace elements required for various biologic functions.

The concentration of Cu in different environmental compartments is indicated in Table 8

Table 8 Concentration of copper in different environmental compartments

Environment	Concentration
Air	~ 10 ng/m ³ ₍₁₎
Water (fresh water)	1- 10µg/L ₍₁₎₍₂₎
Soil	10 - 40 mg/kg ₍₃₎
Sediment	~ 50mg/kg ₍₄₎

(1) ATSDR (1990)

(2) ATSDR (1990) and Juste et al., (1995)

(3) Juste et al., (1995) for french soil

(4) ATSDR (1990) and HSDB (2002)

Copper has two valences: Cu(I) and Cu(II). Copper takes part in the important process of oxidation-reduction reactions as a co-factor (WHO, FAO, IAEA, 1996). Ion Cu(I), reduced state, is not stable in environment unless it is linked with stabilizer ligands such as sulfur, cyanide or fluoride. Ion Cu(II), oxidized state, forms various stable complexes with mineral ligand, chloride or ammonium and organic ligands (ATSDR, 2002). In aquatic environment, many processes influence the behavior of copper: complexation with organic or mineral ligands (especially with group –NH₂, –SH or –OH), adsorption on metallic oxide, clay, or organic particulate, bioaccumulation... Majority of copper released into water is particulate, intends to precipitate and settles to sediment. Particulate Cu represents 40-90% of total Cu (INERIS, 2005). After release of copper into aquatic environment, the equilibrium is generally reached under 24h.

In terms of bioaccumulation and metabolism, BCF is only determined for fish which fluctuates strongly between 20 to 950 with an arithmetic mean 184 (Wepener et al., (2000), Xiarong et al. (1997). Copper is an essential element but it can be even more toxic than such non-essential elements as nickel and cadmium.

1.2.4. Zinc

Zinc is an essential trace element which is considered as a nutritional supplement. Over 100 enzymes are zinc-dependent.

Zinc occurs naturally in environment. Natural sources of zinc include volcanic eruption, vegetal decomposition, forest fires and ocean spray. Anthropogenic sources of zinc can be divided into three groups of activity:

- Mining and industrial sources: mineral processing, refining, galvanizing iron, roof construction, manufacturing gutters, batteries, pigments, plastics, rubber etc.
- Agriculture
- Other activities: Road traffic, erosion of roots, tire wear, waste incineration.

Zinc is widely used in galvanized iron and various alloy. It is also used in different industries such as foundry, welding, electric industry and electronic industry: dry cell battery, electrical fuses, fungicide, dyes and ink. The concentration of Zn in different environmental compartments is indicated in Table 9

Table 9 Concentration of zinc in different environmental compartments

Environment	Concentration
Air	0.01 – 0.2 $\mu\text{g}/\text{m}^3$ ⁽¹⁾
Rivers	10 $\mu\text{g}/\text{L}$ ⁽¹⁾
Lakes	20 $\mu\text{g}/\text{L}$ ⁽¹⁾
Rain	10 $\mu\text{g}/\text{L}$ ⁽¹⁾
Sediment	70 - 140 mg/kg ⁽¹⁾

(1) ADEME(1995), CE (1999), HSD(2000) and, IUCLID (2000)

Zinc is present in aquatic system in different forms: hydrated ion, complexed form with organic ligands (humic and fulvic acid), adsorbed on solid matter, oxide zinc. The speciation of zinc depends on diverse factors and environment conditions such as pH, quantity of organic matter dissolved, and reduction potential. ZnCl_2 and ZnSO_4 are highly soluble in water but can be hydrolyzed and formed precipitate $\text{Zn}(\text{OH})_2$ under reductive condition. A weak pH is necessary to maintain Zn free in the solution. Jansen et al. 1998 estimated in various rivers in Europe that 30% of Zn is free and the other 70% is complexed.

As an oligo element for the life of various aquatic organisms, accumulation of zinc can be regulated by many processes in many species: mollusks, crustaceans, fish and mammals. Many research showed a decreasing BCF when we go up to the food chain. It means that there is an increasing regulation in the superior organisms.

In term of toxicity, LD50 values are in the range 30–600 mg/ kg body weight for animals.

1.2.5. Nickel

Nickel represents around 0.8-0.9% of the Earth's crust (Table 10). Anthropogenic sources include coal or fuel combustion, waste incineration, waste sludge and alloy industry. Nickel and its compounds are widely used in plated coatings, nickel–cadmium batteries, certain pigments, ceramic glazes, and as industrial and laboratory catalysts

Table 10 Concentration of nickel in different environmental compartments

Environment	Concentration
Air	< 3 ng/m ³ ₍₁₎
Fresh water	< 10µg/L _{(1),(3)}
Marine water	< 0.5µg/L ₍₂₎
Rain	< 1µg/L ₍₂₎
Sediment	< 20mg/kg ₍₂₎

(1) OMS IPCS (1991)

(2) HSDB(2000)

(3) ATSDR (1997)

In aquatic environment, nickel is present under ion hexahydrated form, which is weakly absorbed by mostly organisms. Nickel is highly linked to solid matter. Nickel is weakly complexed by natural anions such as OH-, sulfate and chloride. Ni(OH)₂ is dominant at pH 9.5.

In terms of bioaccumulation and metabolism, nickel shows a weak bioaccumulation within aquatic organisms. Nevertheless, in others scientific research, BCF in fresh water is important (Table 11):

Table 11 BCF of nickel of aquatic organisms

	Specie	BCF	Reference
Algal	Eugelna gracilis	2000	Cowgill, 1976
	Scenedesmus obliquus	30-300	Wastras et al., 1985
Vegetal	Elodea densa	200	Mortimer, 1985
	Ipomea aquatic	40	Low et Lee, 1981
Shelfish	Daphilnia putex	4050	Cowgill, 1976
	Daphinia magna	2020	Cowgill, 1976

1.2.6. Lead

Lead is present in the Earth's crust and all compartment of biosphere. Atmospheric pollution of lead comes from industry, lead fusion, road traffic and consummation of lead fuel. Since prohibition of lead in fuel, atmospheric pollution of lead decreased significantly. In aquatic systems, the most important water discharge source is steel industry. In a region subjected to acid rains or water is naturally acid, there will be more risk of corrosion of lead pipe.

Lead and its compounds are widely used throughout industry. They are found in lead acid storage batteries, paints, sheet metal, bearings, solder, piping, and ammunition. Lead arsenate is used in insecticides and herbicides. Lead chromate is used as a yellow pigment in paints, rubber, plastics, and ceramic coatings. House paints must have less than 0.05% of lead. The concentration of Pb in different environmental compartments is indicated in Table 12

Table 12 Concentration of lead in different environmental compartments

Environment	Concentration
Air	0.1 ng/m ³ ₍₁₎
Fresh water	1-10µg/L _{(1),(3)}
Marine water	< 50ng/L ₍₂₎
Rain	< 1µg/L ₍₂₎
Sediment	-

(1) ASTDR (1993) and HSDB (2000)

(2) ASTDR (1993), HSDB (2000) and IUCLID (1996)

In aquatic systems, lead tends to migrate into the sediment by adsorbing on organic matter or clay mineral, co-precipitate with carbonate, sulfate or sulfur or react with hydroxide or MnOx, but the concentration of Pb is influenced by pH.

1.2.7. Comparison of trace metal bioaccumulation

As mentioned above, the bio-concentration factor (BCF) is defined as the ratio of a chemical concentration in an organism to the concentration in the surrounding environment. This ratio is usually determined by laboratory experiences and results from exposure to waterborne chemical (Gobas and Morrison, 2000). We compare here the BCF of each trace metal mentioned above. Here after is a summary of BCF values in literatures (Table 13)

Table 13 Bio-concentration factor of trace metals

Metal	BCF			
	In phytoplankton	Reference	In animal	Reference
Chromium	9100	Wang et al., 1997	1 (Cr(VI))	EPA (1980)
	2300-2900	Braunschweiler et al., 1996	260-800 (Cr (III))	Giesy J.J.P. and Wiener J.G. (1977)
Cobalt	5-15	Warnau et al., 1999, Nolan and Dahlgaard (1991)	< phytoplankton	Yamada et Takayanagi (1995)
Copper	-	-	20 - 950	Wepener et al., (2000), Xiarong et al. (1997)
Zinc	BCF significantly weak due to regulatory process which is especially efficient for organisms at the top of the food chain (Ineris 2005)			
Nickel	2000	Cowgill, 1976	4050	Cowgill, 1976
	30-300	Wastras et al., 1985	2020	Cowgill, 1976
Lead	13.4-31.7	Watling (1983)	30.5-79.5	Nussey et al. (2000)
			300	IAEA (1994)

Table 13 shows that BCF of zinc is particularly weak due to the regulatory processes of the organisms. This regulation is especially more efficient for superior organisms of the food chain (Ineris (2005)). According to OECD, chemical hazard of a component is based on the persistence, bioaccumulation and toxicity profiler (PBT). For example, the toxicity of a metal is more important if it is qualified both as persistent and bioaccumulative (Deforest et al., 2007). The criteria of PBT profiler which allows to determine the bioaccumulation power of a chemical component is defined by United States Environmental Protection Agency (EPA) under the Toxic Substances Control Act (TSCA). According to "Persistent Bioaccumulative Toxic (PBT) Chemicals" by EPA (1999), a trace metal is considered as bioaccumulative if BCF is superior or equal to 1000 and as very bioaccumulative if BCF is superior or equal to 5000. Based on this criterion, cobalt and lead are not bioaccumulative due to their small value of BCF (around 5-15 for cobalt and 13.4-31.7 for lead). Copper might be bioaccumulative in fish depending on studies. Chromium and nickel are both bioaccumulative, even very bioaccumulative, in phytoplankton and aquatic animals in certain cases.

1.3. Biogeochemistry of trace metal in aquatic systems

In this subsection, we will focus on some biogeochemical processes involving the studied trace metals in aquatic ecosystems.

Manganese: Manganese can be present in water in the form of ion Mn^{2+} or $MnOx$ (Mn^{3+} and Mn^{4+}). Metals and nutrients may sorb to or coprecipitate with manganese oxides ($MnOx$). The oxidation of $Mn(II)$ by O_2 to $Mn(III)$ or $Mn(IV)$ is thermodynamically favored under pH and pO_2 conditions present in surface waters but this process is kinetically slow. Another mechanism of

oxidation or reduction of Manganese can be enhanced by light or in the presence of organic matter or biological processes. The dominant reductive and oxidative reactions are the following:

- Reductive dissolution (enhanced by light): MnOx can be reduced to Mn(II) by humic or fulvic acids
- Indirect photoreduction : Under light, H₂O₂ is photoproducted, which can reduce MnOx.
- Oxydation of Mn(II) : Mn(II) can be oxidized to MnOx in the water column. This process can be enhanced by sorption of Mn(II) and biological processes.

Dissolved Mn concentrations decrease in the presence of light and an active photosynthesizing algal community. This can be explained by the fact that in the presence of high algal activity, biological processes and light can decrease Mn(II) concentrations by oxidation. MnOx transformed will precipitate or co-precipitate with nutrients or other metals (Nico et al., 2002, SCOTT et al., 2002).

Iron: In aquatic systems, iron is an essential micronutrient for living organisms. It can be necessary for nitrate reduction and for the assimilation of nitrogen by algae. Iron is found in water under 2 forms: Fe(II) and Fe(III). Most photosynthetic organisms can take up iron only in dissolved and weakly complexed forms. Fe(II) has a high solubility and is not stable in the water bodies containing oxygen and neutral pH. Emmenegger et al. (1998) found that the half-life of Fe(II) in the epilimnion of Greifensee in summer is between 7 and 60 seconds. Fe(II) is rapidly oxidized in the presence of O₂ and H₂O₂. Fe(II) is produced in light-induced processes. Fe(II) concentrations increase during daytime, and decrease during night-time.

Fe(III) is stable but has an extremely low solubility. Reduction of dissolved Fe(III), which is in competition with precipitation can occur (Emmenegger et al., 2001) by:

- photolysis of organic and inorganic Fe(III) complexes
- reduction of dissolved, inorganic Fe(III) by superoxide
- reduction of Fe(III) at cell surfaces due to biological photosynthesis
- thermal, abiotic reduction of Fe(III) by organic reductants (humic acids)

Zinc: Phytoplankton blooms have the potential to deplete first Zn and then Co for enzyme carbonic anhydrase which is involved in the Calvin Cycle. These outcomes are confirmed in situ and in mesocosm experiments. Repartition of Zn between solid and dissolved forms is quite rapid, about 2 weeks whereas it can be until one month for Ni. However, Gee and Bruland (2002) showed that Zn desorbed more quickly than it adsorbed. This can imply an increase of Zn concentration about 20% in a day because of desorption. Remineralization of phytoplankton and reductive dissolution of Fe and Mn oxides can also release dissolved Zn. Note that Zn is strongly bound to hydroxides (Fe or Mn) and a positive correlation between DOC and Zn is often observed.

Morris et al., 2005 showed that diurnal Zn cycling, which means maximum concentration at dawn and minimum concentration in late afternoon, is primarily due to Zn sorption and desorption during photosynthesis activity.

Copper: Researches in San Francisco Bay (Luengen, 2007) showed that strong Cu complexation limits Cu uptake by phytoplankton. Between 80 – 99% of dissolved Cu is complexed to organic ligands: ligands produced by cyanobacteria, natural humic and fulvic substances, and synthetic chelating agents in surface or wastewater inputs. It was reported that during some spring blooms, in presence of chelating agents from anthropogenic activities, Cu was not depleted during algal bloom.

Nickel: In San Francisco Bay, during 1994 spring bloom, dissolved Ni was depleted until 75% of total concentration, but no similar result was found in laboratory experiments. About 25% of Ni surface runoff and 75% of Ni in wastewater runoff are strongly complexed by EDTA. Ni can also be reduced under UV degradation (Luengen, 2007)

Lead: Pb is highly reactive with particles. This is also demonstrated in laboratory experiments. Pb was highly sorbed to phytoplankton (cell surfaces). 95% of Pb is organically complexed in San Francisco Bay which confirmed that Pb was not internally up taken (Luengen, 2007).

Cobalt : Co and Mn have the same pathway of microbial oxidation, therefore their cycling would be linked. Similarly, to Zinc, Cobalt can be depleted by phytoplankton bloom because Zn and Co are used for enzyme carbonic anhydrase in the Calvin Cycle (Pokrovsky et al., 2010).

Cadmium: Cadmium is considered as a potentially harmful metal in freshwaters. Cadmium adsorption is pH dependent. Pokrovsky et al. (2010) showed that the adsorption of Cd by biofilm is pH dependent: pH <2, no adsorption; pH from 2.5 to 6.5, adsorption observed and above pH 7, 100% adsorption. In this study, 2 biofilms were used, one grown in contaminated site (300-2000 μ g/g biofilm dry weight) and the other in non-contaminated site (1-10 μ g/g biofilm dry weight) (Lot river, France). For a high concentration of Cd (0.1 to 10mg/L), no adsorption difference of the biofilms was observed. For a low concentration of Cd (0.5-100g/L), the non-contaminated biofilm sorbed 10 times more than the contaminated one. The main groups responsible for Cd binding at the biofilm surface are probably the carboxylates of the external cell envelopes (Pokrovsky et al., 2010; Luengen et al., 2007).

1.3.1. Trace metal speciation

Total concentration of trace-metals only reflects their quantity in the environment, but their environmental impacts and toxicity depend especially on the nature of the metal species. Speciation refers to distribution of different chemical forms of metal in the environment, which is fundamental to estimate their impact on the biota. Trace metal speciation in the soils and sediments and in the aquatic systems will be explained in the following section.

1.3.1.1. Trace metal speciation in soil and sediment

In soil and sediment, trace metals can migrate from solid phase into soil solution and can be available for the plants and microorganisms. Their speciation in soil and sediment can be defined according to functional or operational criteria.

Operational speciation refers to procedures, reagents and extractants used to quantify and qualify different fractions to which metals are linked (organic matter, iron oxide, manganese oxide, aluminium, carbonate, sulfur...) (Ure et al., 1993). Tessier et al. (1979) proposed a complete scheme of operational metal speciation which are classified into 5 fractions:

- Exchangeable metals: Metals adsorbed on the surface of sediments or their major constituents (clays, hydrated oxides of iron and manganese, humic acids). Sorption-desorption processes of metals are influenced by changes in water ionic composition
- Metals bound to carbonates: Trace metals are associated with sediment carbonates. They can be released as result of pH decrease.
- Metals bound to iron and manganese oxides: Iron and manganese oxides are excellent scavengers for trace metals. They are thermodynamically unstable with potential redox changes and under anoxic conditions.
- Metals bound to organic matter: Organic matter includes living organisms, detritus, coating on mineral particles etc. Oxidizing conditions in natural waters can release soluble metals as a result of organic matter degradation.
- Residual metals: This fraction includes metals embedded in the crystalline structure of minerals. These metals are not expected to be released under normal conditions of natural waters.

Functional speciation gives information concerning mobile forms, available forms for aquatic organisms (Muntau et al., 1992). In this speciation, a unique extractant including diluted acids, organic complexant or saline solutions is used in order to simulate physical-chemical conditions of soil. An example of functional speciation is bioavailability determination of trace metals for biological or microbiological cultures (Varrault, 2012).

1.3.1.2. Trace metal speciation in water bodies

Trace metals have been largely studied in marine (estuarine and coastal) and freshwater (river and lake) systems. Fewer studies focused on trace metal in lake systems. Moreover, trace metals in lakes are largely studied in sediments that are considered as their ultimate destiny. As a result, we have an incomplete image of behaviors of trace metals and their fate in the water column.

In aquatic systems, trace metals are divided between different compartments: water, suspended solids, sediment and biota. Distribution and repartition of metals are mainly influenced by different processes such as dilution, advection, dispersion, sedimentation, adsorption/desorption and bio-uptake. Indeed, they can exist as different chemical forms (Figure 2) free, bound to hydroxides, oxides, sulphates, silicates, adsorbed to clay or dissolved organic matter (Buffle 1998). Depending on the nature of the complexants, trace metals can be free, weakly or strongly bound, which can change their reactivity in aquatic systems towards biota. The qualification and quantification of metals, especially free ion metal, are essential to predict their ecotoxicity and consequences in aquatic environment (Campbell et al., 2006). In aquatic systems, free ion metal concentration depends strongly on water composition, physical chemical conditions and biological factors. For example, metals are complexed by inorganic ligands (chloride, bromide, cyanide, carbonate and hydroxide), dissolved organic matter, biotic ligand. The changes in physical chemical parameters such as ionic strength, pH, potential redox, anoxic conditions can modify trace metal speciation (Buffle 1988; Lead and Wilkinson 2006; Wilkinson and Buffle 2004). Beside dissolved organic matter that could influence significantly trace metal speciation, aquatic microorganisms could have this influence by surface reaction, bio-uptake, synthesis of intracellular chelators and production of extracellular polymeric substances with complexing properties (Worms et al. 2006)

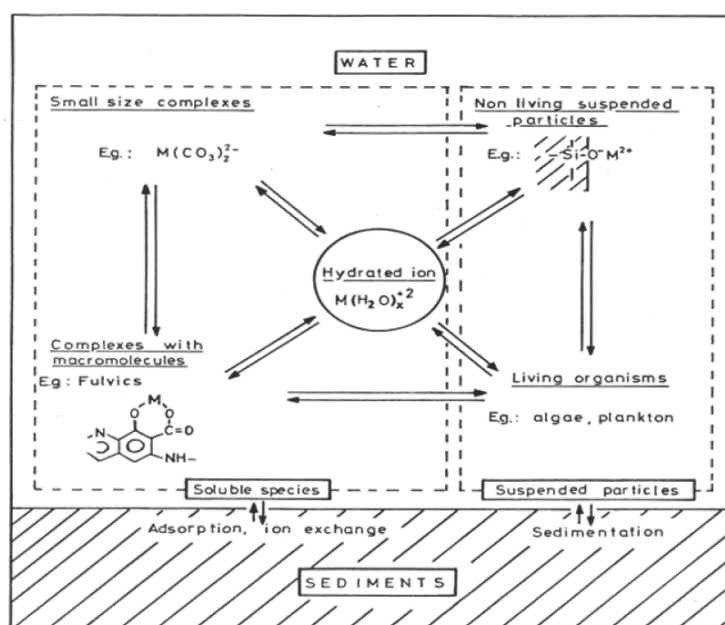


Figure 2 Schematic representation of trace metal in aquatic systems (Buffle 1998)

1.3.2. Dissolved organic matter

Dissolved organic matter (DOM) consists of an incredibly complex mixture of compounds, ranging from simple low molecular weight organic acids (LMWOAs) or sugar to high molecular weight humic acids and the humin fractions (Dudal and Gerard 2004). DOM is operationally defined as the fraction of organic substances that passes the filter (0.45 μ m) and the fraction that remains on the filter is called particulate organic matter (POM) (Mosofa et al., 2013). DOM can be natural or anthropogenic and originates from 2 sources. The allochthonous sources include terrestrial sources that organic matter (vegetation, soil, man-made or industrial activity) leaches from watershed area into rivers and lakes. The autochthonous sources include DOM that is produced in lakes by

phytoplankton and other living organisms. Autochthonous DOM comprised detritus, materials produced or secreted by phytoplankton (EPS) or by heterotrophic organisms such as bacteria or zooplankton. In freshwaters, DOM is distributed in two categories: the humic substances that represent up to 70% of DOM and the non-humic substances including extracellular polymeric substances that represent up to 25% (Thurman 1985, Wilkinson et al., 1997). This ratio can be different in urban or peri-urban lakes. Various scientific studies have been carried for humic substances, especially humic and fulvic acids, while the non-humic substances are less studied.

In aquatic systems, DOM is involved in the global carbon cycle, food webs, the availability of trace metals and other nutrients to the biota (Williamson et al., 1999). Metal-binding complexants can modify trace metal speciation in water. In the next section, we will describe more in details the two categories of DOM: the humic substances and the non-humic substances.

1.3.2.1. Humic substances

Humic substances are major components of the natural organic matter in soil and surface waters. Generally, humic substances are divided in 3 categories: humic acids, fulvic acids and humin. Humic substances are a complex mixture of highly heterogeneous organic matter that contains various functional groups including nitrogen groups (primary amine, imine etc.), oxygenated aliphatic groups (acids, aldehydes, ketones etc.), oxygenated aromatic groups (phenol, quinone, etc.) (Maccarthy and Malcolm, 1989) (Figure 3). Due to its complex nature, the biodegradability of humic substances is low to extremely low. Therefore, they remain in the water column before being mineralized. Their distribution and concentration in soil and aquatic systems depend strongly on physical chemical parameters and environmental conditions. For example, pH can modify humic substances forms. Fulvic substances are soluble at every pH while humic substances precipitate when pH is below 2.

As mentioned above, humic substances are known to be excellent scavengers of trace metals and can influence their speciation. Their ability to bind free metal ions come from two majors sites: carboxylic and phenolic. Indeed, the negative charge of humic substances results from the deprotonation of carboxylic groups (pKa around 4) and phenolic groups (pKa around 10). This negative charge has an ability to bind metals and to be adsorbed to the surface of hydroxides and clays that contain positive charges (Duval et al. 2005). The metal binding ability is influenced by different factors including salt concentration and pH. For example, it will decrease with an increasing salt concentration and decreasing pH (Benedetti et al., 1996a).

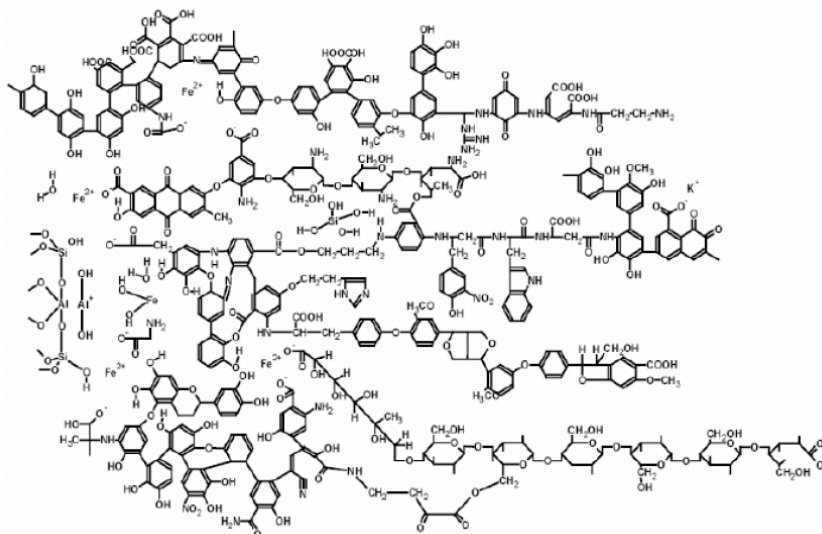


Figure 3 Example of typical humic substances (Buffle 1998)

1.3.2.2. Extracellular polymeric substances

Extracellular polymeric substances (EPS) are generally produced by microorganisms including algae and bacteria during their growth. Many factors can influence the release of extracellular polymeric substances such as pH change, nutrient limitation, toxic substances and cell density of micro-organisms (De Philippis et al. 2003). Indeed, due to EPS binding ability, the efficiency of nutrient uptake is increased in oligotrophic systems. The toxicity of free metal ions is reduced by EPS by adsorbing these metals (Gonzalez et al. 1996). Many studies found a correlation between EPS concentrations and high concentration of Pb, Cu, Cd in the water (Lombardi and Vieira 1998, Gonzalez-Davila et al. 2000, Vasconcelos and Leal 2001b).

EPS are complex high molecular weight mixtures of polymers containing proteins, lipids, polysaccharides, peptides, amino-acids (Fogg 1983). Carbohydrates and proteins are usually found as major components of EPS. Various factors such as culture, growth phase, process parameter, bioreactor type, extraction method, and analytical tool used, influence the composition of the extracted EPS (Nielsen and Jahn, 1999). Mykkestad (1995) showed that 80% of EPS released by the diatom *Chaetoceros affinis* is polysaccharides. Corradi et al. (1998) made a similar observation of EPS of green microalgae. *Scenedesmus actus* was reported to contain 25 times more polysaccharides than proteins.

EPS can contain many sites for the adsorption of metals (e.g. carboxylic, phosphoric, amino, and hydroxylic groups). Indeed, the presence of these functional groups makes EPS to have the ability of binding metals (Flemming and Leis, 2002, Guibaud et al., 2003 and Guibaud et al., 2006). Mayer et al., (1999) showed that the link between EPS and divalent cations, such as Ca(II) and Mg(II) is one of the main interactions in maintaining the microbial aggregate structure. Croot et al., (2000) showed that a decrease of the free Cu(II) concentration to non-toxic values is due to the release of ligands by bacterium *Synechococcus*. Carbohydrates and proteins found in the exudates of *Pseudokirchneriella subcapitata* reduce toxicity of Cd, Cu, Pb and Zn to this algae (Koukal et al. 2007).

EPS is a non-negligible part of DOM and could play a key role in metal binding. The next paragraph presents more details about transparent exopolymeric substances which are a group of EPS and also play a key role in metal binding.

1.3.2.3. Transparent Exopolymeric particles

Carbohydrates (also referred to as glycan) are macromolecules consisting only of carbon, hydrogen and oxygen. Carbohydrates can be divided in 4 groups:

- Monosaccharide - simple sugars, with multiple hydroxyl groups (triose, tetrose, pentose...);
- Disaccharides - two monosaccharides covalently linked;
- Oligosaccharides - a few monosaccharides covalently linked;
- Polysaccharides - polymers consisting of chains of monosaccharide or disaccharide units; Or polymers consisting of many sugars bound with N-osiidique link.

The transparent exopolymer particles (TEP) are at first carbohydrates, and then polysaccharides, more precisely acidic polysaccharides. Acidic polysaccharides are defined as polysaccharides containing carboxyl, phosphate and sulfuric ester groups.

According to Passow (2002), the Transparent Exopolymer Particles (TEP) are polysaccharides. In marine ecosystem, polysaccharide is one major part of labile fraction of dissolved organic carbon. TEP, which is part of exopolymeric substances family (EPS), are operationally defined as transparent particles that are formed from acid polysaccharides, retained on polycarbonate filters and are stainable with alcian blue (Alldredge et al., 1993). TEP differs from other EPS in a way that they have capacity of inter-aggregation to form bigger aggregates that are retained on filters, whereas other forms of EPS are dissolved.

TEPs were discovered and described 40 years ago (Gorden 1970, Wiebe et Pomeroy 1972, Emery et al. 1984). Smetacek et Pollehne (1986) investigated its potential importance in aquatic systems but no adequate analytical techniques were available at that time. When Alldredge et al. (1993) developed their investigation method, TEPs gained again a scientific interest. TEPs are individuals particles and they received a particular scientific attention because a lot of marine organisms, included phytoplankton and cyanobacteria product a large amount of extracellular polysaccharides (Hoagland, Rosowski, Gretz, & Roemaer, 1993; Costerton, 1995; Myklestad, 1995). In particular, diatoms are well known for their capacity of production of these particles (Watt, 1969; Allan, Lewin, & Johnson, 1972; Hellebust, 1974; Hama & Handa, 1983; Sundh, 1989; Williams, 1990).

Some studies have been carried out to investigate the role of TEP in marine and lacustrine ecosystems (Table 14). Their abundance varies from 10^2 to 10^7 particles L^{-1} and their size varies from 2 to 100 μm . TEPs are often positively correlated to phytoplankton biomass and to chlorophyll a concentration.

Table 14 Abundance of TEP in natural lakes

Study site	Sampling depth (m)	Abundance (particles L^{-1})	Reference
Lake Constance	2-25	$0.5 \cdot 10^2 - 1.5 \cdot 10^6$	Grossart <i>et al.</i> (1997)
Lake Constance	6-100	$7.1 \cdot 10^4 - 2.6 \cdot 10^6$	Brachvoege <i>et al.</i> (2001)
Lake Kinneret	15-35	$1.0 \cdot 10^5 - 7.0 \cdot 10^6$	Grossart <i>et al.</i> (1998)
Lake Kinneret	1-38	$4.4 \cdot 10^5 - 2.5 \cdot 10^7$	Berman et Viner-Mozzini (2001)
South California Bay	10	$2.5 \cdot 10^4 - 6.3 \cdot 10^5$	Allredg <i>et al.</i> (1993) Passow et Alldredge (1994)
Lake Pavin	0.5 – 58	$1.9 - 13.4 \cdot 10^5$	Arnous <i>et al.</i> (2010)
Arabian sea	0-1500	$2.0 \cdot 10^6 - 3.5 \cdot 10^7$	Long et Azam (1996)
Mediterranean sea	0-40	$1.0 \cdot 10^7 - 2.2 \cdot 10^8$	Mari <i>et al.</i> (2001)

Studies have shown that the binding of metals to DOM secreted by algae is more significant than the binding of metals on the surface cells and could decrease metal bioavailability and toxicity in aquatic systems (Gonzalez-Davila et al., 1995; Muller and Kester, 1991; Xue and Sigg, 1990, Santana- Casiano et al. (1995), Choueri et al. (2009), Lorenzo et al. (2007), Nogueira et al. (2005). Mechanism of metal binding by DOM secreted by phytoplankton started to be studied recently. Most of these studies consist of laboratory experiments with a specific type of phytoplankton: (1) Carbohydrates fraction dominates over other DOM produced by a toxic planktonic Cyanobacteria *Cylindrospermopsis raciborskii*. This fraction showed a high correlation with ligand concentration and conditional stability constant with Cu, Cd, Zn and Pb (Tonietto et al., 2013); (2) Copper toxicity is lower in batch cultures of *Anabaena spiroides* with the presence of cyanobacteria exudates (Choueri et al., 2009); (3) In batch cultures, *Anabaena spiroides* exudates showed the ability to bind Mn(II) and these algal surfaces have affinity to Cu(II), Pb(II), Hg(II) and Mn(II) (Freire-Nordi et al., 2005). Recently, Pokrovsky and Shirokova (2013) showed that the concentration of Mn decreased during the day due to adsorption onto cyanobacterial cells in the Lake Svyatoo - a boreal lake during summer bloom. Similar patterns were observed for Ba and Fe.

Most of scientific studies about TEP are based on laboratory experiments with simulated environmental conditions.

1.3.2.4. TEPs and the cycle of trace metals

Two processes are involved in TEP production from colloidal precursors: biotic and abiotic processes. TEPs are spontaneously formed from dissolved precursors. This abiotic formation depends

on environmental conditions (turbulence, ionic composition, mineral colloidal concentration) and also depends on the type of precursor.

Precursors of TEPs are fibrils of 1-3 nm diameter and 100nm length. During the state of exponential growth of phytoplankton, surface cells exude these precursors. These free precursors can be able to form aggregates from submicron size (1µm) to bigger aggregates or TEPs.

Formation of submicron particles is favored and stabilized by cations, in particular Ca^{2+} by cationic bridge formation that allows the particles to aggregate more easily. That is the reason why TEP dissociates under presence of strong complexing agents such as EDTA¹ which is a chelating agent of Ca^{2+} and Mg^{2+} . TEPs can also be formed from mucus detached from surface cells of phytoplankton. This occurs during growth state of phytoplankton or during colonies disintegration in senescent state. The peak of TEP production is often associated to phytoplankton bloom (dinoflagellates, cyanobacteria, *Cryptomonas*), in particular during diatom bloom period. Laboratory assays confirm that phytoplankton is a major source of TEPs. TEP production varies in relation to light, CO_2 concentration, nutrients, trace metals and growth state.

1.4. Objectives of the thesis

Trace metals have been largely studied in marine (estuarine and coastal) and freshwater (river and lake) systems. With an increasing economic development, which entails industrial activities in large scale and rapid urbanization, trace metal pollution capture rising public concerns even though it is considered as a “traditional” environmental problem. But few studies focused on trace metals in lake systems. Moreover, the trace metals in lakes are largely studied in sediments that are considered as their ultimate fate. As a result, we have an uncomplete image of behaviors of trace metals and their fate in the water column.

In aquatic systems, trace metals can exist in many different chemical forms, which determine bioavailability and toxicity to aquatic organisms (Hirose, 2006, Morel et al., 2003). The labile metal fraction, which can be easily linked to aquatic organisms, is a good indicator of toxicity. Therefore, it is important to study this fraction of trace metal in aquatic systems.

Our methodology is based on a dense field survey of the aquatic systems in addition to common and specific laboratory analysis. The research has been conducted on three study sites: Lake Créteil in France, Lake Pampulha in Brazil and a panel of 49 peri-urban lakes in the Ile de France region.

Lake Créteil is an urban lake relatively less impacted by anthropogenic pollution than Lake Pampulha. It benefits of a large number of monitoring equipment, which allowed us to collect a part of the data set.

In Lake Pampulha catchment, the anthropogenic pressure is higher. Lake Pampulha has to face with many pollution point and non-point sources. The climate and limnological characteristics of the lakes are also very different.

The panel of 49 lakes of Ile de France was sampled once during three successive summers (2011-2013); they provided us with a synoptic, representative data set of the regional metal contamination in a densely anthropized region.

¹ EDTA Ethylene Diamine Tetraacetic Acid

The key objectives of the thesis can be summarized as follows:

- (1) to analyze the seasonal and spatial evolution of the trace-metal concentrations and their speciation in the water column of the studied lakes;
- (2) to study the potential impact of environmental variables, particularly of autochthonous dissolved organic matter related to phytoplankton production on metal bioavailability in these lakes;
- (3) to link the metal concentrations to the land use in the lake watershed.

In this research, we will try to achieve these objectives using a complete *in situ* environmental monitoring database.

2. Material and Methods

2.1. Presentation of the study sites

2.1.1. Lake Créteil

Lake Créteil is located southeast of the confluence of the rivers Marne and Seine (48°46'37''N, 2°26'47''E), in the alluvial plain limited by these two rivers and the tertiary outcrops of the Mont Mesly hill (NE) and the Bois de la Grange Plateau (SE) (Chesterikoff et al., 1981). The lake is situated in a suburban zone of Paris, in the Val-de-Marne county, nearby a high-density traffic area:highway (A86), roads (D60, N186), high speed trains lines etc.). Lake Créteil was created in a former gravel pit. Its bathymetry is shaped by two simultaneous activities: alluvial gravel extraction until the base of superficial water table and filling with diverse backfill (earthwork materials, rubble, household waste etc.). The definitive form of the lake was defined at the end of the exploitation of gravel pit in 1976. The lake is oriented following a north-south axis. Between 1976 and now, Lake Créteil became a landscape element and a recreation area of city Créteil with a recreational center that organizes outdoor activities including picnic, bicycling, nautical sports etc. Its area is 0.42 km², the length is 1.5km, the mean width is 0.2km with a maximal width of 0.4km. The depth varies from 4 to 4.5m for the major part of the lake with a maximal depth of 6m (Table 15). The volume of the lake is 1.5 10⁶ m³ (Testard, 1983).

Table 15 Characteristics of Lake Créteil

Altitude	34.4 m
Mean depth	4 m
Maximal depth	6 m
Surface	0.42 km ²
Volume	1.5 x 10 ⁶ m ³

2.1.1.1. Geology

Lake Créteil is essentially constituted by modern alluvium (silt, clay, clayey sands) in the first depths from 1.5m to 4.5m and by older alluvium (sand, gravel) in the deeper layer. After extraction of these alluviums, they were replaced by heterogeneous backfill of landfill materials rich in organic matter. The deepest layer consists of marl and limestone of Saint-Ouen and Beauchamps sand (Qualité du lac de Créteil, 2006).

2.1.1.2. Hydrological characteristics

Lake Créteil is totally isolated from the surface hydrologic network. It is essentially fed by an alluvial surface water table flowing from the Marne to the Seine River. The deep aquifer in coarse limestone of Champigny is completely isolated from the surface water table. The fluctuations of the water table level and of the lake are strongly linked. The baseline of the water table is regulated by the Marne and the Seine rivers. For the small floods, there is no significant consequence on variation of water level and volume of the lake. Thus, stormwater coming from the catchment of Mont Mesly and rainfall inputs (around 680mm per year) are the main drivers of the variation of water level. The lake has a unique outlet going into the stormwater network. According to Chesterikoff et al. (1981), the residence time of water is 6 months to 1 year depending on the hydrological conditions. The range of level fluctuation is inferior to 50cm with a maximal water level in March-April and minimal in October-November.

2.1.1.3. Major elements concentration, conductivity and pH

In Lake Créteil water, high concentrations of sulphate, calcium, chloride and sodium (sorted by order) are measured. The salinity of the lake varies from 1.3 to 1.6 g/L while the surface water in France contains generally calcium and bicarbonate and has salinity around 0.5g/L. Consequently, due

to a high mineralization, the lake presents a high conductivity 1250 $\mu\text{S}/\text{cm}$ in 2002, 1490 $\mu\text{S}/\text{cm}$ in 2004 and 1510 in 2013). The lake is slightly alkaline with pH from 6.8 to 8.8 between 2011 and 2013 (our data)

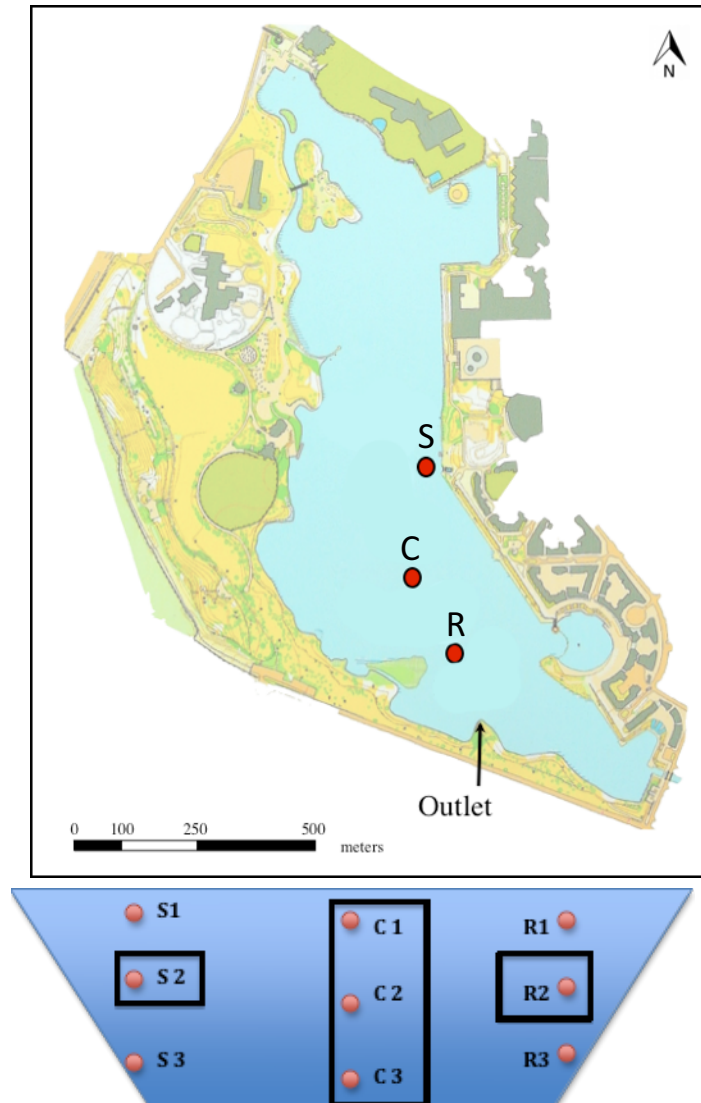


Figure 4 Lake Créteil and monitoring points

2.1.1.4. Monthly monitoring in the Lake Créteil

The monitoring of Lake Créteil was conducted by LEESU (Ecole des Ponts Paris Tech) in partnership with laboratory BIOEMCO with logistic support of the outdoor aquatic center of Lake Créteil. The monitoring started in 2011 and finished in December 2013 in the framework of the research project PULSE - Peri-Urban Lakes Society and Environnement funded by ANR².

² ANR (Agence Nationale de la Recherche) French national agency for research funding

2.1.1.5. Meteorological data

Since May 2012, a weather station has been installed in the point Central of Lake Créteil (Figure 5). This station measures continuously various parameters including meteorological parameters (air temperature, wind direction, wind velocity, barometric pressure, relative humidity, precipitation), physical and biological parameters at 5 different depths (water temperature, chlorophyll-a concentration, photosynthetically active radiation).

2.1.1.6. The field campaigns

The field campaigns, conducted on Lake Créteil, started in October 2011. The frequency is monthly. The monitoring campaigns include three sampling points located on an horizontal transect, from the storm water outlet to the lake outlet : the « S » point is close to the storm water outlet, the « R » point is located next to a reedbed area and the central point « C », is located between S and R (Figure 5). For each sampling point, three depths are defined: surface (0.5 meters), middle (1.5 meters) and bottom (3.5 meters). For each campaign, a “lake average sample”, named “M” is made by mixing 9 samples collected at three depths at the three points (S1, S2, S3, C1, C2, C3, R1, R2, R3). Water samples are collected using a NISKIN bottle.

For each campaign, 6 samples are collected for trace metal and TEP analysis: S2 (middle of the water column at point S), C1, C2, C3 (3 depths at central point), R2 (middle of the water column at point R) and M (lake average point).

2.1.1.7. Probe measurements

Vertical profiles of physical (salinity, temperature, oxygen, conductivity, photosynthetically active radiation (PAR), water transparency) and biological (chlorophyll a) parameters are also monitored *in situ* using probes: CTD Seabird43, LI-COR193 (underwater PAR sensor), Fluoroprobe BBE.

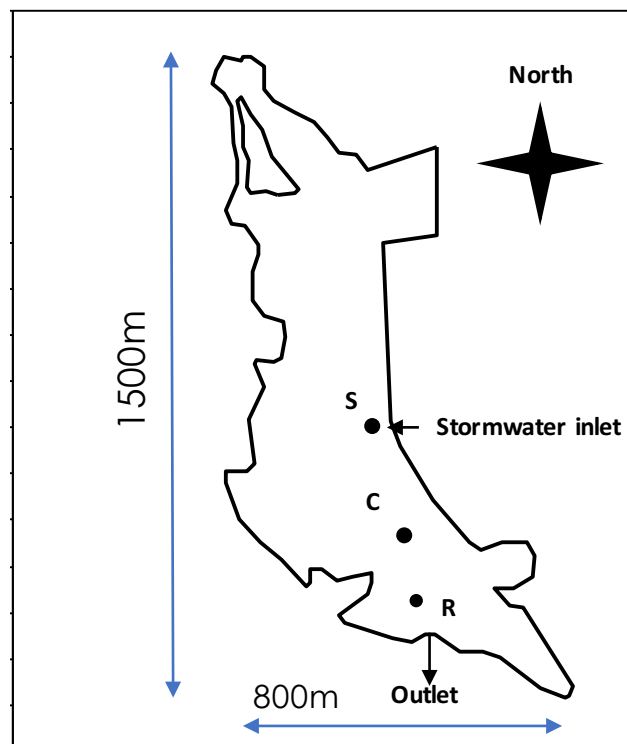


Figure 5 Monitoring physical and biological parameters of the meteorological station (from Soullignac et al. 2014)

2.1.1.8. Monitoring of raining events in the Lake Créteil

Lake Créteil receives the rainfall input from the urbanized catchment Mont-Mesly. Between June and December 2013, 5 rainfall events were monitored. Each rain campaign consists of 2 parts: collecting the runoff water into the lake by using an automatic sampler, sampling at 3 points P, C, R in the lake the day after the raining event.

Table 17 Characteristics of raining events in the Lake Créteil

	Event 1	Event 2	Event 3	Event 4	Event 5	Event 6
Date	19/06/13	28/07/13	14/10/13	16/10/13	20/10/13	03 and 04/11/2013
Raining events						
Max intensity (mm/h)	88.2	34.4	31.4	4.6	52.3	16.7
Cumulative rainfall (mm)	22.7	5.0	4.5	0.4	4.2	4.2
Duration (h)	9.9	0.6	0.6	1.1	0.3	4.7
Return period	5 ans	6 mois	6 mois	15 jours	6 mois	3 mois
Max flow rate (l/s)	435.2	413.9	761.5	279.8	694.7	248.3
Previous days						
Cumulative rainfall j^{-1} (mm)	6.6	0.0	0.0	0.0	0.3	0.8
Cumulative volume j^{-1} (m ³)	1121.7	37.2	97.0	168.8	84.1	624.2
Cumulative rainfall j^{-7} (mm)	19.9	24.2	2.0	6.5	5.4	9.9
Cumulative volume j^{-7} (m ³)	3940.8	3452.0	1317.7	2743.8	3319.4	7957.0
Concentrations						
[Pt] (µgP/L)	1389.06	1000.5	2720.22	562.25	2834.42	439.87
[PO ₄] (µgP/L)	50.67	194.8	102.44	89.88	118.66	75.48
[NO ₃] (mgN/L)	0.33	0.37	0.33	0.34	0.19	0.17
[DOC] (mg/L)	4.18	11.57	9.26	6.56	9.09	3.94
[SM] (mg/L)	275.96	134.4	544.8	85.1	380.1	43.2
[POC] (mgC/L)	44.19	25.3	97.82	17.32	58.95	9.3
[POC] (gC/gMES)	16.01	18.83	17.95	20.36	15.51	21.52

Table 18 Laboratory analysis for raining event monitoring and punctual tributaries campaign

Analysis	Method
TSS	Gravimetry (ALPHA, 1998)
Turbidity	Turbidimeter (TB-1000P, TECNOPON)
Amonical nitrogen macro	Mineralization and titration (ALPHA, 1998)
Nitrogen Kjeldahl macro	Mineralization, distillation and titration (ALPHA, 1998)
Amonical nitrogen semi-micro	Distillation and colorimetry (ALPHA, 1998)
Nitrogen Kjeldahl semi-micro	Mineralization, distillation and titration (ALPHA, 1998)
TOC, TC, IC and nitrogen total	TOC – VCPN, SHIMADZU and TNM-1, SHIMADZU
Anions (fluoride, nitrate, nitrite, phosphate, sulphate, chloride)	Inionic chromatography (ICS-1000, DIONEX)
Total phosphorus	Mineralization and colorimetry (ALPHA, 1998)
Trace metal	Conservation and analyzed in ICP-MS

2.1.2. Lake Pampulha

Lake Pampulha is located in the city of Belo Horizonte southeast of Brazil, capital of the state of Minas Gerais. The population of Belo Horizonte reaches 2.4 million inhabitants. The city, which is located in a mountainous region, has an altitude of 750 to 1,300 meters. Lake Pampulha is considered one of the most important components of the urban development of the region. The reservoir has an area of approximately 1.9 km² and a volume of at about 10 million m³. Its maximum depth is 16m and the average depth is 5 m. The climate is tropical highland, with a high yearly rainfall of 1600mm of which 90% occurs mainly during the raining season from October to March. Typical rainfall intensities are relatively high: 200 mm/h (10-year return period event with 5 minutes duration) and 70mm/h (50-year return period and 1h duration event) (Table 19)

The Lake Pampulha was constructed in 1938 and firstly conceived to supply drinking water for the north part of the city. After the dam failure due to a major rainfall event in 1954, the lake was reconstructed in 1958 with the following multi-objectives: water supply, flood control, recreation activities. From the 1970s, rapid urbanization occurred when population increased significantly and industry has developed. Lack of sanitation network infrastructure has led to the degradation of the water quality of Lake Pampulha. Until 1980, the lake water was treated and distributed as drinking water for different regions of the city. Indeed, from 1980 up to now, the water quality of the Lake Pampulha has been heavily impacted due to many factors: the intense and disorganized urbanization of the region which resulted in a population increase of 300,000 inhabitants in a 30 year period (Silva 2014); lack of adequate sanitation and solid waste management; uncontrolled illicit domestic and industrial sewage discharge into the lake. One of the main consequences of the degradation of water quality in Lake Pampulha is eutrophication due to the excessive discharge of nutrients (phosphorus and nitrogen), which results in a permanent state of algal blooms. The Pampulha Reservoir has also to struggle against the loss of water surface area within the reservoir due to silting problem, estimated to vary between 200,000 – 400,000 m³ of sediment deposition annually. Moreover, scientific studies showed high heavy metals pollution in the main streams (Ressaca and Sarandi) and in the lake (water column and sediment) (Friese et al., 2010, Rietzlet et al., 2001).

Since the 1980s, due to degradation of water quality by eutrophication, many limnological studies have been conducted to improve the knowledge about: (1) seasonal cycle of nitrogen and phosphorus (Pinto Coelho and Giani, 1992), (2) mesozooplankton community (Pinto Coelho, 1998), (3) carbon production and consumption of planktonic community (Araújo and Pinto-Coelho 1998), (4) phytoplanktonic community (Giani et al., 1999, Figueredo and Giani, 2001), (5) Biochemical composition and nutrient (Boëchat and Giani, 2000; Torres et al., 2007), (6) Heavy metal (Rietzler et al., 2001; Sabino et al., 2004, Friese et al., 2010), (7) Bathymetry (Resck et al., 2007).

Table 19 Physical characteristics of Lake Pampulha and Pampulha watershed

Altitude	801 m
Mean depth	5.1 m
Maximal depth	16.2 m
Surface	1.97 x 10 ⁶ m ²
Volume	9.9 x 10 ⁶ m ³
Pampulha Watershed**	
Population (inhabitants)	424 000
Total surface	98 km ²
Sub-catchment Ressaca	20 km ²
Sub-catchment Sarandi	49 km ²
Mean flow dry season Ressaca + Sarandi	0.65 m ³ /s
Mean flow raining season Ressaca + Sarandi	1.63 m ³ /s

* Resck et al. (2007) ** Silva (2014)

The Pampulha catchment has an area of 98 km², 44 km² of which is located in the territory of Belo Horizonte municipality while the other 56 km² is located in Contagem municipality. The outlet of the reservoir is Pampulha stream, a tributary to the river Onça, which after rejoins the river Velhas. The Lake Pampulha is fed by 8 streams: Olhos d'Água, AABB, Baraúna, Água Funda, Tijuco, Mergulhão, Sarrandi et Resseca. Ressaca and Sarandi streams are the two principal tributaries to the lake, contributing with at about 70% of the volume inflow to the lake. According to Friese et al., (2010), Ressaca and Sarandi are responsible for trace metal contamination in the lake originating from steel industry (Fe, Cr, Ni, Co), solvent and paint industry (Ni, Cr, Pb) and landfill dump (Cu, Fe, Mn, Ni, Cd, Pb, Zn) of the cities of Belo Horizonte and Contagem. In 1930, the Pampulha catchment was still a rural area while it is highly urbanized nowadays. Based on aerial photographs, CPRM estimated in 42% the urban area in the Pampulha catchment for the period 1994-1995 (CPRM, 2001). In 2013, only urbanized zones of subcatchment Ressaca and Sarandi correspond itself up to 50% of total surface (Silva , 2014). Currently, the urbanized part of the watershed contains a residential, with shopping centers on main roads and an industrial center south of the sub-watershed Sarandi.

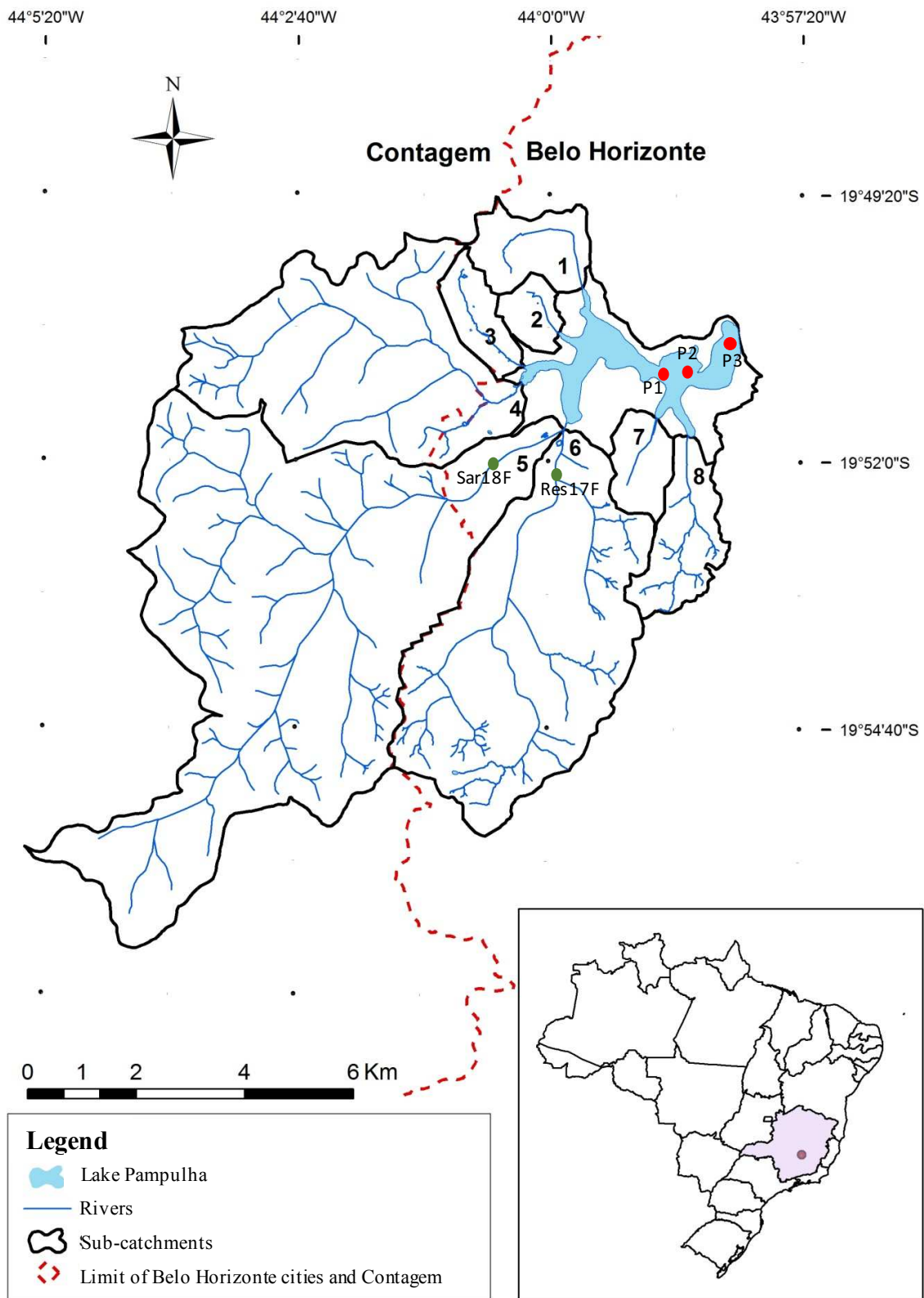


Figure 6 Localisation of Lake Pampulha. Tributaries : (1) Olhos d'água ; (2) AABB ; (3) Bráunas ; (4) Água Funda ; (5) Sarandi ; (6) Ressaca; (7) Tijuco et (8) Mergulhão (Silva et al., 2014)

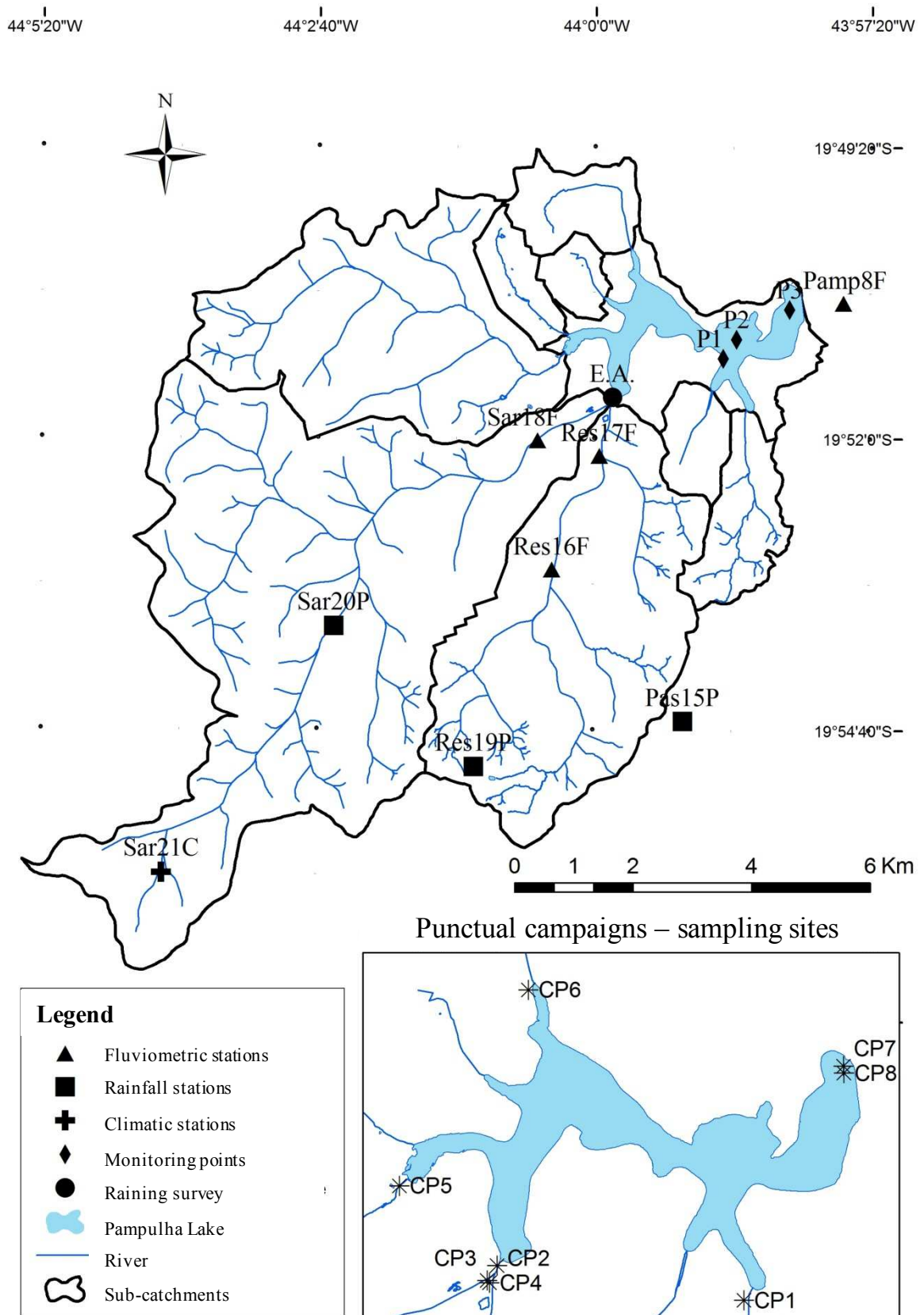


Figure 7 Sampling points of Lake Pampulha, measure stations of PBH, localization of automatic sampler. Adaptation from Silva, 2014

2.1.2.1. Environmental monitoring of Lake Pampulha

The monitoring of Lake Pampulha has been conducted in partnership with the laboratory of Phycology of the Instituto de Ciências Biológicas (ICB) of UFMG and the municipality of Belo Horizonte. The monitoring began in 2011 in the framework of Talita Silva's thesis (Silva, 2014). The present thesis followed and continued the framework already established for common parameters and introduced protocols for the parameters: trace-metals and TEP.

2.1.2.1.1. Meteorological data

Meteorological data is provided by the Instituto Nacional de Meteorologia do Brasil (INMET). The nearest weather station is located inside UFMG Campus, about 3 km from Lake Pampulha. This station registers hourly the minimum, maximum and instantaneous temperature, air moisture, wind direction, cumulative solar radiation and precipitation over 1 hour. The data is updated every hour on the website of INMET (www.inmet.gov.br) and is freely used up to 3 months after its online publication. After this period, it is necessary to contact INMET to obtain the data (Silva, 2014).

2.1.2.1.2. The field campaigns

The field campaigns, conducted on Lake Pampulha, have started in October 2011 under the framework of the research project MAPLU (Storm water management project, funded by the Brazilian Agency for Funding Study and Projects – FINEP). Three sampling points were selected in the lake, located as follows: the point “P1” close to the Igreja da Pampulha P1(19°51,399'S; 43°58,751'W), the point “P2” close to Casa do Baile (19°51,197'S; 43°58,548'W) and the point “P3” close to the lake outlet (19°50,698'S; 43°58,071'W). (Figure 6).

From December 2011 to June 2013, the field campaigns were conducted with a frequency of twice per week. Water samplings were collected at a depth of 50cm at three points P1, P2 and P3 using the Van Dorn bottle. From January 2013 up to June 2014, only the point P2 has been monitored because we decided to investigate the distribution of physical chemical and biological parameters at different depths. Water samplings were collected at 4 depths: 0.50m, 1.50m, 3.50m and 7.0m. Concerning trace metal speciation, the samplings were collected at 3 depths and defined as surface (0.50m), middle (3.50m) and bottom (7.0m).

2.1.2.1.3. Probe measurements

Vertical profiles of water temperature, conductivity, pH, dissolved oxygen and redox potential (ORP) are conducted *in-situ* using the multi-parameter probe YSI 556 (YSI, EUA). From June 2012 to January 2013, we couldn't measure these vertical profiles because the probe was out of service.

Chlorophyll a concentration was also monitored *in situ* using Fluoroprobe BBE for 2 periods: from September to November 2011 and from August to November 2012 and Fluoroprobe AlgaTorch from January to June 2013 with monthly frequency.

Water transparency was determined by using Secchi disk. Water sampling is performed by using Van Dorn bottle. Samples are conserved in polyethylene bottle 2L at 4°C in a cooler, protected from light until analysis. Laboratory analyses include (TSS, NO₃-N, NO₂-N, NH₄-N, SO₄-S, N-total, P-total, PO₄³⁻ and DOC), main anions (F⁻, Cl⁻, Br⁻) and trace metal (Fe, Mn, Si, As, Cd, Co, Cr, Cu, Pb, Sb, Sn, Zn). Analyses for physical chemical parameters are conducted according to the Standard Methods for the Examination of Water and Wastewater (Greenberg et al. 1992). Trace metal speciation and TEP concentration determination are described in next sections.

Chlorophyll a analysis is performed by photospectrometer according to Nusch, 1980. Phytoplankton identification and counting are prepared following Utermöhl, 1958 and conducted following the method developed by laboratory of phycology of ICB since the 1980s.

2.1.2.2. Horizontal transect

With the purpose of assessing the influence of the water flow on the transport of pollutants in the lake, 2 horizontal transects were conducted in September 2012 and January 2013. In these transect campaigns; water was collected under the surface (0.5m) and above (0.5m) the bottom of 6 points from the outlet (point A) to the inlet of the lake (point F) (Figure 8). We expected that an increasing concentration gradient goes in this direction.

The first campaign in 5 September 2012 occurred during the dry season. The most recent raining event at tributaries Ressaca and Sarandi was registered 114 days before with 34 mm rainfall. The second campaign in 22 January 2013 occurred during the rain season: there were 3 raining events registered from 6 mm to 52 mm, 2 days before the second campaign. The first campaign in 5 September 2012 is representative of the dry period and the second campaign in 22 January 2013 is representative of the raining period. (Table 20).

We remind that the localization of the rainfall stations are indicated in Figure 7



Figure 8 Localization of the sampling points of the horizontal transect (Google Earth ©)

Table 20 Hydrological of characteristics of the campaigns.
Rainfall stations Res17F and Sar18 F are localized in Figure 7

September 2012	Rainfall station (Res17F)	Rainfall station (Sar 18F)
Rain during the day of campaign	No rain	No rain
Preceding raining events (mm daily rainfall)	14/05/2012: 34mm Period without rain: 114 days	14/05/2012: 38mm Period without rain : 114 days
January 2013	Rainfall station (Res17F)	Rainfall station (Sar 18F)
Rain during the day of campaign	No rain	No rain
Preceding raining events (mm daily rainfall)	20/01/2013: 5.2 mm 17/01/2013: 22mm 11/01/2013: 51.6 mm Period without rain: 2 days	20/01/2013: 5.6 mm 17/01/2013: 21.5 mm 11/01/2013: 54mm Period without rain: 2 days

2.1.2.3. Continuous hydrological monitoring

Due to the importance of sub-catchments Ressaca and Sarandi in term of volume contribution to the Lake Pampulha, continuous hydrological monitoring has been conducted at the confluence of tributaries Ressaca and Sarandi. The sensors (Global Water, EUA) measured continuously with frequency of 5 minutes temperature, turbidity, electrical conductivity and water level at the confluence of Ressaca and Sarandi (ETAF), upstream of Lake Pampulha. The localization of the station corresponds to the point E.A in Figure 7 . In order to monitor hydrological parameters downstream of Lake Pampulha, the similar system is installed at the outlet of the lake (TULIPA). The localization of this station corresponds to the points CP7, CP8 in Figure 7. Hydrological monitoring at ETAF and TULIPA has been conducted between mid-February and mid-June 2013. From March 2014, hydrological monitoring has been conducted by a new monitoring system (Campbell) (Table 21)

The municipality of Belo Horizonte (PBH) made available their own hydrological monitoring system which includes: (1) four automatic stations which register water level of the tributaries and precipitation, (2) three stations which measure precipitation in the sub-catchments, (3) one weather station upstream of sub catchment Sarandi which measure different meteorological parameters (precipitation, atmospheric pressure, wind direction and speed, temperature and humidity) (Silva, 2014). The monitoring frequency of these stations is of 10 mins. The monitoring system started at the end of 2011. All data are real-time accessible from website of PBH (Figure 7)

Table 21 Hydrological monitoring system (MAPLU)

Station	System	Period	Measure
ETAF	Global Water	Mid-Feb to Mid-June 2013	Water level, conductivity, turbidity
TULIPA	Global Water	Mid-Feb to Mid-June 2013	Water level, conductivity, turbidity, dissolved oxygen*
ETAF	Campbell	March to August 2014	Water level, conductivity, turbidity
TULIPA	Campbell	March to August 2014	Water level, conductivity, turbidity, dissolved oxygen*

* Dissolved oxygen concentration was not measured at ETAF due to permanent wastewater discharge at ETAF

Table 22 Monthly monitoring of Lake Pampulha from 2011 to 2012

Measure	2011				2012											
	Set*	Oct*	Nov*	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Set	Oct	Nov	Dec
Monitoring points																
P1, P2 e P3 - depth 50 cm																
P2 – depth: 0.5; 1.5; 3.5 e 7.0 m																
Vertical profiles																
Phytoplankton 4 families (bbe fluoro)																
Phytoplankton Chla totale + Cyano (AlgaeT)																
Light PAR (Licor)																
Conductivity, pH, Oxygen dissolved, ORP																
Temperature																
Buoy SMATCH																
Laboratory analysis																
Chlorophyll-a spectrophotometry																
Nutrient																
Phytoplankton counting et identification																
Suspension Matter																
Trace metals																
TEP																
Secchi																

* weekly frequency

Table 23 Monthly monitoring of Lake Pampulha from 2013 to June 2014

	2013												2014					
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun
Monitoring points																		
P1, P2, P3 depth 0.5m	■																	
P2 depths: 0.5; 1.5; 3.5; 7.0 m		■	■	■	■	■							■	■	■	■	■	■
Vertical profiles																		
Phytoplankton 4 families (bbe fluoro)																		
Phytoplankton total Chla + Cyano (AlgaeT)	■	■	■	■	■	■							■	■	■	■	■	■
Light PAR (Licor)																	■	■
Conductivity, pH, Oxygen dissolved, ORP		■	■	■	■	■							■	■	■	■	■	■
Temperature	■	■	■	■	■	■							■	■	■	■	■	■
Buoy SMATCH			■	■	■	■												
Laboratory analysis																		
Chlorophyll-a spectrophotometry	■	■	■	■	■	■							■	■	■	■	■	■
Nutrient	■	■	■	■	■	■							■	■	■	■	■	■
Suspension Matter	■	■	■	■	■	■							■	■	■	■	■	■
Trace metals	■	■	■	■	■	■							■	■	■	■	■	■
TEP			■	■	■	■							■	■	■	■		
Secchi	■	■	■	■	■	■							■	■	■	■	■	■

2.1.2.4. Monitoring of rain events in the Lake Pampulha

Rain events monitoring

Water sampling during rainfall-runoff events has been conducted using an automatic sampler ISCO 3700 (Teledyne ISCO, EUA) in conjunction with 1640 Liquid Level Sampler Activator. The sampling routine is triggered when the water in the stream reaches a previously established level. The determined triggered water level corresponds to a weak and medium rain event.

The sampling program aims at sampling stream water during rainfall-runoff events. Taking into account the existing time series of rainfall and water levels monitored in the Ressaca and Sarandi tributaries, the water sampler located at the mouth of these tributaries in the lake was programmed to sample water during 4 hours with a sampling frequency of 10 minutes. A typical flood hydrograph having a base time of 4 hours. This sampling duration is chosen to be able to follow the intergrity of rain event.

The water sampler contains 24 high-density polyethylene bottles with 1L capacity. During 4 hours, 800mL of water is sampled each 10 minutes. At the end of the sampling, the 24 bottles are put in a cooler and transported to laboratory for the analysis

In the laboratory, we undertake measures of electrical conductivity, turbidity and pH of each sample. Based on these parameters and on the characteristics of the corresponding flood hydrograph (base time, time to peak, recession time, peak flow), the number of samples can be reduced to 12 bottles by regrouping two or more raw samples having similar conductivity, turbidity and pH. After regrouping the samples, water quality analysis can be conducted (Table 24).

Table 24 Laboratory analysis for raining event monitoring and punctual tributaries campaign (Silva 2014)

Analysis	Method
TSS	Gravimetry (ALPHA, 1998)
Turbidity	Turbidimeter (TB-1000P, TECNOPON)
Amonical nitrogen macro	Mineralization and titration (ALPHA, 1998)
Nitrogen Kjeldahl macro	Mineralization, distillation and titration (ALPHA, 1998)
Amonical nitrogen semi-micro	Distillation and colorimetry (ALPHA, 1998)
Nitrogen Kjeldahl semi-micro	Mineralization, distillation and titration (ALPHA, 1998)
TOC, TC, IC and nitrogen total	TOC – VCPN, SHIMADZU and TNM-1, SHIMADZU
Anions (fluoride, nitrate, nitrite, phosphate, sulphate, chloride)	Inonic chromatography (ICS-1000, DIONEX)
Total phosphorus	Mineralization and colorimetry (ALPHA, 1998)
Trace metal	Conservation and analyzed in ICP-MS

Lake Pampulha tributaries campaigns

From October 2011, Pampulha tributaries monitoring aims at surveying water quality of the Pampulha Lake tributaries during dry and wet weather conditions. Up to now, the sampling frequency has been bi-monthly. Four tributaries are monitored: Mergulhão; Ressaca and Sarandi; Água Funda and, downstream the lake, the Ribeirão Pampulha. The contributing area of the monitored tributaries to the lake represents more than 90% of the total Pampulha Lake catchment. Water samples were analyzed in the laboratory to determine nutrient (total phosphorus, phosphate, nitrate, nitrite, ammonium, total nitrogen) as well as physical chemical parameters (TSS, DOC, DIC) (Table 24).

In order to quantify the trace metal input during the dry season, we have conducted 2 campaigns of tributaries monitoring during the dry period (June 2013). The first campaign consisted in collecting punctually water at 5 different tributaries: Agua Funda, Mergulhão, Riberão, Ressaca, Sarandi and the confluence of Ressaca and Sarandi tributary. The second campaign consists in collecting water at the confluence of Ressaca and Sarandi by using an automatic storm sampler ISCO with 1h frequency during 24h. Temperature, conductivity and water level were also monitored continuously *in situ* with measurement time step of 5 minutes using GlobalWater instruments

2.1.3. Urban lakes in Ile-de-France region

49 urban lakes in Ile-de-France region of the PULSE project were selected according to (Catherine, 2009). The objective of the sampling strategy is to select a number of urban lakes who can represent the urban lakes population of the Ile-de-France region. According to Catherine et al 2008, the RNDE (Réseau National des Données sur l'Eau, France) defined 990 surface water units (lakes, reservoirs and ponds) in the Ile-de-France region. Among these surfaces, the 49 urban lakes are the results of a multi criteria selection.

At first, only water bodies more than 5 ha were retained by using the Carthage 3.0© GIS database (IGN, Paris, France) and their hydrographical zones entirely comprised within the IDF region. Based on this population of water bodies, the similarity and hierarchical analysis were performed on the land use, urban impervious, non-agricultural pervious, relative size of the hydrological zones, drainage index and altitude index to define the different stratas (cluster). Finally, the 49 urban lakes were selected by using the stratified simple random sampling design.

2.1.3.1. Annual monitoring of 49 lakes in Ile-de-France

The field campaigns, conducted on 49 urban lakes of IDF region, have started in July 2011 under the framework of the research project Peri-Urban Lakes Society and Environment (PULSE) funded by the Agence National de Recherche. During 3 years (2011 – 2013), the sampling campaigns were conducted at 49 lakes during 2 weeks every year from the last week of July to the first week of August (Figure 9). For each lake, three sampled stations are selected and located with a maximal distance between stations according to Catherine et al 2008. Water samplings were collected at 3 depths of each station using a NISKIN bottom: 0.5m below the surface, middle of the water column and 0.5m above at the bottom. The water samplings at 3 depths of 3 stations were mixed to an average sample which is representative of the lake. Concerning metals, samples are conserved in polyethylene bottle 2L at 4°C in a cooler, protected from light until the acidification in laboratory.

The water samples are analyzed in laboratory to determine a various set of parameters: biological parameters (Chlorophyll-a, Cyanobacteria biomass, Escherichia coli densities, Zooplankton, Haptophytes, Heterotrophic prokaryotes, Heterotrophic and phototrophic eukaryotes) and micro pollutant concentrations (Polycyclic Aromatic Hydrocarbons (13 congeners) in dissolved and particulate fractions, and the trace metals (9 elements) intotal, dissolved, labile fractions.

Vertical profiles of physical (salinity, temperature, oxygen, conductivity, photosynthetically active radiation (PAR), water transparency) and biological (chlorophyll a) parameters are also monitored *in situ* using probes: CTD Seabird43, LI-COR193 (underwater PAR sensor), Fluoroprobe BBE. Water transparency was determined by using Secchi disk.

The general characteristics of 49 lakes in Ile-de-France region are shown in Table 25

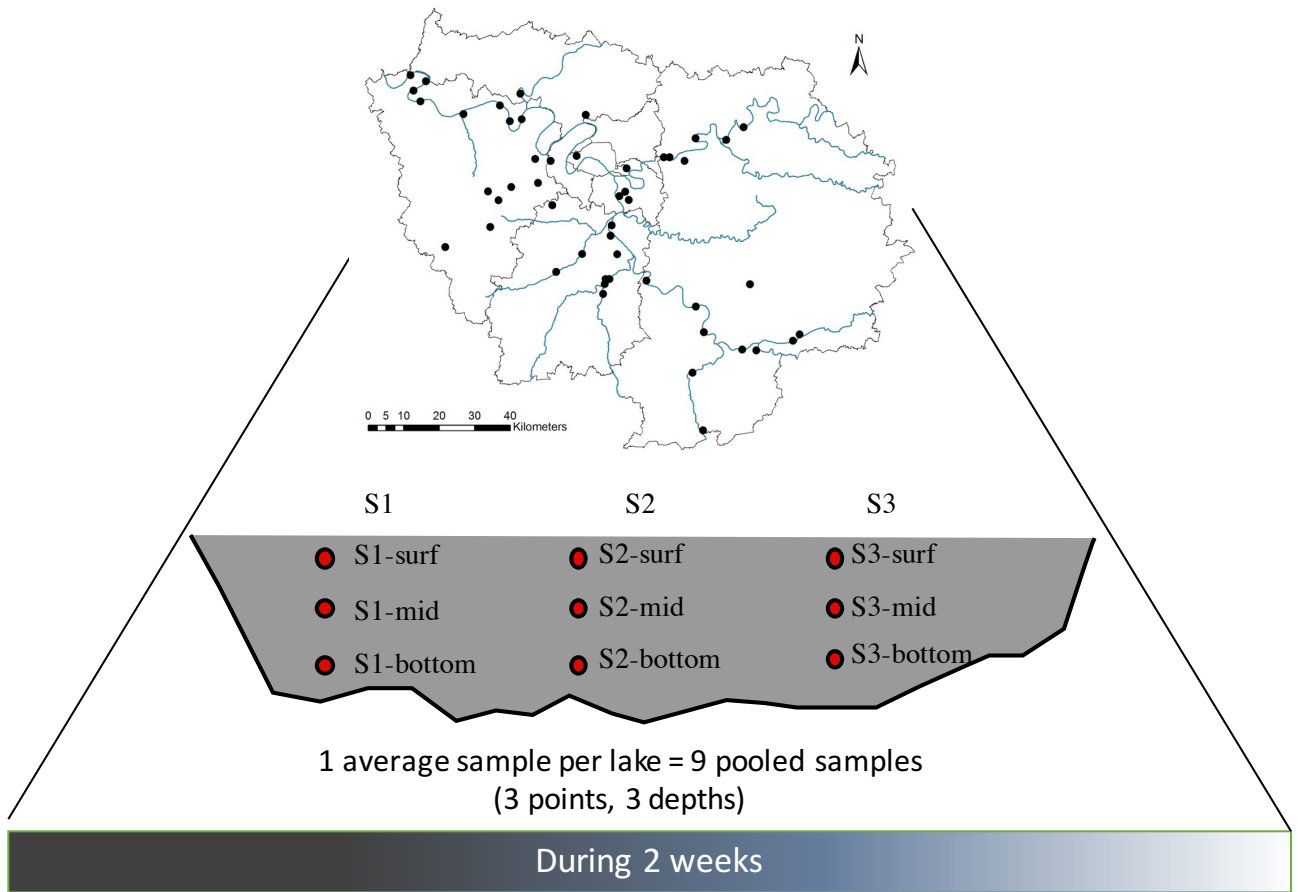


Figure 9 Sampling periods of 49 lakes in IDF region

Table 25 General characteristics of 49 lakes in Ile-de-France region

Lake ID	Name	Localization		Abbreviation	Lake surface (ha)	Catchment surface (ha)	Altitude (m)	Linked
5438	Freneuse cove	49° 4'19.92"N	1°37'22.46"E	FreC	14.00	16.1	14.2	1
5545	Grand lavacourt Pond	49° 3'17.04"N	1°40'52.38"E	Lava	111.50	97.0	14.5	0
5777	Les Galets Pond	49° 1'29.99"N	2° 2'45.62"E	Galet	10.60	7.7	24.9	0
5906	ASM Club cove	49° 0'12.92"N	1°39'41.79"E	ASMC	13.22	49.8	19.6	1
5959	Grosse Pierre Pond	48°59'43.64"N	1°58'5.80"E	Gpier	46.20	33.7	19.4	0
6161	Bout du monde pond	48°58'22.64"N	1°49'41.56"E	BduM	27.60	38253.6	19.3	0
6164	Enghien Lake	48°58'16.49"N	2°17'59.14"E	Enghien	33.80	-	-	1
6266	Gaule Achéroise Pond	48°57'37.11"N	2° 3'7.46"E	Acher	5.30	9.5	19.9	0
6274	Triel Pond	48°57'18.51"N	2° 0'23.75"E	Triel	34.22	78.2	19.8	0
6559	Jabline-Anet Lake	48°54'43.86"N	2°43'21.66"E	Jablin	77.10	63.2	39.5	0
6631	Isles-les Villenoy Pond	48°54'24.26"N	2°50'24.43"E	Isles	41.60	54.9	44.0	0
6901	Lake Inferieur	48°51'47.69"N	2°15'37.63"E	Infer	9.50	146547.0	44.6	1
6926	Les Pâtis Pond	48°51'49.80"N	2°35'51.81"E	PetitP	9.80	1460.1	39.6	0
6929	Torcy Lake	48°51'56.72"N	2°39'17.41"E	Torcy	25.53	-	-	1
6935	UCPA Centre Pond	48°51'48.96"N	2°37'21.33"E	UCPA	92.00	103.0	39.8	0
6974	UTE Louveciennes	48°51'21.79"N	2° 6'16.18"E	UTELo	7.50	3.2	166.8	0
6982	Loy Pond	48°51'14.00"N	2°40'47.59"E	LoyP	6.90	2228.7	50.4	1
6986	Saint-Cucufa Pond	48°51'16.85"N	2° 9'49.94"E	Cucuf	5.40	61.6	114.6	0
7080	Lake Minimés	48°50'9.62"N	2°27'29.56"E	Minim	5.80	173.4	52.4	1
7329	Swiss Pond	48°47'53.45"N	2° 6'57.02"E	Swiss	14.40	9.2	119.4	0
7383	Saint Quentin Pond	48°47'15.04"N	2° 0'52.74"E	Quentin	120.10	4059.4	157.4	1
7419	Creteil Lake	48°46'30.54"N	2°27'3.69"E	Créteil	40.80	258.3	34.4	0
7448	Maurepas reservoir	48°46'34.53"N	1°55'26.36"E	Maure	7.60	430.2	-	1
7489	Choisy Pond	48°45'49.33"N	2°25'42.80"E	Choisy	21.60	152.5	34.7	0
7556	Plage Bleue Pond	48°45'18.60"N	2°27'52.40"E	Pblue	9.30	65.3	34.4	0
7559	Noes Pond	48°45'13.53"N	1°57'46.33"E	Noes	27.70	3425.1	165.2	0
7628	Saclay Pond	48°44'29.43"N	2°10'17.77"E	Saclay	30.20	3201.2	122.3	0
7968	Laveyssière Pond	48°41'26.69"N	2°23'53.52"E	Lavey	27.10	495.9	34.5	0
8015	Vaux-de-Cernay Pond	48°41'8.42"N	1°55'52.39"E	Vaux	6.50	4270.5	120.5	1
8201	Noues de seine Pond	48°39'57.56"N	2°23'23.52"E	Noues	73.20	2271.4	34.4	1
8498	Gazeran Pond	48°38'0.88"N	1°45'34.89"E	Gazeran	8.12	4525.9	134.3	1
8620	Courcouronnes Pond	48°37'6.43"N	2°25'5.54"E	Courco	6.50	548.6	79.4	0
8627	Epinoche Pond	48°37'1.88"N	2°17'3.79"E	Epino	5.70	53876.4	44.2	0
8889	Port-Sud Pond	48°34'22.33"N	2°11'22.00"E	PortS	6.50	20871.5	54.4	1
9031	Vert le petit Pond	48°33'14.98"N	2°22'30.37"E	VertP	1.48	10.1	49.3	0
9032	Seine Port Pond	48°32'59.62"N	2°31'54.77"E	SeineP	5.90	87.3	39.2	0
9050	Fleuri Pond	48°32'28.11"N	2°22'18.63"E	Fleuri	8.96	184168.4	49.3	1
9086	Villefermoy Pond	48°32'19.49"N	2°55'42.42"E	Villefe	21.70	2690.8	100.6	1
9205	Saint-Blaise Pond	48°31'2.69"N	2°21'55.78"E	Blaise	5.20	105814.8	49.4	0
9391	Boi-le-Roi Pond	48°29'0.61"N	2°43'20.75"E	BoiRoi	8.30	31.6	44.4	0
9726	Samoreau Pond	48°25'4.61"N	2°44'58.87"E	Samor	10.20	16.1	44.7	0
9799	Delomez Pond	48°24'36.62"N	3° 6'55.55"E	Delom	6.70	3.6	55.0	0
9910	Leclerc Pond	48°23'38.88"N	3° 5'25.94"E	Leclerc	5.40	4.8	51.6	0
10026	Grande-Paroisse Pond	48°22'23.58"N	2°53'47.72"E	Paroisse	52.70	67.5	50.0	0
10338	Clarette Pond	48°18'54.22"N	2°42'21.21"E	ClaretP	13.90	21.5	54.6	0
10987	Souppes/Loing Pond	48°10'3.01"N	2°44'37.55"E	Loing	21.10	20445.9	66.0	1
45982	Grand Marais Pond	48°22'12.56"N	2°56'58.26"E	Marais	16.50	69.8	49.8	0
46136	Fontenay/Vic Pond	48°33'13.06"N	2°23'19.99"E	Fonte	13.84	185528.7	49.3	1
46600	Ilon cove	49° 1'51.98"N	1°37'58.67"E	Ilon	70.16	100.0	16.2	1

2.2. Trace metal sampling and analysis

2.2.1. Trace metal speciation method

Trace metal samples are divided for analyzing total metal, particulate, dissolved labile and dissolved inert metal. Total metal corresponds to unfiltered sample. Particulate and total dissolved metal fractions are separated using cellulose acetate membrane filter with 0.45 μ m porosity. We differentiate total dissolved metal into dissolved inert and dissolved labile using chelating disk EMPORE constituted of polystyrene divinylbenzene with presence of chelating resin imino-diacetic (Figure 11). The chelating disk retains dissolved labile metals during filtration. Their concentrations are calculated as the difference between total dissolved and dissolved inert concentrations (Bracmort, 2010, Varrault et al, 2012). Dissolved inert metals are considered as metal species that are strongly linked to chelating substances and dissolved labile metals as species that are weakly linked to inorganic or organic complexes (Zhang and Davison, 2000)

2.2.1.1. Total, dissolved and particulate metal determination

Trace metals are determined using inductively coupled plasma mass spectrometry (ICP-MS) with detection limit until 10ng/L for Cd, Co, Pb and 100ng/L for Cr, Ni, Cu and Zn. Analyses are validated with the standard reference material NIST 1640a (<http://www.nist.gov/srm/>). All the material used for the sampler were pre-cleaned in 5% (v/v) detergent Extran, rinsed many times with ultrapure water and pre-cleaned again in 10% (v/v) nitric acid (Vetec 65% metal ultrapure) to avoid metal contamination.

For total metal concentrations correspond to 50mL of unfiltered water were acidified with ultrapure HNO₃ 65% VETEC (pH<2) and conserved at 4°C temperature. Total metal was mineralized with HNO₃ 65% and HCl 30% using a graphite digestion block (DigiPrep of SCP SCIENCE) programmed to reach 95°C and maintain during 150 minutes. After digestion, samples were refilled with Milli-Q ultrapure water to 50mL and then filtered through 0.45 μ m Teflon filter. A blank with Milli-Q ultrapure water is systematically done for each mineralization cycle to estimate eventual contamination. Mineralized samples were analyzed using ICP-MS.

Total dissolved concentrations correspond to 20mL of filtered water acidified with 500 μ L ultrapure HNO₃ 65% (pH<2) and conserved at 4°C temperature to be analyzed in ICP-MS.

Particulate metal concentrations are calculated as the difference between total and dissolved concentrations

2.2.1.2. Dissolved labile and dissolved inert metal determination

Filtering total dissolved through chelating disk EMPORE separates dissolved labile and inert metals. Labile metals are retained by chelating disk while inert metals are not (Figure 10). Inert metals are acidified with 500 μ L ultrapure HNO₃ 65% (pH<2) and conserved at 4°C temperature and determined in ICP-MS. Labile metal concentrations are calculated as the difference between total dissolved and inert concentrations.

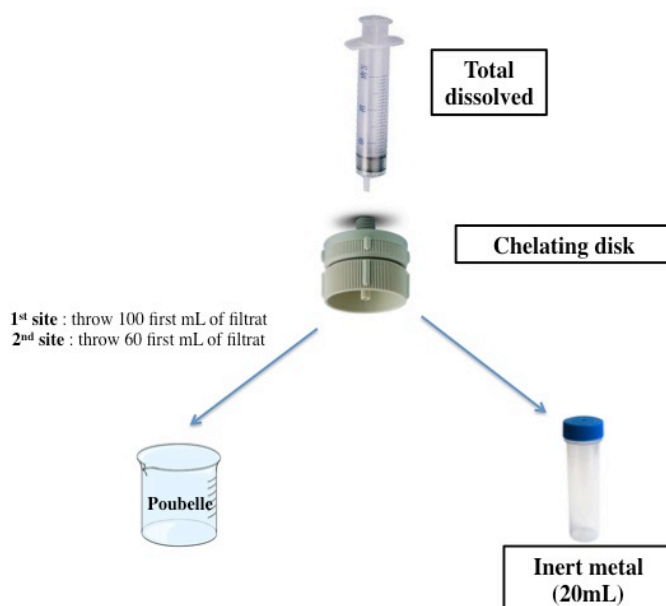


Figure 10 Separation inert metal from total dissolved

2.2.1.3. Presentation of chelant disk

The chelant disk is constituted of a polymer support (polystyrene divinylbenzene) functionalized by chelating groups imino-diacetate (IDA) (Figure 11). The iminodiacetate chelating group has an affinity for multivalent (primarily 2+ and 3+) transition elements. The IDA groups are also used in the Chelex 100 resin which are well-known in metal speciation (Florence, 1982). The chelant disk was used by Chaminda et al., 2008 and Chaminda et al., 2010 to study the complexation of Zn and Cu in waste water treatment plant effluent and comparison of metal (Zn and Cu) complexation characteristics of DOM in urban runoff, domestic, waste water and secondary effluent. Varrault et al., 2012 optimized the method of determination of labile metal concentrations. The innovation of the method of Varrault et al., 2012 is the extraction of labile metals by using the chelant groups as a simple filtration disk. This method suggested a practical operational method for punctual measures.

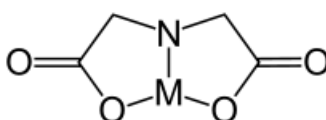


Figure 11 Complexation of metal with imino-diacetic group

2.2.1.4. Protocol of materials preparation

Bracmort, 2010 suggested a laboratory protocol for using the chelant disk.

2.2.1.4.1. Material cleaning

Analysis of trace metal presents a high risk of contamination. Every procedure must be conducted with specific protocols to avoid any metal contamination from exterior. Before and after every field campaign, the material needs to be specifically cleaned to minimize the contamination. An ideal washing is conducted in a clean room that has a low level of pollutants such as dust, airborne microbes, aerosol particles, and chemical vapors. Level of contamination is specified by the number of particles per cubic meter at a specified particle size.

The washing cycle lasts 48h. The material is firstly soaked in a detergent solution Extran (diluted with osmosed water) at 15 % during 24h. Then the material is cleaned at least 3 times with ultra pure water before being soaked in a HNO₃ solution 5% diluted with ultra pure water during 24h. After washing with acid, the material is washed with ultra pure water many times and dried under the hood of the cleanroom. The material is finally put in a clean sac and kept isolated.

2.2.2. Preparation of chelating disk

The metal bind site of chelating disk is totally active only after a treatment in the cleanroom. This treatment consists of different steps:

- Inject 20 mL suprapur nitric acid through chelating disk. We need to assure 1 minutes of contact between membrane and acid
- Empty remaining acid by sending a vacuum into the syringe through the disk
- Inject 50 mL of ultrapure water
- Empty the disk
- Inject 100 mL of ammonium acetate buffer at pH = 5.3
- Rinse with ultrapure water several times. Put under the hood to dry

2.2.2.1. Acidification

After separating different fractions, we conserve sample with nitric acid. We add 500 µL nitric acid OPTIMAL for 50mL of total metal and 600 µL nitric acid for 20mL total dissolved and inert metal. Samples are conserved at 4°C until their analysis in ICP-MS.

2.3. TEP sampling and analysis

2.3.1. Determination of TEP

TEP is operationally defined as particles, which are retained on a polycarbonate filter and colorable by using blue alcian (cationic colorant that adheres to polysaccharides negatively charged). At the moment, there are 2 methods allowing quantifying TEP. These 2 methods use blue alcian to color: (1) microscopy method allowing counting and determining size distribution, (2) spectrometry method allowing quantifying colored particles retained on filter.

Microscopic counting

The sample is filtered by using a polycarbonate filter of 0.4 or 0.2 µm. The humid filter is colored with blue alcian. The counting and size distributions are carried by using microscopy in a manual or semi automatic way using an image analysis system. TEP determination is better if total surface and volume are both well estimated. Total surface is estimated basing on hypothesis that colored particles retained on filter are only spherical. Total volume can be estimated by using a empiric relation with fractal dimension equal 2.55 (Passow, 2002). The size distribution can be estimated by a power law.

Spectrometry

TEP is colored by using blue alcian. 3-50mL of sample is filtered under low pression constant (<100mmHg) using polycarbonate filters of 0.4µm. The humid filter is colored with 500µL of blue alcian 0.02% (m/v) prepared in acetic acid (pH 2.5). After being stained, filter is rinsed once with distilled water to remove excess dye. Filters are then transferred into 25-ml beakers. Six milliliters of 80% H₂SO₄, are added and filters soaked for 2 h. The beakers should be gently agitated 3-5 times over this period. The absorption maximum of the solution lies at 787 nm and absorption is measured in a 1-cm cuvette against distilled water as a reference.

This method is semi quantitative because quantity of blue alcian adsorbed depends directly on weight of specific polysaccharide. In order to normalize the weight of polysaccharide, gum xanthan is used as reference. Quantity of TEP is expressed in μg gum xanthan equivalent per liter.

2.3.1.1. Trace metal incertitude

Each sample is analyzed 3 times in ICP-MS. Mean value is retained and validated if value of relative standard deviation is inferior to 5%. As trace metal analysis is extremely sensitive to contamination during preparation, filtration and analysis, we consider incertitude of preparation and filtration around 10%. Total incertitude is maximal at 15% of mean value.

2.4. Data processing and statistical methods

2.4.1. Database validation

The trace metals concentrations were analyzed with ICP-MS. The validation of the results is meticulous and time consuming. The raw data given by ICP-MS has been treated through different steps as follows.

2.4.1.1. Verification of calibration curve

The calibration solutions were prepared from 1ppt to 20ppb or 100ppb depending on metals. After analyzing, we need to refine the calibration curve of each trace metal element by excluding some calibration points in order to obtain the best coefficient R^2 of this curve. The example in the Figure 12 showed the calibration curve of Cobalt. By excluding the point at 100ppb, we obtained a better R^2 .

Additionally, this step also gave the information about the quantification limit of the experiment by considering the intensity signal for each calibration solutions. The intensity signal is expressed by the average count per second (mean CPS). In this example, there is no difference in term of count per second between the HNO_3 , Blank and Pcal 1ppt. The intensity signal is significant from 10ppt to 20 ppb for the Cobalt. The quantification limit does not change drastically from one experiment to the other. However, it can be different between the Lake Créteil samples and the Lake Pampulha samples. This primary step is essential to obtain reliable results.

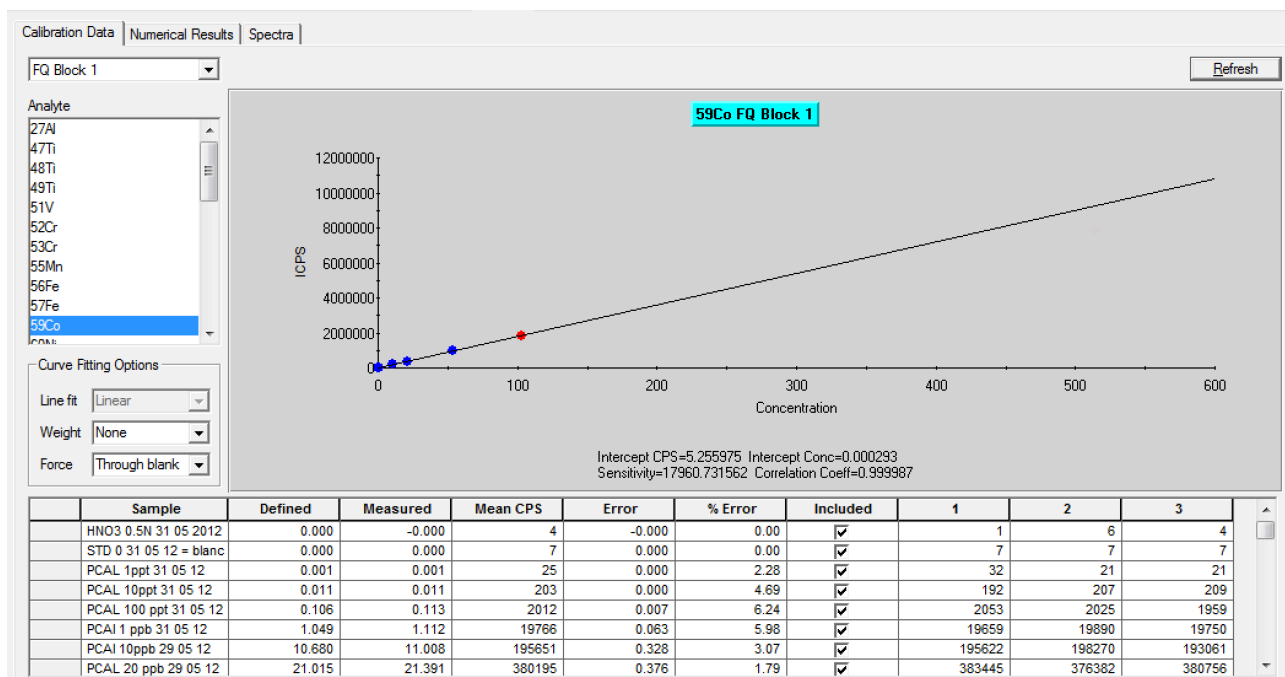


Figure 12 calibration curve for Cobalt

2.4.1.2. Comparison to standard values

To validate the quantification of trace metals, we used the standard reference material (SRM) 1640a for the trace elements in natural water certificated by the National Institute of Standards and Technology (NIST). If the measure was correct, the measured value of Nist should be similar to the certified value of Nist. If the measure was not correct, the analytical mode in the calibration data should be done. In ICP-MS, there are 2 analytical models: Pulse counting and analog. The pulse counting mode provides a high sensitivity detection for the elements at low concentrations. The analog mode provides an adequate signal for the elements at high concentrations. It is not possible to have both pulse counting and analog mod for the same calibration curve. The point in analog mode should be excluded.

2.4.1.3. Pulse counting and analog

If for one element, the values in analog mode are excluded from the calibration curve. All the measures in analog of the samples will be considered as incorrect consequently. In order to deal with this problem, the sample is diluted.

2.4.1.4. Validation of the obtained measures

In order to validate the obtained measures, all the cases as follows should be checked:

1. Detection and quantification limits: For the concentrations which are not comprised within the calibration curve range, the high concentration is diluted and the low concentration is considered as the same level of blank sample
2. Interferences: For one element, the measure is done for a multiple isotope (for eg. ^{63}Cu and ^{65}Cu). When there is an interference in the measure, the values of the isotopes are not the same. In the case of the Lake Créteil, we encountered a strong interference effect due to the composition of the water. In order to limit the interference effect, the analysis can be conducted in Collision Cell Technology (CCT) with the mix of gas H_2 and He. Another option is to dilute the samples to avoid the interference
3. Matrix effect: The internal standards rectify the matrix effect. However, the percentage of the internal standards can decrease or increase in comparison to the percentage observed in the blank (HNO_3 0.5N). To avoid this fluctuation, the samples need to be diluted or analyzed with CCT.
4. Derivation of device: During the analysis, incident can happen such as the cone is clogged due to the matrix of the samples. This incident can be observed through the percentage of internal standard of the blank or the Nist sample which are periodically analyzed during the experiment. The theoretical percentage is around 100%. In case of derivation, it can be 120% or 70%. Even though we observe the derivation, but we can continue the analysis until the value of the Nist standard is correct. Otherwise, another calibration curve should be repeated. By analogy, if a same sample at the end of the experiment does not give the same results as at the beginning of the experiment, this sample should be analyzed in the next experiment in order to compare.
5. Comparison of the same sample: In addition, we did 2 tests of validation for a same sample: dilution and repeat analysis in different experiments. For the same sample randomly selected, the value before, after the dilution with correction, at the beginning, at the end of the experiment, in the next day of the experiment, CCT or normal should remain unchanged.
6. Blank: For each campaign, we collected 2 blanks : at the beginning of the sampling and at the end of the sampling.
7. Relative standard deviation: Each measure in ICP-MS was repeated 3 times. The relative standard deviation for a sample should not exceed 5%.

2.4.1.5. Scientific validation

After validating the analytical values, we performed different tests to validate scientifically the values.

1. Boxplot: The total concentration of metal is always superior to the dissolved concentration who is always superior to the labile concentration. If this is not verified, some further verifications should be checked.
2. Empirical Distribution Curve: the empirical distribution curve gives a better visualization if some aberrant values are observed (Figure 13)
3. Ratio verification: The third verification is to calculate the ration of Dissolved/ Total and Labile/Dissolved. If the ratio is greater than 1, the exceedance of the ratio must be comprised in the interval of evaluated uncertainty (Figure 14)

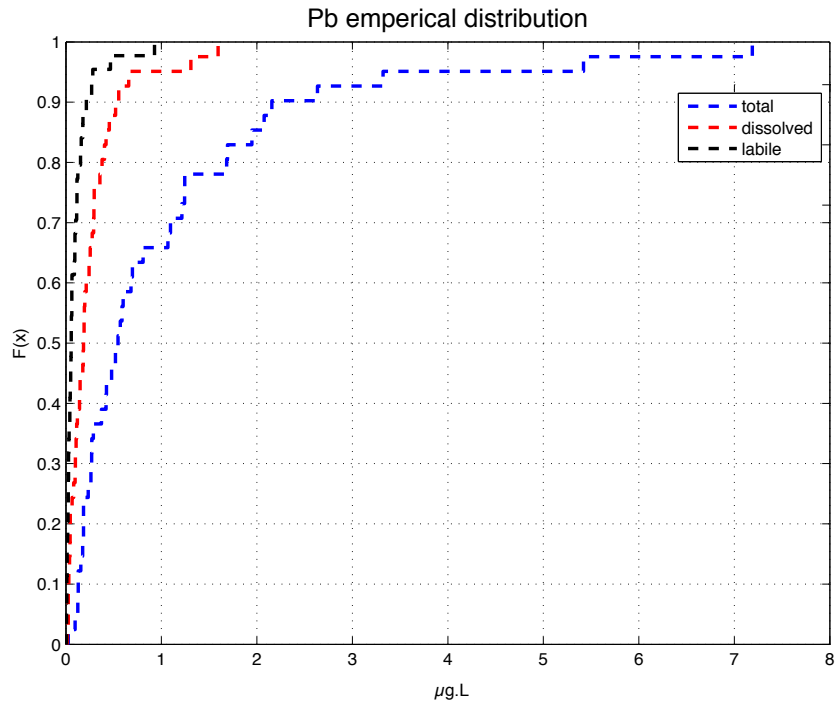


Figure 13 Emperical distribution of lead

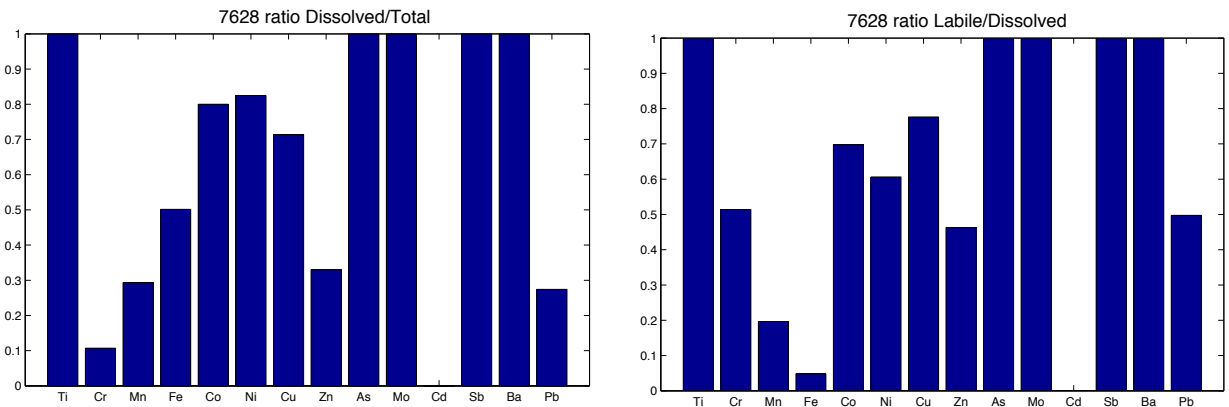


Figure 14 Ratio verification for the lake 7628

2.4.2. Statistical methods

2.4.2.1. Regression and classification

Regression and classification are two approaches in statistics but have the same objective, which is investigating the relationship between two variables. Regression aims to predict a continuous response variable for a new value of predictor variable such as predicting chlorophyll a concentration based on temperature, light conditions and nutrient availability. Various regression methods are used in statistics such as linear and nonlinear regressions, non-parametric regressions (kernel smoothing, spline methods, Tree (1984)), or machine learning regression (boosting, bagging, random forests). Classification is used to predict a categorical response variable for a given predictor variable. For example, predict a person's 5-year survival based on their age, height, weight etc. (Adele (2013)).

Different classification methods are listed as linear discriminant, logistic regression, non-parametric methods (nearest neighbor classifiers, trees) and machine learning methods (bagging, random forest, support vectors machines)

As we could notice, random forests are figured as a machine learning methods in both regression and classification approach. Over the past two decades, machine learning has enjoyed growing attention in computer science. Machine learning consists in exploring data, constructing algorithms that can learn from and make predictions of data (Kohavi and Provost (1998)). Applications of machine learning are various that go from web page ranking, face recognition to scientific purposes (Smola and Vishwanathan (2008)). In regression and classification of ensemble machine learning, besides boosting and bagging methods, random forest is developed and gaining gradually attention of researchers as an efficient approach of machine learning.

2.4.2.2. Introduction to the Random Forest model

Ensemble learning is another definition of methods that generate many classifiers and aggregate their results (Polikar 2012). Two well-known methods are boosting (Shapire et al., 1998) and bagging Brieman (1996) of classification trees. In boosting, the output is calculated taking an average weight given by successive trees into account. Bagging (stands for Bootstrap Aggregation) means that successive trees are independent and each tree is generated using a bootstrap sample of the data set. The output is based on the majority of vote (Liaw and Wiener, 2002).

Random forests were introduced by Leo Brieman who was inspired by earlier work by Amit and Geman. Random forests are a continuity of Brieman's bagging idea and were developed as an alternative to boosting. Random forests are both classification and regression methods, which mean that they can be applied on continuous response variable as well as on categorical variable.

Random Forests draw attention from a computational standpoint because they can handle both regression and classification, are relatively fast to train and to predict, can be used directly for big data problem, can be robust again overfitting. Statistically, Random Forests are interesting because they can measure variance importance, work with no distributional assumption, can handle missing value imputation (Brieman 2001, Cutler et al., 2011).

2.4.2.3. Random Forests algorithm

This paragraph here after is a synthesis of 3 main documents: Brieman 2001, Cutler et al.,2001 and Liaw and Weiner (2002).

Before mentioning the Random Forests algorithm, it is important to understand firstly classification and regression trees in Random Forests. The trees used in Random Forests are the binary recursive trees. As its name suggest, the predictor space is separated into binary partition on individual variables. The root of node of the trees or the node at the top of the tree represents the entire predictor space. A node splits into two descendant nodes which are qualified left node and right node. This separation is based on the value of one of the predictor variables. We remind that in Random Forest, a number of predictor variables is chosen at each node. The splitting predictor variable can be categorical or continuous. For example, it could be a categorical variable such as sex (male or female), survival (yes or no). In case of continuous predictor variable, the split-point is a precise value for which all the predictors, which are smaller than the split-point, are at the left and the others at the right. The node at the end of each division is called terminal node.

The algorithm 1 here after can resume the binary recursive partitioning procedures:

- Let $D = \{(x_1, y_1), \dots, (x_N, y_N)\}$ denote the training data, with $x_i = (x_{i,1}, \dots, x_{i,p})^T$.
 1. Start with all observations $(x_1, y_1), \dots, (x_N, y_N)$ in a single node.

2. Repeat the following steps recursively for each unsplit node until the stopping criterion is met: a. Find the best binary split among all binary splits on all p predictors. b. Split the node into two descendant nodes using the best split (step 2a).
3. For prediction at x , pass x down the tree until it lands in a terminal node. Let k denote the terminal node and let y_{k_1}, \dots, y_{k_n} denote the response values of the training data in node k . Predicted values of the response variable are given by:
 - $\hat{h}(x) = \bar{y}_k = \frac{1}{n} \sum_{i=1}^n y_{k_i}$ for regression
 - $\hat{h}(x) = \arg \max_y \sum_{i=1}^n I(y_{k_i} = y)$ for classification, where $I(y_{k_i} = y) = 1$ if $y_{k_i} = y$ and 0 otherwise.

Random Forests is a tree-based ensemble with each tree is totally randomly selected from the dataset. For a p -dimensional random vector $X = X(X_1 \dots X_p)^T$ representing input variables or predictor variables, we want to predict a random variable Y representing output variable or response variable. We assume an unknown joint distribution of X and Y . The objective is to predict Y value from a function of X . This prediction function is determined by a loss function $L(Y, f(X))$. Many choices to minimize error of expected value. One of them is *squared error loss* which is $L(Y, f(X)) = (Y - f(X))^2$ for regression and zero-one loss for classification :

$$L(Y, f(X)) = I(Y \neq f(X)) = \begin{cases} 0 & \text{if } Y = f(X) \\ 1 & \text{otherwise} \end{cases}$$

Construction of an ensemble function f based on a collection of so-called “base learners” $h_1(x), \dots, h_f(x)$, which are combined to give the “ensemble predictor” $f(x)$. In regression, $f(x)$ is the average of all the base learners while in classification $f(x)$ is the most frequent “vote” of ensemble trees.

Random Forests algorithm for both classification and regression follow:

1. Take a bootstrap of n_{tree} from original data set
2. Bootstrap samples are used as training data. For each bootstrap samples, grow an unpruned classification or regression tree using binary recursive partitioning. At each node, we randomly sample m_{try} of the predictors and find the best binary split among those.
3. Split the node into descendant level and repeat all over from this node.
4. Predict new data by aggregating the prediction of n_{tree} trees (most frequent vote for classification and average for regression)

2.4.2.4. Out-of-bag predictions

In order to avoid the overfitting problem if the model is trained on all the data, the evaluation of the random forest is based on the out-of-bag predictions. At each iteration, the bootstrap process generate a bootstrap sample which does not contain the totality of the data. The rest of data, which are not into the bootstrap sample, is called out-of-bag sample. The out-of-bag prediction is defined as the prediction of the variable response using the model trained with the bootstrap sample and the observation of the out-of-bag samples.

For the regression with squared error loss, the generalization error is estimated by the out-of-bag mean square error (MSE). For the classification, the generalization error is estimated by the out-of-bag error rate which correspond to the misclassification of each class through the out-of-bag confusion matrix.

2.4.2.5. Variable importance

One of the feature of Random Forest is the possibility to rank the variable importance. This feature is very helpful for variable selection and the interpretation of the results. The measure of the variable importance in Random Forest is performed at each tree. The algorithm of this measure is called permutation variable importance. First, after on iteration, the model computed the out-of-bag prediction. Next, the values of the variable k is randomly permuted in the out-of-bag data while the other predictor variables remain unchanged. The model generated thus a new out-of-bag sample with the changed variable k . The model computed again the out-of-bag prediction. For each iteration, the model generated 2 sets of out-of-bag predictions: one from the real data, the other from the variable k permuted data. The average difference of out-of-bag error rate or MSE of these two sets correspond to the variable importance

2.4.2.6. What to retain from Random Forest?

Random Forest is a supervised machine learning or ensemble learning method. It can treat both regression and classification problem. The term “random” refers to 2 random processes of the model:

- tree bagging: generate randomly with replacement the bootstrap sample from the data
- feature sampling: select randomly k predictors variables at each node of the tree.

The term “Forest” indicates the model generate randomly many decision trees independent. Each tree represents a part of vision of the data. The result of the model take into account the forest of trees. The prediction corresponds to an average value in regression or a major vote in classification

PART 2

Results and Discussion

In this part, the principal results will be presented in the first chapter for Lake Pampulha, in the following chapter for Lake Créteil, in the third for 49 lakes of Ile de France region and the last chapter is devoted to discussion of these results and conclusion.

3. Results on Lake Pampulha

Based on the data of Lake Pampulha monitoring conducted from August 2012 to June 2013 (see section 3.2.1), we will first focus on the limnologic functioning of the lake, then we will describe the time evolution of trace metal speciation in the water column. The third sub-section will be devoted to the tributaries monitoring, principally to the the presentation of the evolution of metal concentration during dry and raining periods. Finally, we will try to assess the impact of the influence of environmental variables on trace metal bioavailability through a statistical analysis.

3.1. Seasonal lake functioning

In lake ecosystems, the environmental conditions can play an essential role on biological processes (*e. g.* phytoplankton development or cyanobacteria bloom due to an excess of nutriments, a favorable temperature and light conditions), on chemical processes (*e.g.* modification of metal speciation under oxygen conditions) or on physical processes (*e.g.* modification of stratification and mixing patterns). Before analyzing the evolution of trace metal concentrations, understanding the limnologic functioning will help us to explain the behavior of these metals in the water column

3.1.1. Water temperature evolution

The evolution of the water temperature at 3 depths, between August 2012 and June 2013, is shown in Figure 15. The water column is thermally stratified between August 2012 and March 2013 and mixed from the end of March to the beginning of August 2013. This corresponds to the air temperature evolution. The water temperature varied from 20 to 28 °C at 0.5m depth and from 21 to 24°C at 7 m. The difference of water temperature between surface and middle of the water column can be up to 2.5 °C.

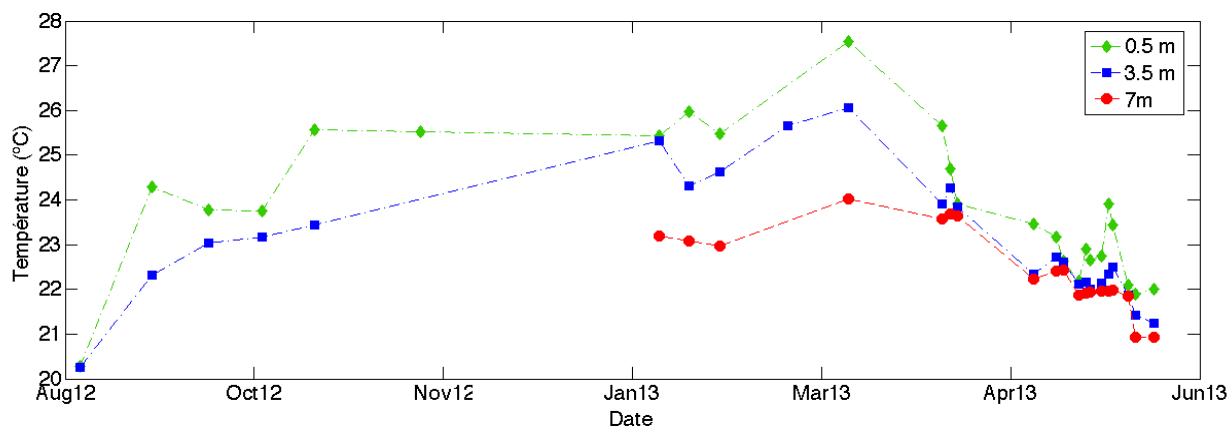


Figure 15 Evolution of temperature at 0.5m, 3.5m and 7m depth

The typical water temperature profiles at the point P2 are shown in Figure 16. The lake water column started to be stratified in August and the overturn occurs in June. Our sampling campaigns were performed during this period of almost 1 year, which corresponds to 1 annual cycle of stratification and overturn.

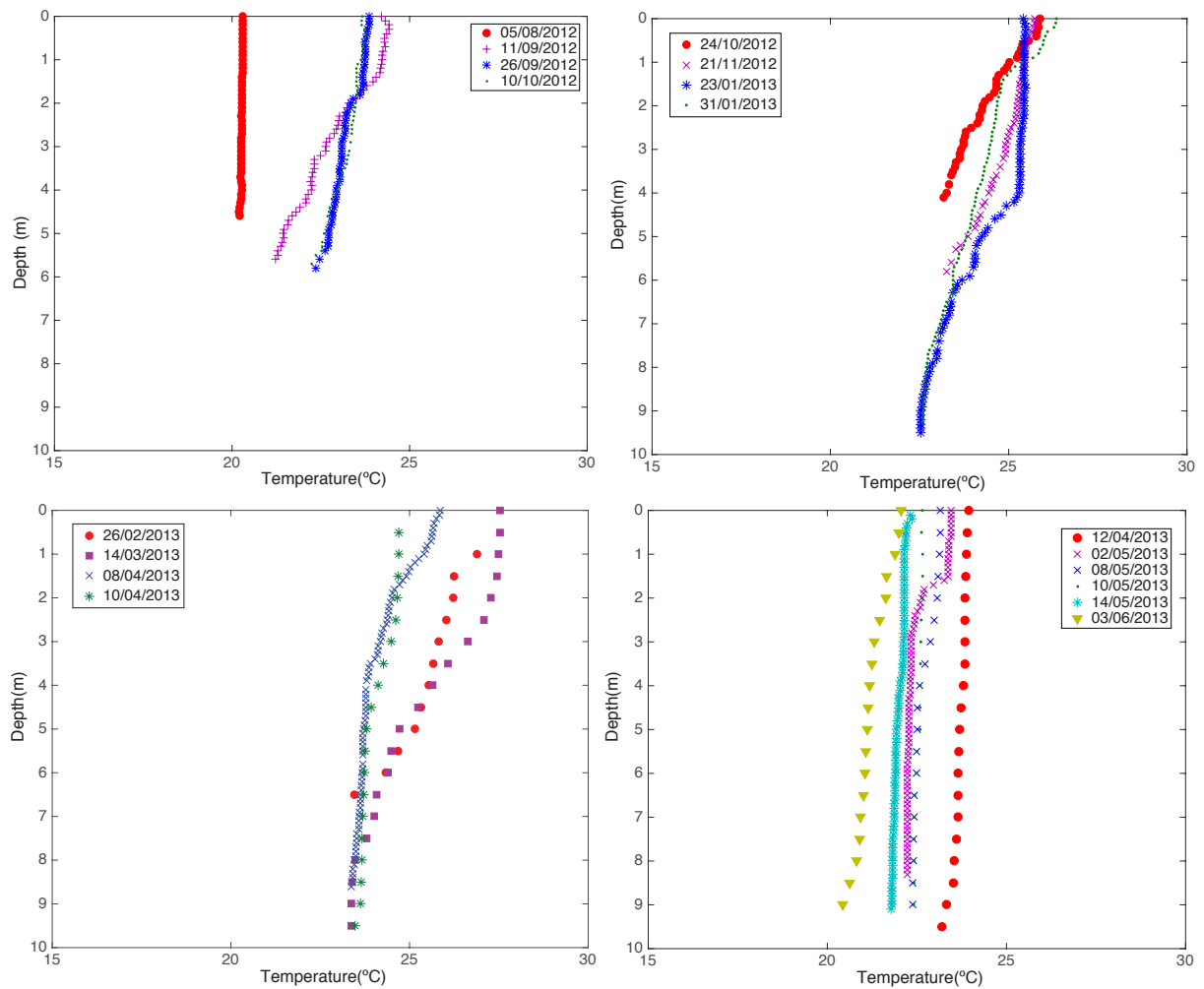


Figure 16 Water temperature profiles

3.1.2. Chlorophyll-a concentration

The concentration of chlorophyll-a in the Figure 17 and Figure 18 corresponds to the measurements *in-situ* performed with the probe AlgaeTorch. According to the AlgaeTorch algorithm, cyanobacteria contribute to 60-80% of total chlorophyll-a concentration. This result is within the same range of the measurements of chlorophyll-a by spectrophotometry (Silva, 2014; Silva et al., 2016). The evolution of chlorophyll-a concentration at 0.5 m and 7 m depth is shown in Figure 17. Total concentration of chlorophyll-a varied from 37 to 220 $\mu\text{g/L}$ at the surface and from 5 and 63 $\mu\text{g/L}$ at the bottom. The temperature and cyanobacteria development are highly correlated. The difference of chlorophyll-a concentration between the surface and the bottom are related with the stratification and mixing pattern. During the stratification period, the highest concentration of chlorophyll-a (220 $\mu\text{g/L}$) was measured. Chlorophyll-a decreases at the surface and increase at the bottom (63 $\mu\text{g/L}$ at 7m) during mixing period.

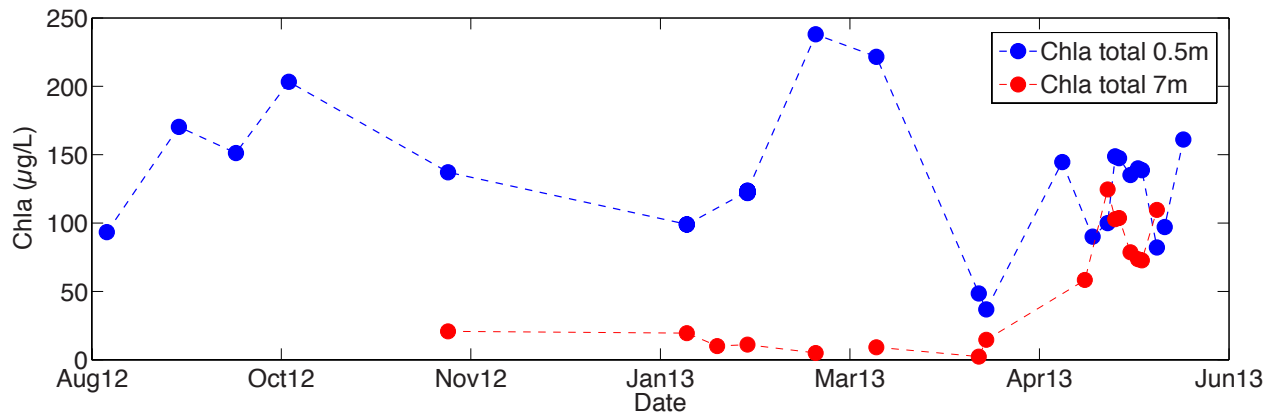


Figure 17 Evolution of chlorophyll-a concentration at 0.5m and 7m depth

Two typical profiles of chlorophyll-a concentration on 14/03/2013 and 12/04/2013 are shown in Figure 18. This figure confirmed that the chlorophyll-a concentration profile is in concordance with the vertical temperature distribution.

According to trophic state index for lakes (Carlson et al., 1996), total phosphorus (maximum value 700 µg/L) and chlorophyll-a (maximum value 220 µg/L) confirm that Lake Pampulha is hypereutrophic.

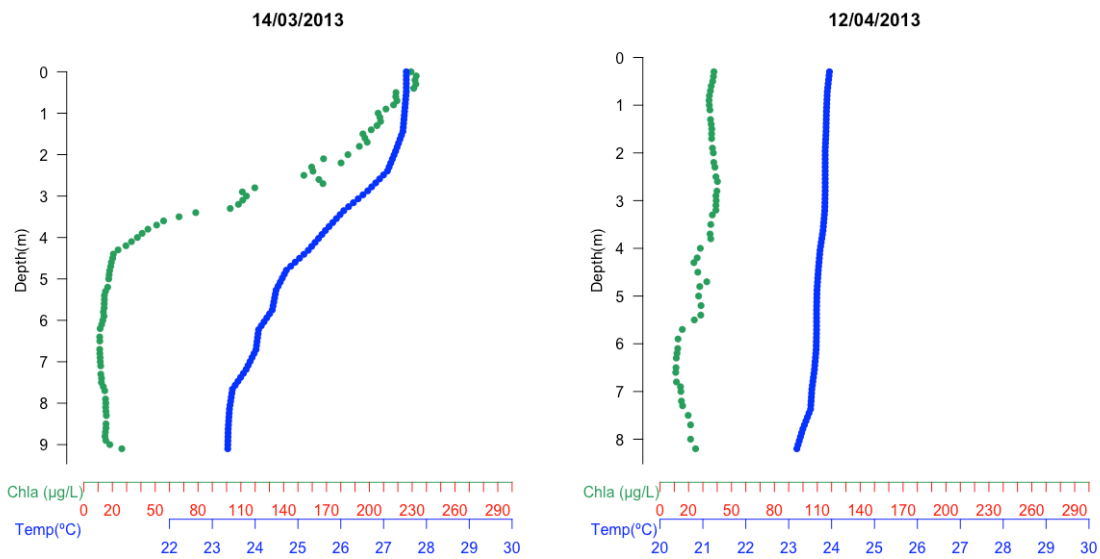


Figure 18 Chlorophyll a (µg/L) and temperature (°C) profiles of the point P2

3.1.3. Other physical chemical parameters

The evolution of conductivity, oxygen dissolved, pH and suspended matter at three depths of the point P2 is shown in Figure 19

The conductivity varies between 217 and 326 µS/cm. We observe more variation of conductivity at the surface and the bottom of the water column.

Our data show that the lake is anoxic below 3.5 m depth from February to June 2013. Before February 2013, we do not have oxygen measurements but according to Friese et al (2010), the lake is permanently anoxic below 3m. In the surface layer, the dissolved oxygen concentration can be over-saturated when photosynthesis activity is high. On the other hand, the surface water can be

anoxic during mixing period. Due to an oxygen-free hypolimnion below 3m, the redox potential (Eh) is strongly negative (-50mV to -150mV). Dissolved oxygen profile separates the lake into an oxidizing zone (surface layer) and reducing zone (below 3m).

The pH is comprised in the usual range of pH in lake ecosystems between 6.8 to 8.85. It is higher at the surface and decreases at the bottom. This basic pH corresponds to a high chlorophyll-a concentration at the surface (pH = 8.85 for [Chla] = 204 µg/L). the pH is lower for low chlorophyll-a concentration at the bottom (pH = 6.8 for [Chla] =9.2 µg/L).

Suspended matter (SM) concentration varies from 5 to 55 mg/L. A high value of SM at the surface corresponds to high biomass of phytoplankton ([SM] = 32.5 mg/L for [Chla] = 221 µg/L). A high value of SM at the surface can also be due to other particles or to resuspension process.

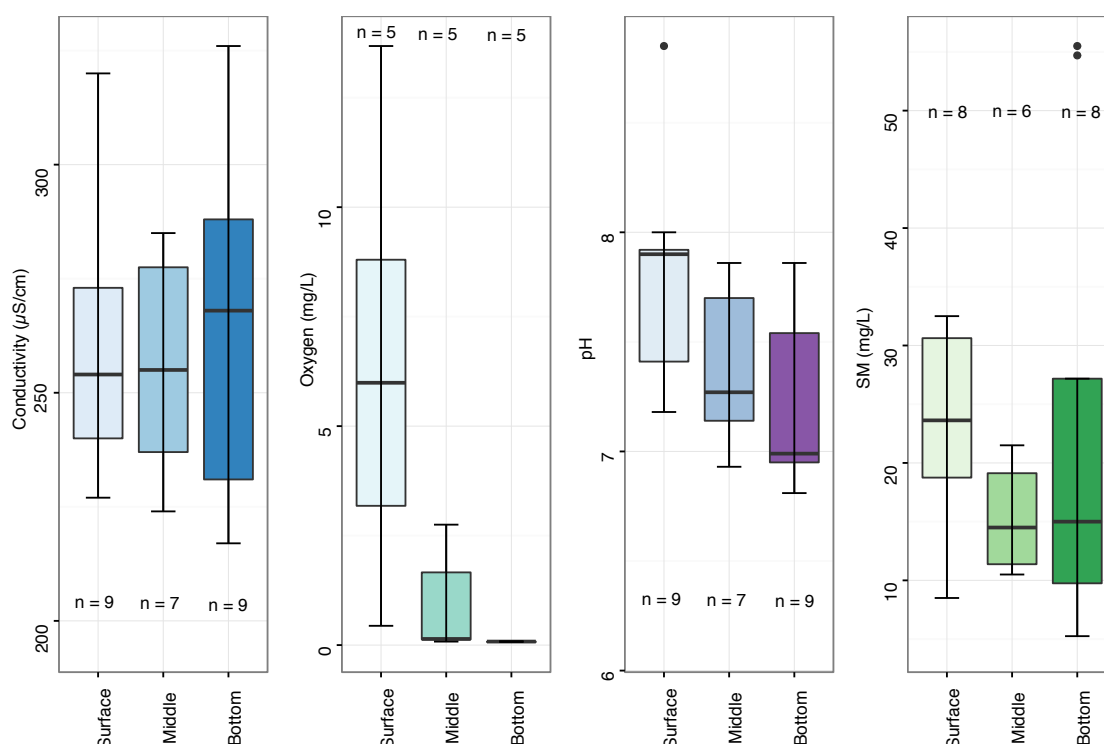


Figure 19 Evolution of conductivity, oxygen, pH and SM at 3 depths of point P2

3.2. Trace metal speciation in the Lake Pampulha

As mentioned before, in the next paragraphs, we will only consider 7 trace metals which are more associated with human activities: chromium (Cr), cobalt (Co), copper (Cu), cadmium (Cd), lead (Pb), nickel (Ni) and zinc (Zn). These metals come from various anthropogenic sources such as metallurgy, dyeing industry, production of paint, coloring agents, catalyst, wood conservation, petroleum industry etc. They present an ecotoxicity hazard and are progressively controlled by regulation. Lake Pampulha has been increasingly affected by pollution from urban and industrial sources (Friese et al., 2010).

The evolution of the principal tributary Ressaca's flow, the precipitation during all monitoring period and the dates of all the campaigns are presented on Figure 20.

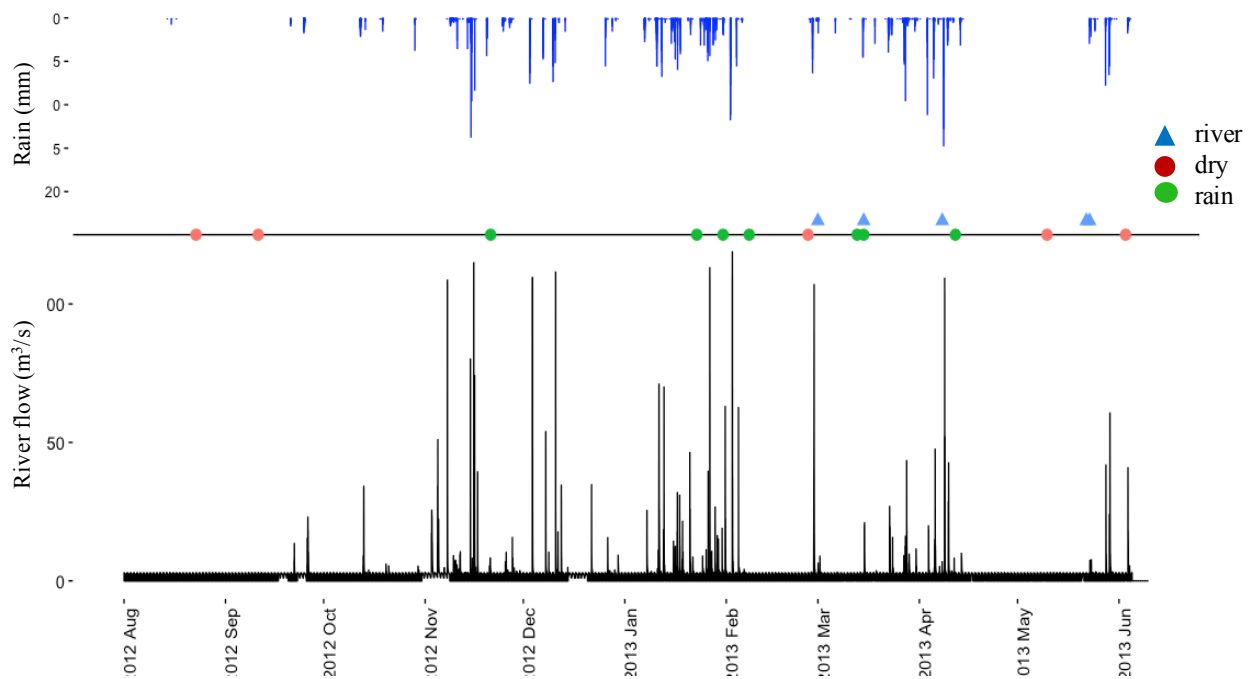


Figure 20 Ressaca's daily flow (lower panel, black), daily precipitation(upper panel, blue) and the campaign dates (colored points)

The principal two tributaries Ressaca and Sanrandi contribute up to 70% of total flow into the lake. The entering flow and the rain are measured at the station Res17F and Sar18F (Figure 20) upstream of the sampling point for the river monitoring campaigns. In the Figure 20, we only present the Ressaca's flow and the rainfall at the station Res17F.

From August to November 2012, almost no rainfall is registered and the flow is low and constant. From November 2012 to February 2013, there is a raining period with river flow higher than $100\text{m}^3/\text{s}$ for certain events. From February to June 2013, the rain is intermittent, but strong for certain events.

Based on the precipitation and flow data, we define the monthly campaigns as “dry” after a period without raining or “rain” campaigns during the raining periods.

3.2.1. Trace metal concentrations in Lake Pampulha and in the tributary Ressaca/Sarandi

The total metal concentrations in the principal tributary during the dry period are presented on the boxplots in Figure 21. The concentrations correspond to a 24-hour sampling during the dry campaigns. For Lake Pampulha, dry and raining campaigns are presented together.

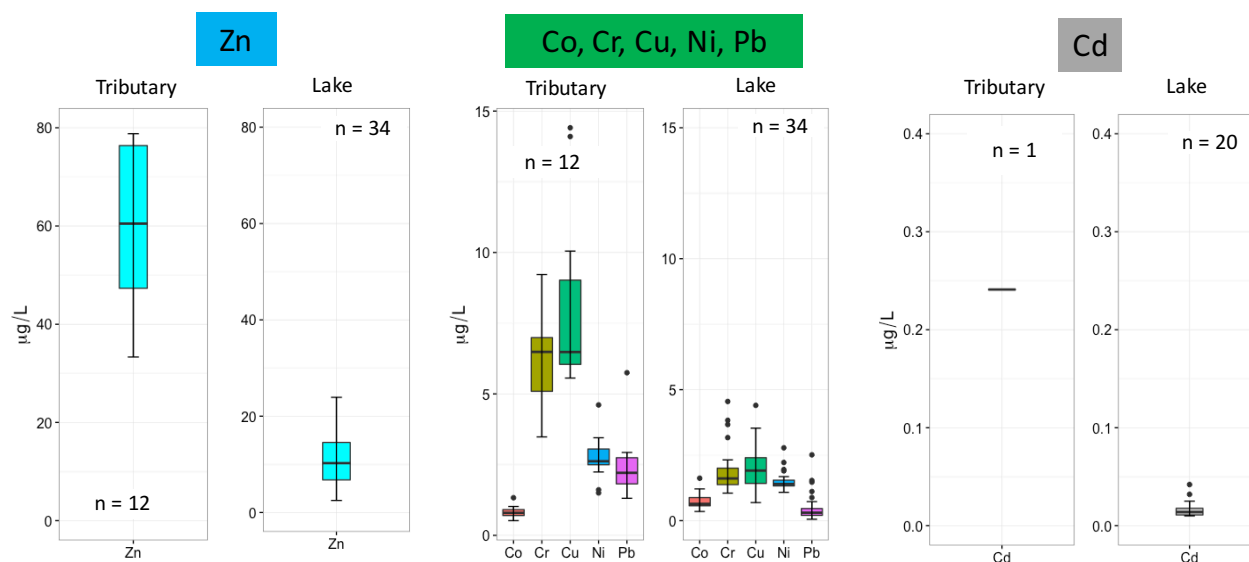


Figure 21 Box plot of total metals concentration in the tributary Ressaca/Sarandi and in the water column of Lake Pampulha

In general, we observe more variation of the metal concentrations in the river than in Lake Pampulha. For Cr, Ni, Cu, Zn, Cd and Pb, the total concentrations are higher in the river, particularly for the Zn and Cu. For Co, the variation of total concentration is higher in the lake. For Cd, we have only one value in the river, because during analysis with ICP-MS, we diluted systematically all the sampling from tributary. This dilution allowed us to quantify correctly the concentration of other metals but make us to lose information for Cd. We cannot conclude that Cd in the river is higher than in the lake, but the only value of Cd is around 10 times stronger than the concentration in the lake.

As all the metals, do not have a normal distribution, we performed the Wilcoxon Mann Whitney test for the average comparison between the river and the lake (Table 26).

Table 26 Mean comparison of total concentrations between river and lake according to Wilcoxon Mann Whitney test (threshold 5%)

	p value	Significant difference
Cr	$4.1 \cdot 10^{-6}$	River > Lake
Co	0.3	No difference
Ni	$4.4 \cdot 10^{-5}$	River > Lake
Cu	$1.7 \cdot 10^{-6}$	River >> Lake
Zn	$1.8 \cdot 10^{-6}$	River >> Lake
Pb	$1.1 \cdot 10^{-5}$	River > Lake

3.2.2. Total, dissolved and labile concentrations of trace metals in Lake Pampulha

In this paragraph, we will present the variation of metal concentrations of 3 fractions (total, dissolved, labile) in the water column of Lake Pampulha during the dry and raining periods (Figure 22)

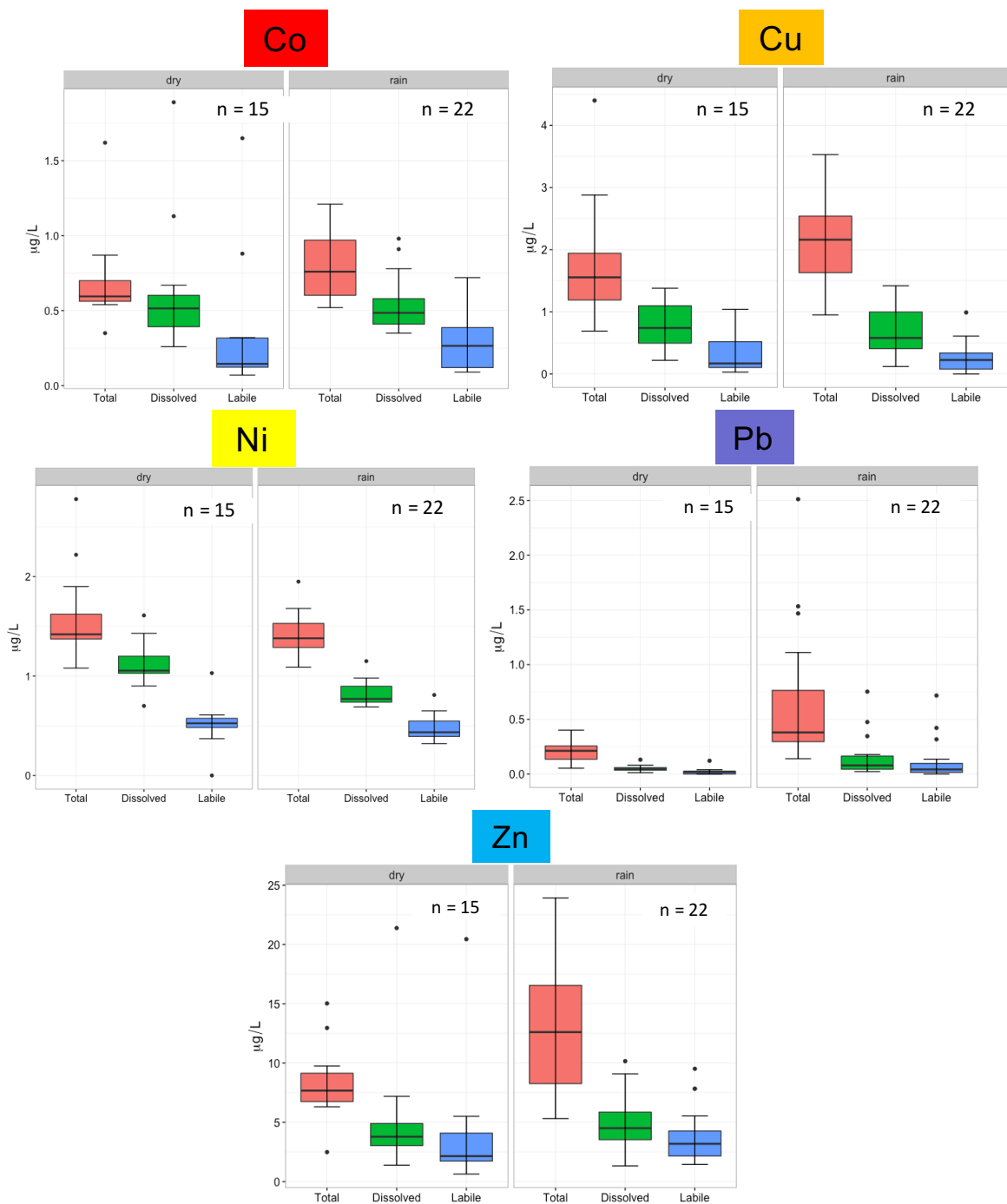


Figure 22 Boxplots of Co, Cu, Ni, Pb and Zn in total, dissolved and labile fraction in Lake Pampulha during dry and raining periods

In general, we observe a higher variation for all fractions in the raining period for all metals. During the raining period, the total concentration is higher, except for Ni. In fact, for the total concentration, the concentration of Cr, Zn and Pb is significantly higher during the raining period. For the dissolved concentrations, Cr and Pb are significantly higher during the raining period. Contrary to Cr and Pb, Ni is significantly lower during the raining period. No significant difference of the labile fraction appeared (Table 27).

The impact of raining period is observed for the total and dissolved concentrations. We do not observe an increasing labile concentration during the raining period. For Ni, the boxplot showed a

stable concentration of the total and labile fractions and a lower concentration in the raining period may be due to the dilution effect.

Table 27 Mean comparison of concentrations (total, dissolved, labile) between dry and raining period using Wilcoxon Mann Whitney test (threshold 5%)

	Total		Dissolved		Labile	
	p value	Difference	p value	Difference	p value	Difference
Cr	$7 \cdot 10^{-3}$	rain > dry	0.01	rain > dry	-	-
Co	0.17	no difference	0.96	no difference	0.61	no difference
Ni	0.23	no difference	$4 \cdot 10^{-3}$	rain < dry	0.26	no difference
Cu	0.06	no difference	0.49	no difference	0.92	no difference
Zn	0.05	rain > dry	0.39	no difference	0.22	no difference
Pb	$1 \cdot 10^{-3}$	rain > dry	0.04	rain > dry	0.13	no difference

- **Trace metal standards in freshwaters**

Water standards regarding trace metals in freshwaters in Brazil (resolution CONAMA 357, 17/03/2005) and in Europe (Water Framework Directive 2008/105/CE, EU WFD) are presented respectively in Table 28 and Table 29. There are two main differences between CONAMA resolution and the European Union Water Framework Directive. Firstly, CONAMA states a classification framework to water bodies according to their intentional use. The decision on which water quality class is assigned to a particular water body is influenced by a participatory process organized by the concerned river basin committee where stakeholders (representatives of water users, the civil society and the government) have seat. The European Water Framework Directive aims at the good chemical and ecological status at Community level and national level depending on each substance.

Secondly, CONAMA resolution sets the thresholds based on metal total fraction (in mg/L), except for Cu, while in the WFD the limits for good chemical status are based on the metal dissolved fraction (in µg/L). WFD also considers a maximum acceptable concentration (MAC) and an annual average (AA). Depending on the legislative context, trace metal concentrations in Lake Pampulha could exceed the limit of these water standards. Considering the CONAMA resolution, high cyanobacteria biomass and low dissolved oxygen concentration in Lake Pampulha would lead to classifying it in class 3 for freshwaters, meaning that this water can be used for drinking water after advanced water treatment, for irrigation of trees, but not of greenery. No primary neither secondary contact with water is allowed in this class. According to CONAMA resolution, all trace metal values measured in Lake Pampulha are also under the limits for class 3 water-bodies. Considering European WFD, only dissolved copper exceeded the maximum acceptable value in one sample among the 26 collected samples and no dissolved metal exceeded the annual average concentration.

Table 28 Maximum concentrations according to CONAMA resolution 357 for freshwater class 3

	Co total	Cu dissolved	Cd total	Ni total	Pb total	Zn total
Maximum concentration (mg/L)	0.2	0.013	0.01	0.025	0.033	5

Table 29 Water standards for surface water in Europe (MAC:Maximum concentration, AA :Annual average)

	Cr dissolved	Co dissolved	Cu dissolved	Cd dissolved	Ni dissolved	Pb dissolved	Zn dissolved
MAC (µg/L)	-	-	1.4	1.5	34	14	-
AA (µg/L)	-	-	1.4	0.25	4	1.2	7.8

- **Trace metal concentration measured in Lake Pampulha in 2001**

In this paragraph, we present the total metal concentrations at the surface, middle and bottom of the water column at point P2, measured in May 2011 (Friese et al.2010) and May 2013 (our data) in the Table 30.

Table 30 Total metal concentrations at three depths of point P2 in May 2001 (Friese et al.2010) and May 2013 (our data)

Depth	Cr (µg/L)		Co (µg/L)		Ni (µg/L)		Cu (µg/L)		Zn (µg/L)		Cd (µg/L)		Pb (µg/L)	
	2011	2013	2011	2013	2011	2013	2011	2013	2011	2013	2011	2013	2011	2013
Surface	0.94	1.07	0.73	0.54	-	1.43	1.24	4.4	18.1	15.03	0.17	0.12	0.94	0.20
Middle	<0.03	1.05	0.58	0.54	-	1.38	0.61	1.32	5.2	6.31	0.07	NA	0.41	0.14
Bottom	0.07	1.14	0.85	0.6	-	1.34	17.1	1.45	14.4	7.73	0.07	NA	0.96	0.12

In general, we find the same range of concentration in Lake Pampulha 12 years later except for Cu, Zn and Pb. Cu concentration at the surface in 2013 is higher but it is lower at the bottom. For Zn, we have the same range of concentration for the surface and middle of the water column. The concentration is lower at the bottom in 2013. Only Pb showed a lower concentration for all the depths. The lower Pb concentration in the lake probably result from the prohibition of Pb in gasoline in Brazil.

- **Comparison with other urban water bodies**

For comparison with other urban water bodies, we present the 1st quartile, median and 3rd quartile of the total metal concentrations in Lake Pampulha, in 49 lakes in Ile-de-France region during 2011-2013 (PULSE project, see chapter 6) and the minimum and maximum of Marne river. The range of metal concentrations is shown in the Figure 23

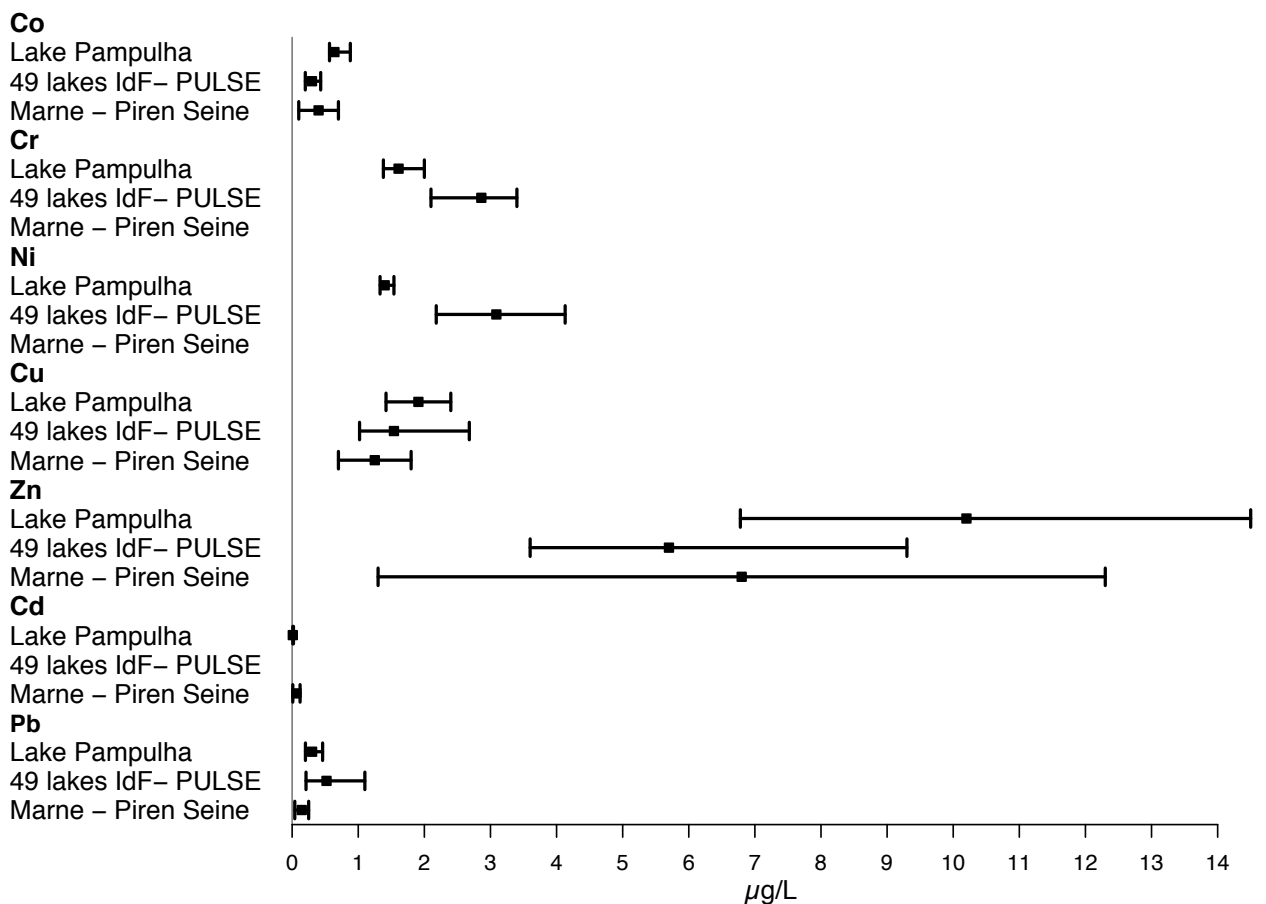


Figure 23 Range of total metal concentrations (1st – 3rd quartile) in Lake Pampulha, 49 lakes in IdF and Marne river

For Co, Cu, Zn, the concentrations are higher in comparison to 49 lakes and Marne river, especially for Zn. Cr and Pb values in Lake Pampulha are lower. Concerning Cd, we cannot really compare because most of analyses of Cd are under the quantification limits.

3.2.3. Trace metal speciation in the water column

In this section, we will focus on the distribution of total, dissolved and labile metal concentrations in the water column of Lake Pampulha. We remind that in most samples, Cd concentrations were under quantification limits, they will not be presented here. In this analysis, we only consider 2 depths: surface (0.5m) and bottom (7m) of the water column.

At first we present the mean total and dissolved concentrations at the surface and bottom of 12 monthly campaigns in the Table 31

Table 31 Mean concentration of total and dissolved metals at 0.5 and 7m depth, n = 12

Depth	Co Total μg/L	Co Diss. μg/L	Ni Total μg/L	Ni Diss. μg/L	Cu Total μg/L	Cu Diss. μg/L	Zn Total μg/L	Zn Diss. μg/L	Pb Total μg/L	Pb Diss. μg/L
Surface	0.65 ±0.20	0.45 ±0.12	1.58 ±0.42	0.94 ±0.26	2.53 ±1.05	0.90 ± 0.38	10.48 ± 4.25	4.54 ± 1.44	0.29 ± 0.15	0.06 ± 0.04
Bottom	0.88 ±0.32	0.64 ±0.22	1.49 ±0.35	0.91 ±0.22	1.69 ±0.61	0.54 ± 0.38	11.44 ± 6.17	4.05 ± 2.83	0.77 ± 0.78	0.14 ± 0.21

The mean concentration of total and dissolved fractions of Co, Cu and Pb is significantly different between the surface and the bottom ($p < 0.05$). The standard deviation indicated that there is more variation for Cu at the surface, for Zn at both depths and particularly for Pb at the bottom (Relative Standard Deviation ~ 100%).

For assessing the distribution of particulate and dissolved metals, we calculated the ratio between dissolved and total fractions (Table 32 and Figure 24 left). This distribution is very variable among the metals. Dissolved fraction varies between 21% for Pb and 72% for Co. Ni is also highly dissolved, around 60%. For Cu and Zn, the dissolved and particulate fractions at the surface are nearly equal, between 40 and 50%. The distribution between dissolved and particulate fractions is rather similar at surface and bottom of the water column for Co and Pb. The standard deviation of these ratios varies from 8% to 28% for the 5 trace metals. The distribution between the particulate and dissolved fractions of Ni and Co is rather constant over the study period while the distribution of Cu and Zn is much variable.

For estimating the fraction of metal that is potentially bioavailable, we calculated the ratios between labile and dissolved fractions of the 5 metals (Table 33 and Figure 24 Right). The standard deviation of these ratios varies from 7% to 34%, indicating a low to medium seasonal variability of the metal bioavailability. Bioavailability is variable between metals but also between the surface and the bottom of the water column. At the surface, the labile fraction varies between 9% and 26% and at the bottom of the water column, between 7% and 34%. Cobalt is the less labile in the surface layer. The lowest ratio of Co labile fraction (16%) was measured during a period of phytoplankton bloom, when the concentration of chlorophyll a was particularly high (220 μg/L). This result suggests that biological activity in the lake can have an impact on the bioavailability of Cobalt but additional data are required to confirm this hypothesis.

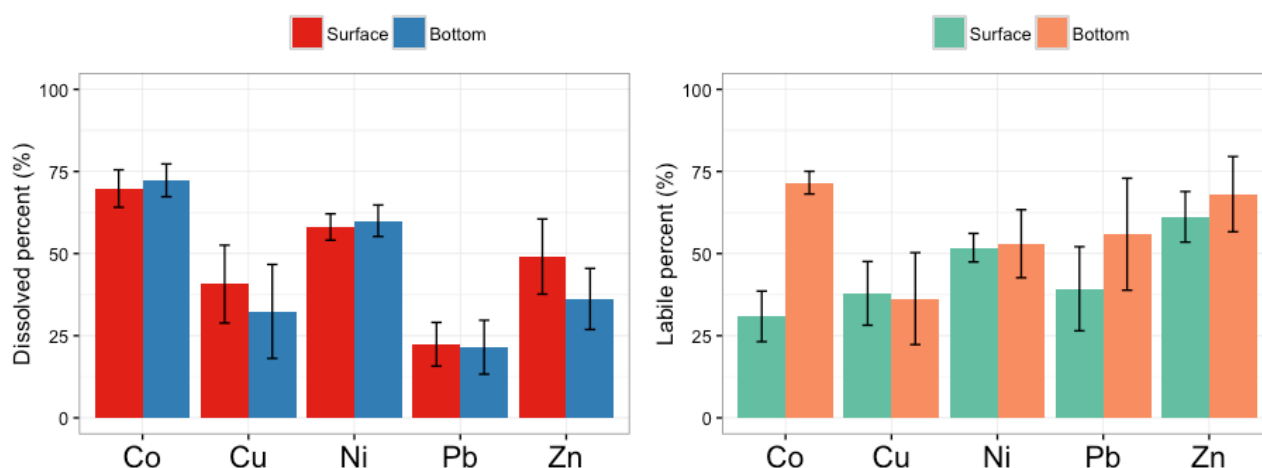
**Figure 24 (Left) Dissolved percent and (Right) labile percent of metal concentrations at the surface and the bottom**

Table 32 Mean ratio of dissolved to total metals at 0.5m and 7m depth

Mean ratio Dissolved/Total	Co (%)	Ni (%)	Cu (%)	Zn (%)	Pb (%)
Surface (0.5m)	69.8 ± 11.4	58.1 ± 8.0	40.7 ± 23.8	49.1 ± 22.9	22.4 ± 13.3
Bottom (7m)	72.3 ± 10.0	60.0 ± 9.6	32.4 ± 28.6	36.2 ± 18.6	21.5 ± 16.4

Table 33 Mean ratio of labile to dissolved metals at 0.5m and 7m depth

Mean ratio Labile/Dissolved	Co (%)	Ni (%)	Cu (%)	Zn (%)	Pb (%)
Surface (0.5m)	30.9 ± 15.4	51.8 ± 8.7	37.9 ± 19.4	61.2 ± 15.4	39.3 ± 25.6
Bottom (7m)	71.6 ± 6.9	53.0 ± 20.7	36.3 ± 28.0	68.1 ± 22.9	55.9 ± 34.1

3.2.4. Seasonal variation of trace metal

In this paragraph, we present the evolution of the concentrations of total, dissolved and labile metals at 3 depths of the point P2 during the 12 monthly campaigns.

3.2.4.1. Chromium

The Cr labile concentration was not correctly quantified with the chelant disk (see § 3.2.1.3 --- in Material & Methods section). We only present the temporal evolution of total and dissolved concentrations of Cr in the Figure 25. The total Cr concentration at the surface varies slightly from 1 to 2 µg/L while it varies from 1 to 5 µg/L at the bottom. During the dry period, the total concentration does not vary with depths. However, it increases at the bottom during the raining campaigns (21/22/2012 – 08/02/2013).

Only around 20% of Cr is dissolved in the water column. There is a slight difference between the concentration of dissolved Cr at 0.5m and 7m depth during the whole monitoring periods. The dissolved concentration increases slightly during the raining campaigns. Taking into account the variation of the total and dissolved concentrations, we can deduce that the particulate concentration is higher during the raining period.

Lake Pampulha has a neutral pH while the layer below 3m is depleted in oxygen. Fe and Mn oxides are known as excellent scavengers for Cr to the bottom (Delaune et al., 1997; Levy et al., 1992). This condition can explain why Cr is more particulate than dissolved. When arriving at the bottom under strong reducing conditions, Fe and Mn oxides will be dissolved and release scavenged Cr. Due to the strongly negative Oxido-Reduction Potential (ORP), this effect can explain a slight increase of Cr dissolved at the bottom during the stratification period.

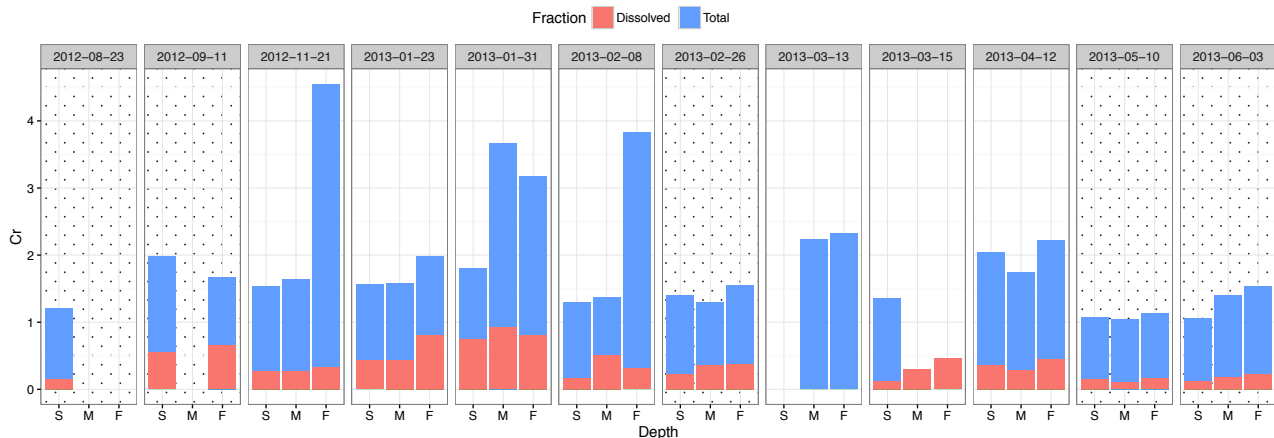


Figure 25 Total and dissolved concentration of Cr at the surface (S), middle (M) and bottom (F), for dry period (dotted background) and raining period (blank background)

3.2.4.2. Cadmium

Total concentration of cadmium is very low in the water column. For most campaigns, we could only quantify the total fraction. During the raining period, Cd concentration is higher at the middle and the bottom of the water column (Figure 26).

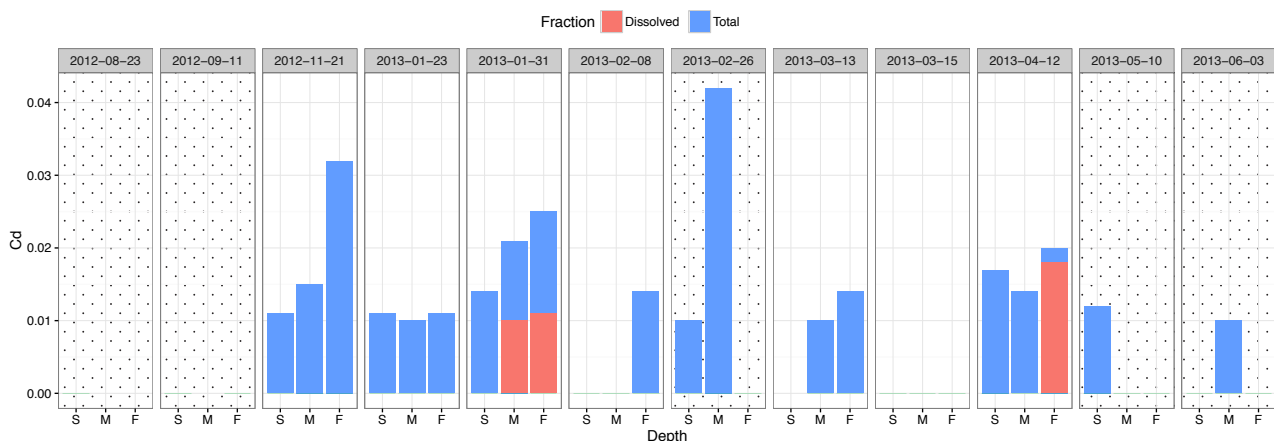


Figure 26 Total and dissolved concentration of Cd at the surface (S), middle (M) and bottom (F), for dry period (dotted background) and raining period (blank background)

3.2.4.3. Cobalt

Cobalt is highly dissolved at 3 depths during the sampling periods (Figure 27). The total concentration varies around 0.5 $\mu\text{g/L}$ at the surface. Concentration is higher at the middle and bottom during both dry and raining periods. For example, at 7m, the total concentration of cobalt can be above 1 $\mu\text{g/L}$ for a dry campaign (26/02/2013) and it can be close to the average concentration for another dry campaign (10/05/2013). Cobalt reaches its highest concentration during the 26/02/2013 campaign when the phytoplankton biomass is also the highest.

For the dissolved and labile concentrations, cobalt is less labile at the surface and more at the bottom for most of campaigns: around 20 - 40% labile at the surface and around 70% labile at the bottom. Cobalt labile concentration is lower at the surface layer for the campaign 26/02/2013 when chlorophyll-a concentration is 220 $\mu\text{g/L}$. Meanwhile, for the campaigns of 12/04/2013 and

10/05/2013 when the water column was completely mixed and the phytoplankton activity was weak, cobalt is less labile in the surface layer Figure 27)

In rivers, lakes or marine waters, cobalt is heavily adsorbed by sediments; it is adsorbed by carbonate, hydroxide or oxide minerals present in water (ATSDR, 2001). Cobalt can also adsorb on humic substances, organic matter or organic pollutants, however this process depends on the local pH. An acid pH favors cobalt in the form of free ions. An increasing pH will favor the complexation of cobalt, especially with carbonate (ATSDR, 2001). On 26/02/2013, a high chlorophyll-a concentration indicates an active photosynthesis activity leading to a high pH (8,85) at the surface and a low labile fraction compared to the bottom.

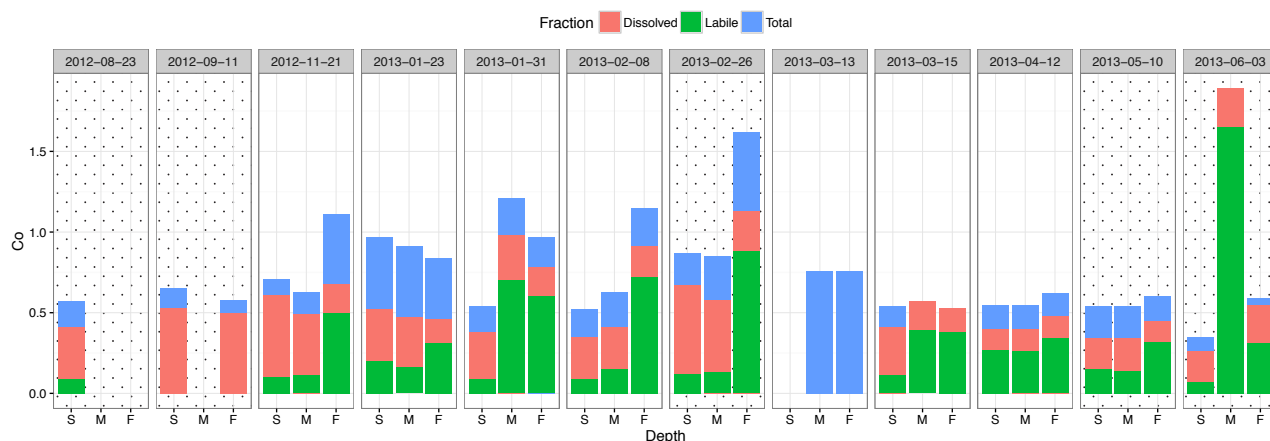


Figure 27 Total and dissolved concentration of Co at the surface (S), middle (M) and bottom (F), for dry period (dotted background) and raining period (blank background)

3.2.4.4. Nickel

The total, dissolved and labile concentrations of Nickel are shown in the Figure 28. In general, nickel concentrations are stable during the time. Around 60% of nickel is dissolved and 40-50% of nickel is labile at 3 depths. There is a slight difference of nickel total concentration between the surface and the bottom. We do not observe a difference between the dry and raining period.

In water bodies, nickel is weakly absorbed by aquatic organisms while it is highly linked to solid matter. Nickel is weakly complexed by natural anions such as OH⁻, sulfate and chloride. Ni(OH)₂ is dominant in solution at pH 9.5 (Kabata-Pendias et Pendias, 1992 ; ATSDR, 1997). This behavior can explain that the labile Ni fraction is not influenced by the phytoplankton production.

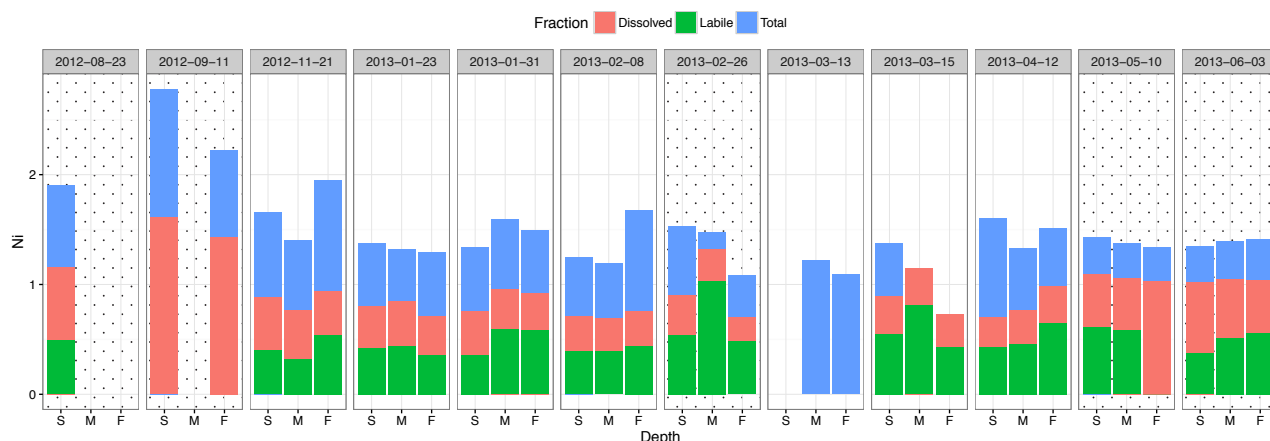


Figure 28 Total and dissolved concentration of Ni at the surface (S), middle (M) and bottom (F), for dry period (dotted background) and raining period (blank background)

3.2.4.5. Copper

We do not observe differences of Cu total concentration during the dry and raining periods (Figure 29). Copper shows a slight difference at the middle of the water column comparing with both surface and bottom. Copper is more particulate during most of campaigns. The labile concentration remains low at 3 depths except for 31/01/2013 ($>0.5 \mu\text{g/L}$) at 3 depths and for 26/02/2013 ($\sim 1 \mu\text{g/L}$) at the middle depth.

Copper is present in environment under various forms: ions, complexed by organic matter (humic and fulvic matter), oxides or adsorbed by particulate matter. Processes of complexation of copper depend on various factors such as pH, quantity of dissolved organic matter, redox potential etc. Copper is often discharged into environment under particulate form and tends to settle, adsorb to organic matter, oxides... (ATSDR, 1990 ; Dameron et Howe, 1998). In freshwaters, particulate copper represents from 40 to 90% of total concentration.

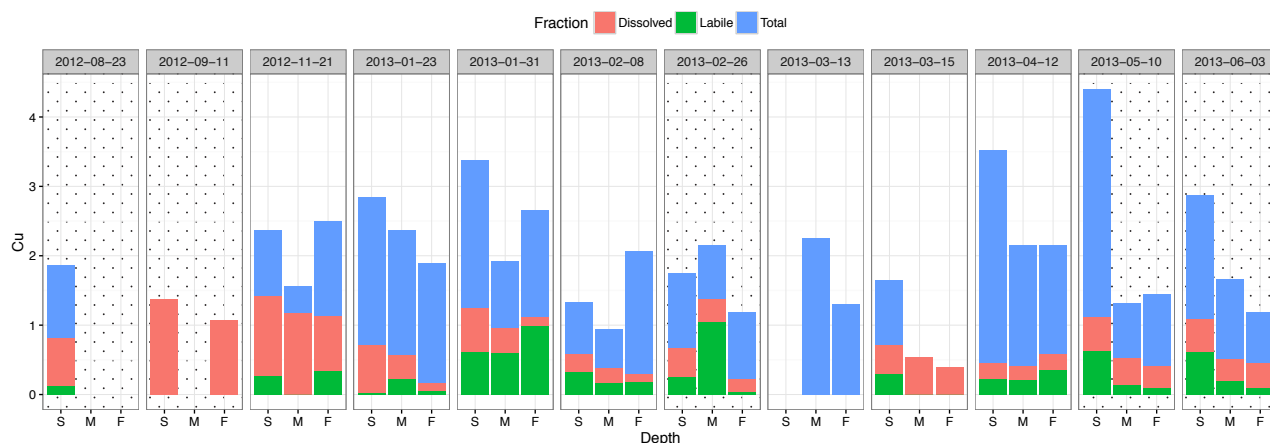


Figure 29 Total and dissolved concentration of Cu at the surface (S), middle (M) and bottom (F), for dry period (dotted background) and raining period (blank background)

- Zinc

The total, dissolved and labile concentrations of Zn are presented in the Figure 30. The total concentration is higher during the raining periods. During the dry periods, the total concentration is

lower than $10\mu\text{g/L}$ while it can be higher during the raining period. We observe a difference between the surface and the bottom of the water column during the raining period.

Zinc is more particulate during the raining campaigns. The labile concentration varies more for the raining period except for the dry campaign on 26/02/1203 where we observe a peak of labile concentration up to $20\mu\text{g/L}$. The field blank sample confirmed that it is not a contamination.

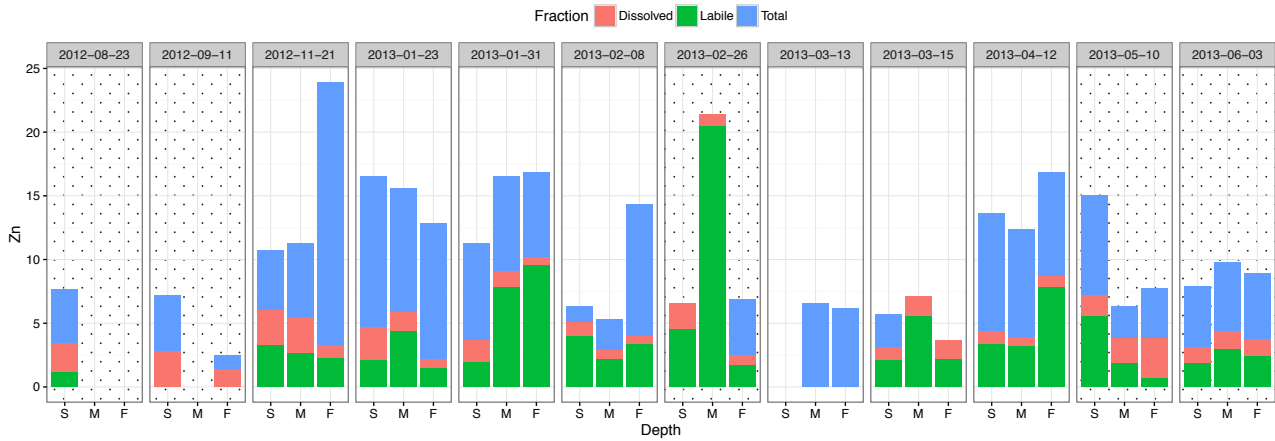


Figure 30 Total and dissolved concentration of Zn at the surface (S), middle (M) and bottom (F), for dry period (dotted background) and raining period (blank background)

Zinc has a similar distribution and complexation processes as copper in the environment. In various rivers in Europe, the distribution of zinc is 30% of ion and 70% complexed (Jansen et al. 1998).

- Lead

In the Figure 31, we observe that the total concentration during the raining period is much higher than during the dry periods and Pb is often more particulate, at the bottom of the water column. Particularly on 31/01/2013, the labile concentration at the middle and bottom is highest.

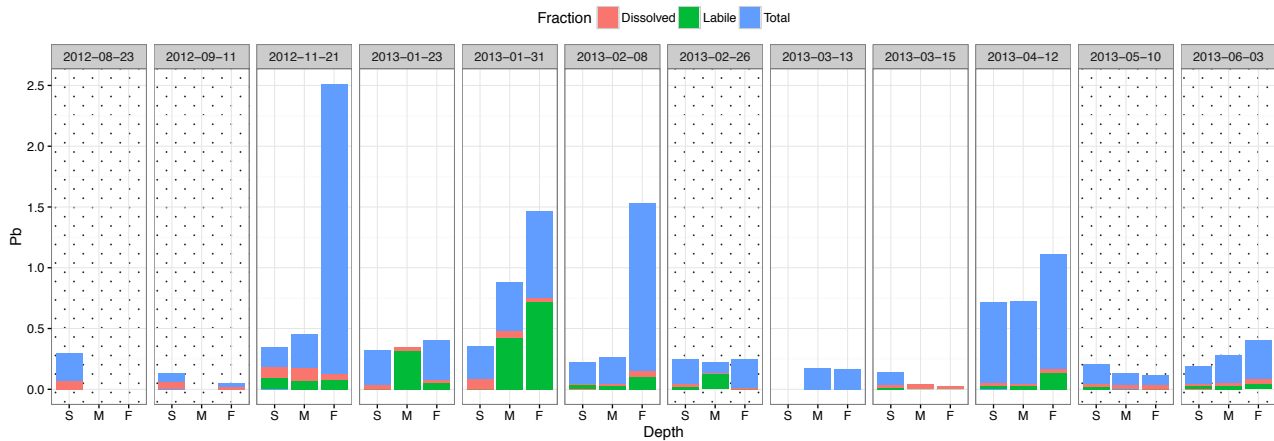


Figure 31 Total and dissolved concentration of Pb at the surface (S), middle (M) and bottom (F), for dry period (dotted background) and raining period (blank background)

3.3. Nutrient and trace metal input by tributaries

In this section, we present the results of nutrient and trace metal total concentration during the dry period, providing a rough assessment of the contribution of the tributaries into Lake Pampulha. Lake Pampulha is fed by 7 tributaries. We only present the results for the principal tributary Ressaca/Sarandi and the main tributaries Agua Funda, Mergulhão and Riberão. In order to easily compare the magnitude of the river concentrations, we present also the average concentration in the lake..

- Nutrients during the dry period

We present the concentration of total phosphorus, suspended matter (SM), chloride, nitrate and sulfate in the mentioned tributaries above and the average value in Lake Pampulha at the last position of the series of bar plots (Figure 32).

Mergulhao and AguaFunda creeks have a total phosphorus concentration higher than the average concentration in the lake. In the lake phytoplankton biomass contributes to the suspended matter. Mergulhao creek presents a particularly high SM concentration (10 times higher than in Lake Pampulha). We cannot confirm this high concentration because it is a single measurement. Chloride concentration is higher in the lake than in the tributaries. Sulfate concentrations are the same in the tributaries and in Lake Pampulha.

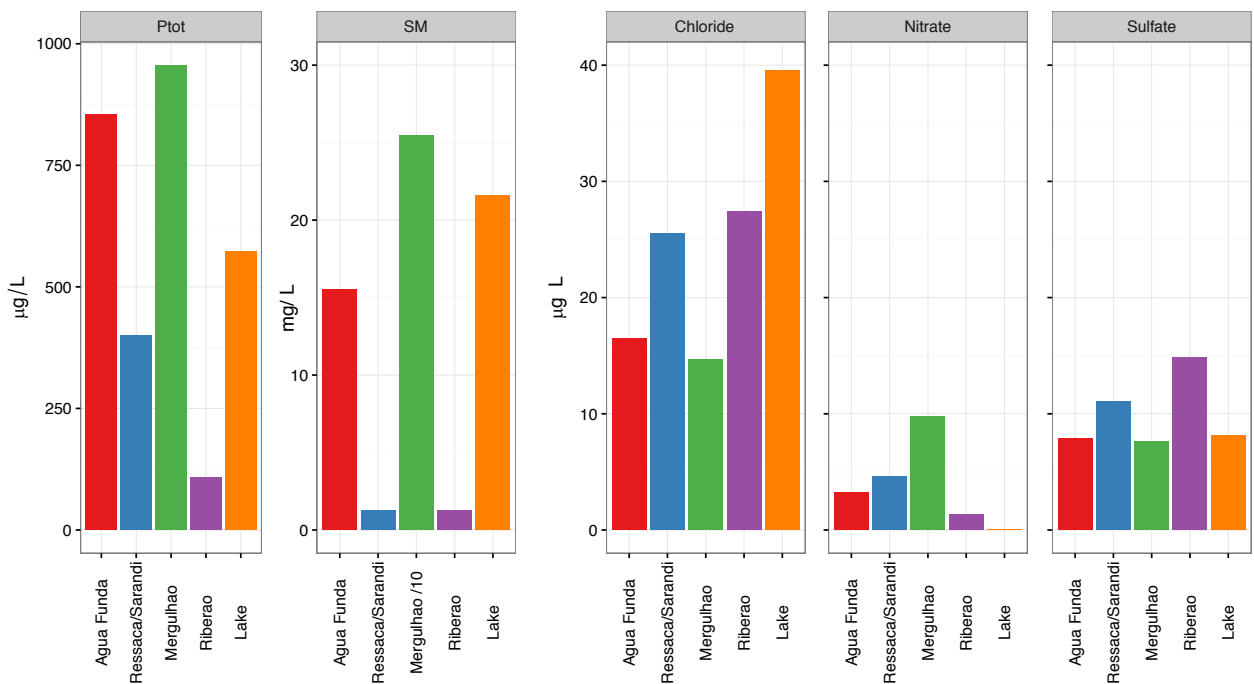


Figure 32 Concentration of total phosphorus, SM, chloride, nitrate and sulfate for 4 tributaries and Lake Pampulha

- **Total metal concentrations during the dry period**

The total concentration of Cr, Co, Ni, Cu Pb and Zn in the tributaries and the lake are presented in the Figure 33. For all metals, the concentrations in the Mergulhao creek is divided by 10 to be scaled with the other tributaries.

As observed above, Mergulhao creek presented a high concentration of nutrients compared to the other tributaries. The total concentration found in Mergulhao can be from 5 times higher (Ni) to 10 times (Cr, Co, Cu, Zn) or 30 times higher (Pb). Among these metals, they have a similar concentration to the average concentration in the lake.

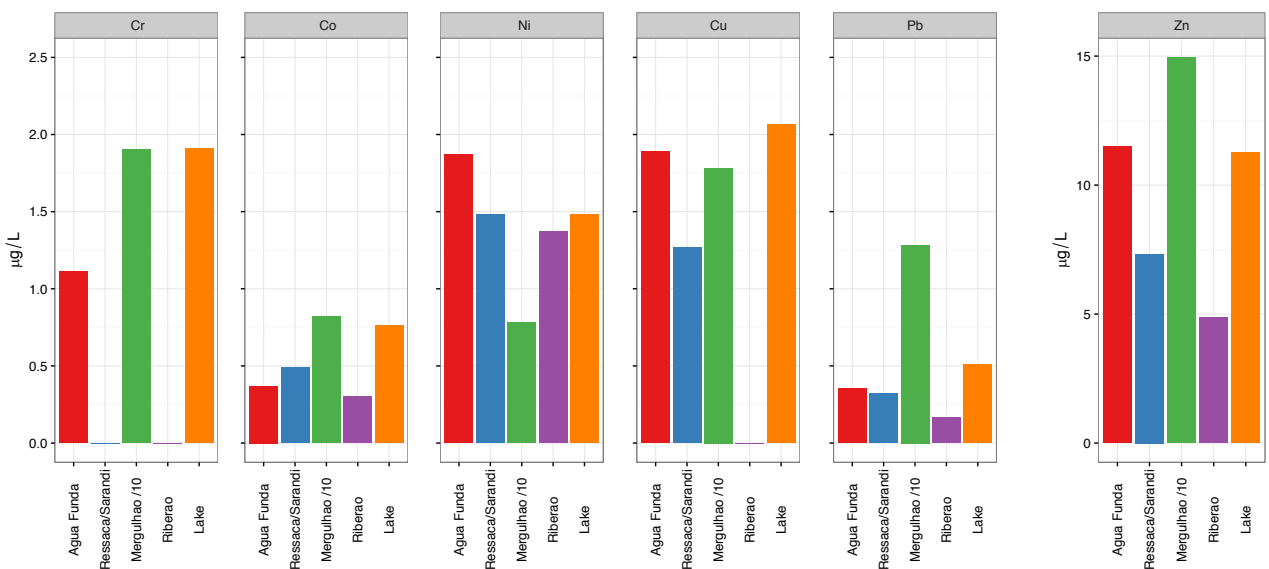


Figure 33 Concentration of total metal for 4 tributaries and Lake Pampulha

3.3.1. Total metal concentrations in the lake main tributary

According to Friese et al.(2010), the main tributary Ressaca-Sarandi contributes up to 70% of the total flow into Lake Pampulha. The concentrations measured in Ressaca-Sarandi is not particularly high (see § 4.1.3). In order to better quantify the contribution of this principal tributary, we present hereafter the nutrient and total metal concentrations in samples collected from 11h20 am to 9h20 am the next day. The campaign was conducted on 19/06/2013 with a previous dry period of 16 days.

The evolution of physical chemical variables at Ressaca and Sarandi during 24h is presented in the Figure 35. The conductivity range is between 280 and 420 μ S/cm. We observed a declining conductivity between 15h20 and 19h20. This modification corresponds to a reduced flow between 14h and 19h (Figure 34). The variation of other variables follows closely the evolution of the hourly average flow except for nitrate.

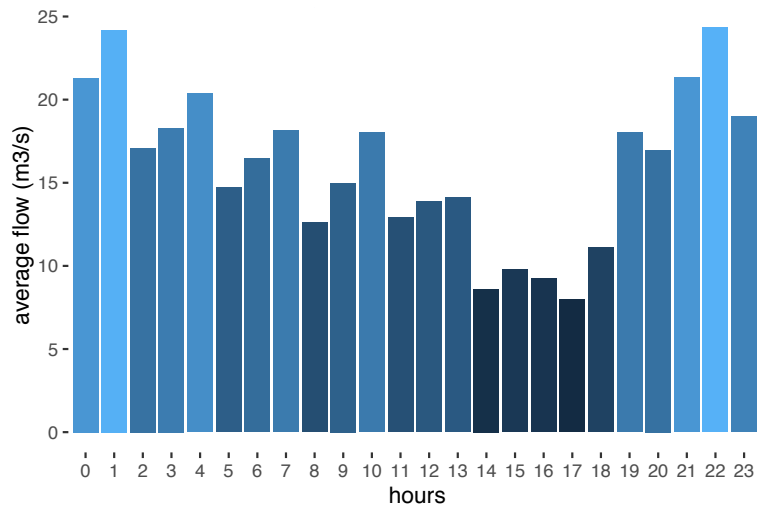


Figure 34 Average flow from 29/01/2012 to 04/06/2013 at Ressaca and Sarandi

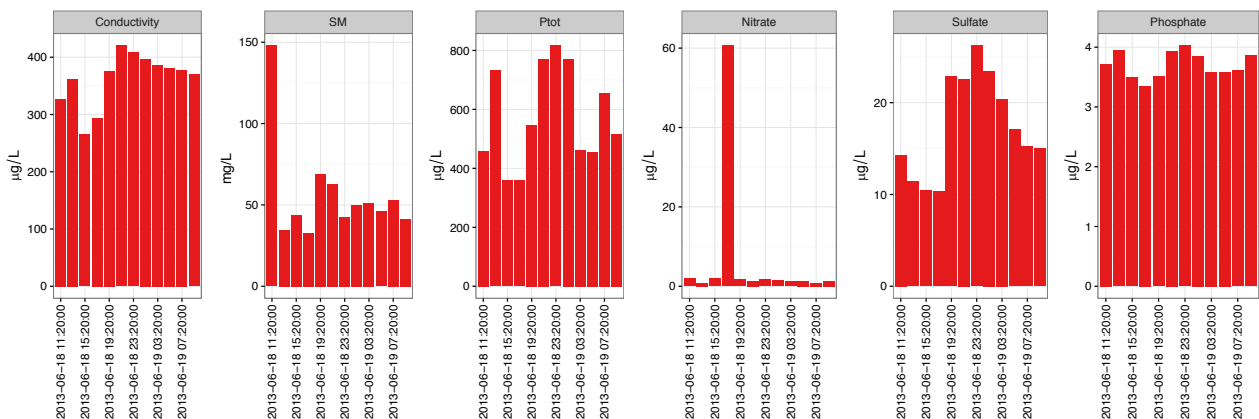


Figure 35 Evolution of conductivity, SM, total phosphorus, nitrate, sulfate and phosphate during 24h in Ressaca and Sarandi

The evolution of the total metal concentrations during 24h at the principal tributary Ressaca and Sarandi is presented in the Figure 36. We observed similar concentrations for Co, Ni, Cu, slightly stronger concentrations for Cr, Pb and a strongly higher concentration for Zn (10 times higher). The hourly evolution of Co, Ni, Zn and Pb corresponds to the evolution of the daily average flow. At that day, we find a particularly higher concentration of Zn in the river and an increasing peak around 5am the next day. It can suggest that there is eventually an industrial or domestic discharge during this moment.

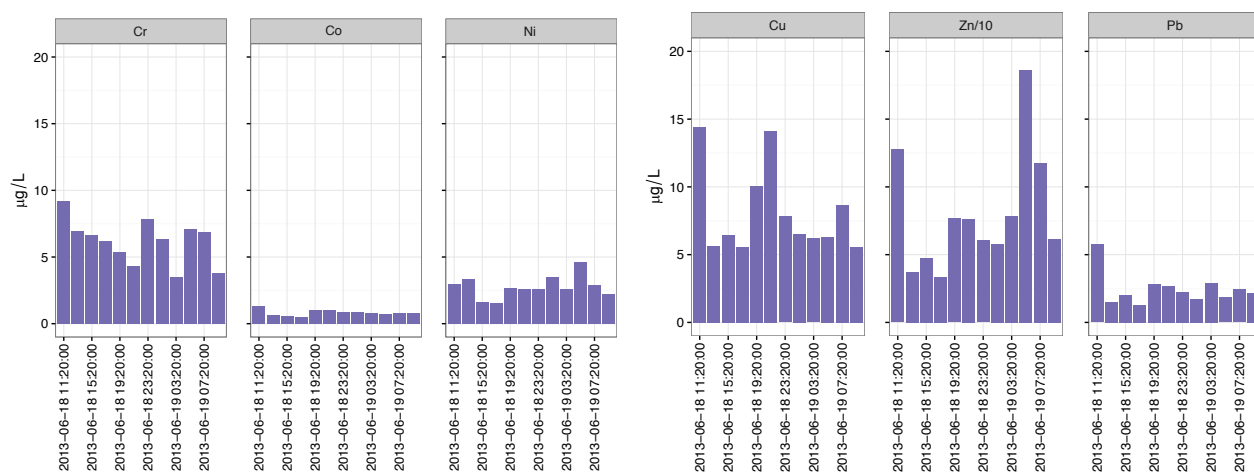


Figure 36 Evolution of total metal concentration during 24h in Ressaca and Sarandi

3.3.2. Impact of raining events

In this section, we will present the data collected during 5 raining events in the principal tributary. We present at first the characteristics of the five raining events (Table 34). The rain 1 and rain 5 have the same characteristics in term of rainfalls, return period and dry days before the sampled rain event. The rain 3 is the most important with 37mm height, 22 mm/h intensity and 3 months of return period. On the other hand, in term of the number of previous days without rain, the rain 4 is the only raining event after a long dry period (40 days)

Table 34 Characteristics of 5 rainfall events (Silva et al., 2014)

	Date	Precipitation(mm)	Intensity (mm/h)	Return period (month)	Days without rain
Rain1	01/03/2013	2.8	1.53	0.13	0
Rain2	15/03/2013	13.2	7.2	1	4
Rain3	08/04/2013	37	22.2	3	3
Rain4	22/05/2013	4.8	7.2	1	40
Rain5	23/05/2013	2.0	6.0	0.13	0

Table 35 summarize the min, max, average and cumulative load of total metal for 5 events. In general, we found higher concentrations during the raining events compared to the monthly campaigns. We found a strong peak of concentration of Cu, Zn and Pb. Between the raining events, the rain 3 carried the most pollutants due to its rain fall intensity. After the rain1, the 4 and 5 rains

present strong loading due to the accumulation of pollutants during 40 days before the raining event. The raining intensity and the number of days before the raining event are the most important parameters.

Table 35 Min, max, average load, cumulative load of total metal for 5 raining events

Rain 1	Cr	Co	Ni	Cu	Zn	Cd	Pb
Min (µg/L)	3.42	0.96	2.95	4.61	39.05	0.28	1.91
Max (µg/L)	6.07	6.89	4.41	7.15	139.56	4.17	12.49
Average(mg/s)	15.19	6.83	10.27	16.62	192.93	3.75	12.24
Sum(mg)	75.94	34.17	51.34	83.12	964.67	18.74	61.17
Rain 2							
Min (µg/L)	7.80	1.58	3.09	11.48	88.84	0.20	7.13
Max (µg/L)	35.61	7.40	13.13	72.18	518.70	0.95	43.54
Average(mg/s)	87.07	17.59	32.69	147.60	1122.93	2.25	92.02
Sum(mg)	435.35	87.97	163.46	738.00	5614.67	11.25	460.12
Rain 3							
Min (µg/L)	14.89	2.24	5.02	14.50	122.80	0.18	11.96
Max (µg/L)	33.72	4.73	13.13	28.35	240.80	0.63	28.14
Average(mg/s)	231.63	43.72	82.61	223.85	1878.51	2.89	188.19
Sum(mg)	1853.04	349.78	660.88	1790.81	15028.05	23.09	1505.55
Rain 4							
Min (µg/L)	7.15	1.27	3.30	7.85	50.05	0.27	2.68
Max (µg/L)	53.79	10.83	20.26	97.70	730.53	3.95	78.78
Average(mg/s)	79.63	14.64	28.51	134.38	935.85	NA	59.84
Sum(mg)	875.91	161.03	313.60	1478.13	10294.33	NA	658.25
Rain 5							
Min (µg/L)	7.00	1.71	3.23	11.30	111.10	0.22	5.30
Max (µg/L)	44.65	10.90	19.38	114.10	820.60	1.26	58.26
Average(mg/s)	79.68	17.20	28.68	156.53	1587.96	1.83	80.06
Sum(mg)	956.19	206.46	344.18	1878.30	19055.56	21.94	960.75

3.4. Metal bioavailability in Lake Pampulha and environmental variables

In this section, we investigate how metal availability in Lake Pampulha can be related to environmental variables. We consider the metal labile fraction as the ratio labile/dissolved and we present the linear Spearman correlation of this ratio with environmental variables. All the insignificant correlations with p value <0.05 are omitted. The degree of correlation corresponds to the color gradient and size of symbol.

- All depths

The correlation coefficients at the point P2 with all the data obtained during the monthly campaigns at all depths pooled in the Figure 37. A strong correlation is observed between physical chemical variables themselves. Chlorophyll-a concentration correlates positively with O₂, pH, ORP, Nitrate ($r \in [0.53, 0.83]$). Oxygen concentration correlates strongly with other variables such as pH,

ORP, SM, Nitrate ($r = 0.65-0.84$). The labile fraction of metals correlate weakly between themselves except for Zn which correlate with Ni, Cu and Pb labile fractions.

The correlation of labile fraction of metals and other variables showed a strong negative correlation with all variables ($r = -0.4$ to -0.64) except for phosphate and total phosphorus.

The correlation of suspended matter and metals is observed for Cu and Zn ($r = 0.59$ and $r = 0.47$)

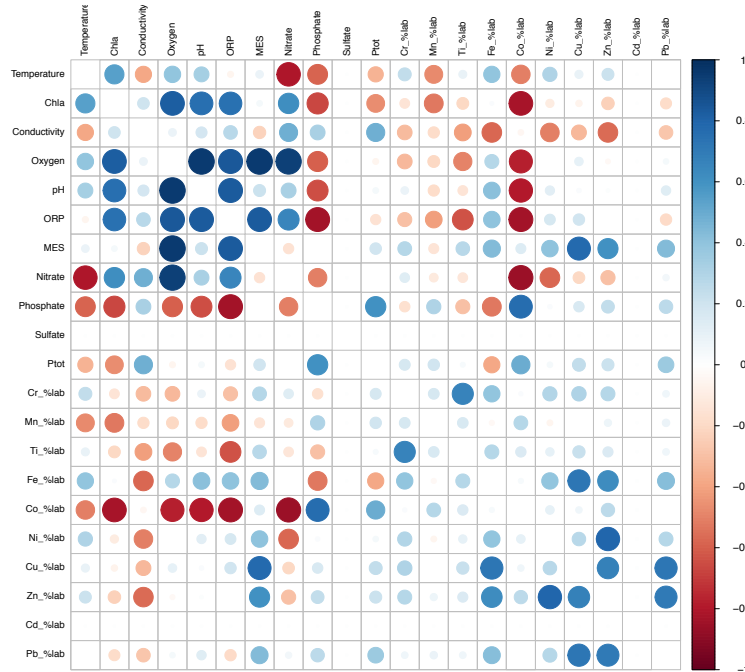


Figure 37 Correlation of labile fraction and physical chemical variables with all depths pooled

Due to a high vertical heterogeneity of temperature, chlorophyll-a and oxygen distribution, we then investigated the correlation of the labile metal fractions with the environmental variables separately at the surface and the bottom

1. At the lake surface

At first, we observe a strong correlation of chlorophyll-a concentration with other environmental variables ($r = 0.7-0.84$) (Figure 38), especially for the surface layer. Labile Cobalt fraction showed a negative correlation with chlorophyll-a, oxygen, pH, ORP, SM and Nitrate. This negative correlation is stronger for all depth pooled ($r = -0.55$ to -0.90). On the other hand, labile cobalt showed a strong positive correlation with phosphate ($r = 0.96$). Nickel labile showed a strong negative correlation with ORP and Nitrate ($r = -0.63$ for both). Zinc labile showed a strong negative correlation with Oxygen and ORP ($r = -0.63$ and $r = -0.83$). The suspended matter correlates negatively with most labile metals except for Cu. Phytoplankton biomass is the major contribution of suspended matter at the surface layer. The negative correlation of chlorophyll a concentration and suspended matter concentration with the labile metals indicates that when these concentrations increase, the labile metal concentrations decrease.

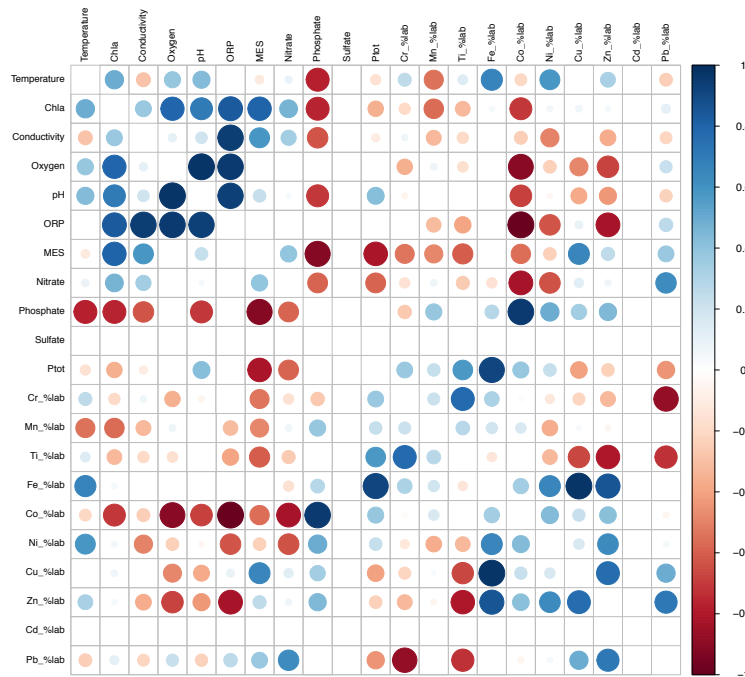


Figure 38 Correlation of labile metal fraction and physical chemical parameters at the surface

2. Correlation at the bottom

At the bottom layer, the temperature correlates negatively with other environmental variables ($r = -0.54$ to -0.85). The chlorophyll-a concentration does not show high correlation with other variables. The suspended matter shows high positive correlation with the labile metals ($r = 0.61$ to 0.94). This correlation can indicate the dominance of particulate metals at the bottom of the lake (Figure 39).

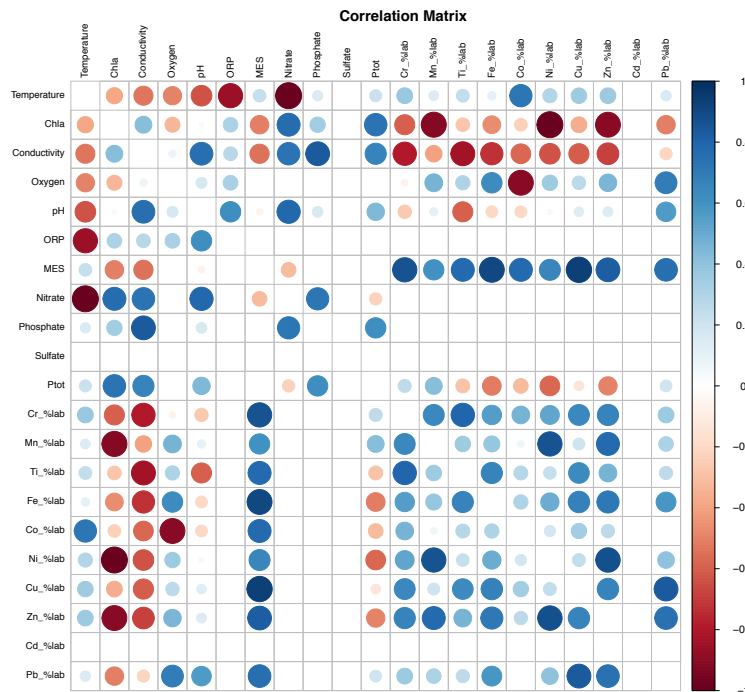


Figure 39 Correlation of labile metal percent and physical chemical parameters with all depths pooled at the bottom

Conclusion:

We observe differences between the surface layer, where the phytoplankton development dominates and the bottom layer where oxygen is permanently low and the metals are principally particulate.

Labile Cobalt showed a high correlation with chlorophyll-a concentration at the surface. The correlation is negative and can be explained by the fact that Co and Mn have similar pathways of microbial oxidation, therefore their cycles would be linked. Similarly, to Cobalt, Zinc can be depleted by phytoplankton because Zn and Co are used for enzyme carbonic anhydrase in Calvin Cycle.

Labile Nickel only strongly correlates with chlorophyll a and conductivity at the bottom layer. In the literature, nickel shows rarely any relation with the medium (Bisson et al., 2006).

Labile Zinc and chlorophyll-a concentration showed no correlation at the surface but high negative correlation at the bottom layer. It means that when the phytoplankton develops, the percent of Zn labile decrease at the surface and when the phytoplankton is weak, this percent can be strong at the bottom layer. Phytoplankton production can deplete first Zn and then Co for enzyme carbonic anhydrase which is involved in Calvin Cycle. Transfer of Zn between solid and dissolved forms is quite rapid, about 2 weeks whereas it can be until 1 month for Ni. However, Gee and Bruland (2002) showed that Zn desorbed more quickly than it absorbed. This can imply an increase of Zn concentrations of about 20% in a day because of desorption. Mineralization of phytoplankton biomass and reductive dissolution of Fe and Mn oxides can also release dissolved Zn. Zn is strongly binded to hydroxides (Fe or Mn) and the relationship high DOC – high Zn is often observed. Morris et al. (2005) showed that diurnal Zn cycle, with maximum concentration at dawn and minimum concentration in late afternoon, is primarily due to Zn sorption and desorption during photosynthesis activity.

Lead showed no strong correlation at the surface layer and strong negative correlation with Oxygen, pH and SM. We do not observe a correlation with the chlorophyll-a concentration. However it was demonstrated in laboratory experiments that Pb was highly sorbed to phytoplankton, principally on the cell surfaces). 95% of Pb are organically complexed in San Francisco Bay, which confirmed that Pb was not internally up taken (Pokrovsky et al., 2010; Luengen et al., 2007)

3.5. Statistical analysis

The objectives of this section are to present the different steps to constitute the data set analyzed with the statistical model Random Forest (RF); to present the parametrization of the RF model and to present the modelling results.

The main objective in this statistical analysis is to study the influence of environmental variables on the fraction potentially bioavailable of the metals.

3.5.1. Missing values

The missing values of the monthly monitoring of the dataset at the point P2 must be treated before their introduction in the Random Forest model. The missing values of the environmental variables are presented in Figure 40. The left zone of the graph corresponds to the proportion of missing values for each variable. The right zone corresponds to the proportion of missing values for a combination of variables (yellow = missing, and blue = not missing). The variation of the environmental variables and the percent of missing values for each variable are presented in Table 36.

For the environmental data, the missing values vary from less than 10% to 60%. Temperature and chlorophyll-a are the most complete in the data set. ORP is the most uncomplete of the dataset (more than 60% of missing values). At the right zone of the graph, the first below row mean that there are 9 times for a combination: the ORP and Oxygen are missing and the other variables (total phosphorus + SM + Conductivity + NH4 + Chla and Temperature) are available.

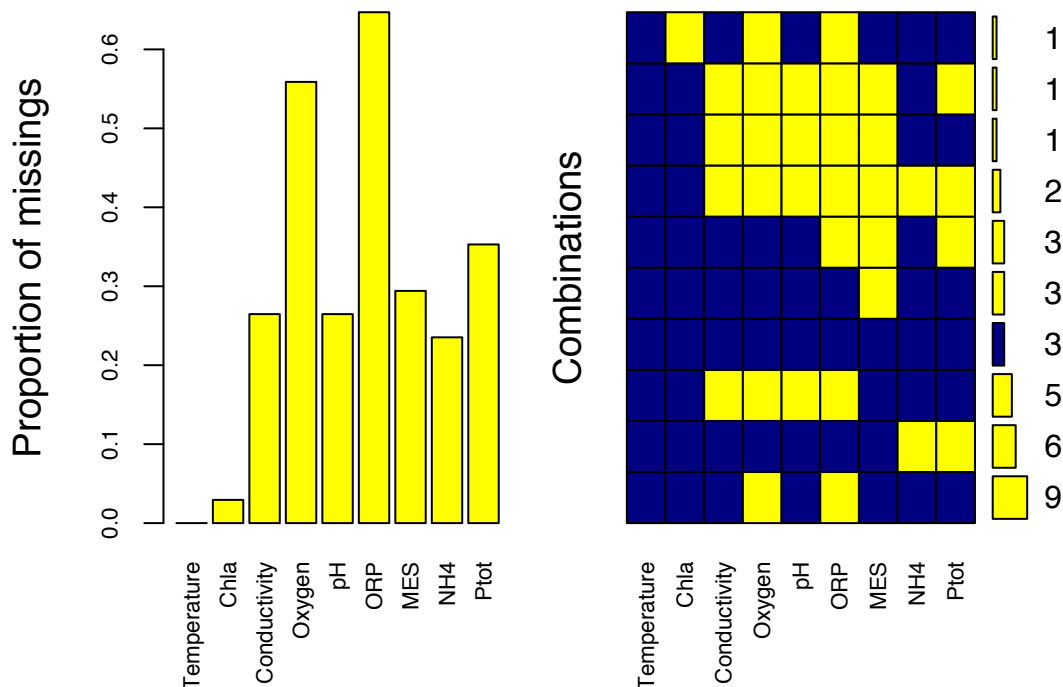


Figure 40 Proportion of missing values (left) and combination of environmental variables (right)

Table 36 Summary table of environmental data

Parameters	mean	sd	median	max	min	missing (%)
Temperature	23.8	2.0	23.9	27.5	17.3	0
Chla	75.1	59.8	71.0	221.6	5.0	3
Conductivity	261.1	30.9	255.0	326.0	217.0	26
Oxygen	2.5	4.0	0.1	13.7	0.1	56
pH	7.5	0.5	7.4	8.9	6.8	26
ORP	-31.7	135.5	-47.9	176.5	-217.9	65
MES	21.6	13.1	18.5	55.5	5.3	29
NH4	4.1	2.4	4.3	10.6	1.0	24
Ptot	572.9	644.5	320.3	2162.1	22.7	35

The metal dataset is more complete than the environmental dataset. After verification and validation of the dataset, the percentage of missing values of the total and dissolved metal concentrations is around 6%. For the labile concentrations, the percentage of missing values is higher, 19% for Pb and 17% for the other metals. The right zone of the Figure 41 indicates that all metal concentrations are available for 27 samples.

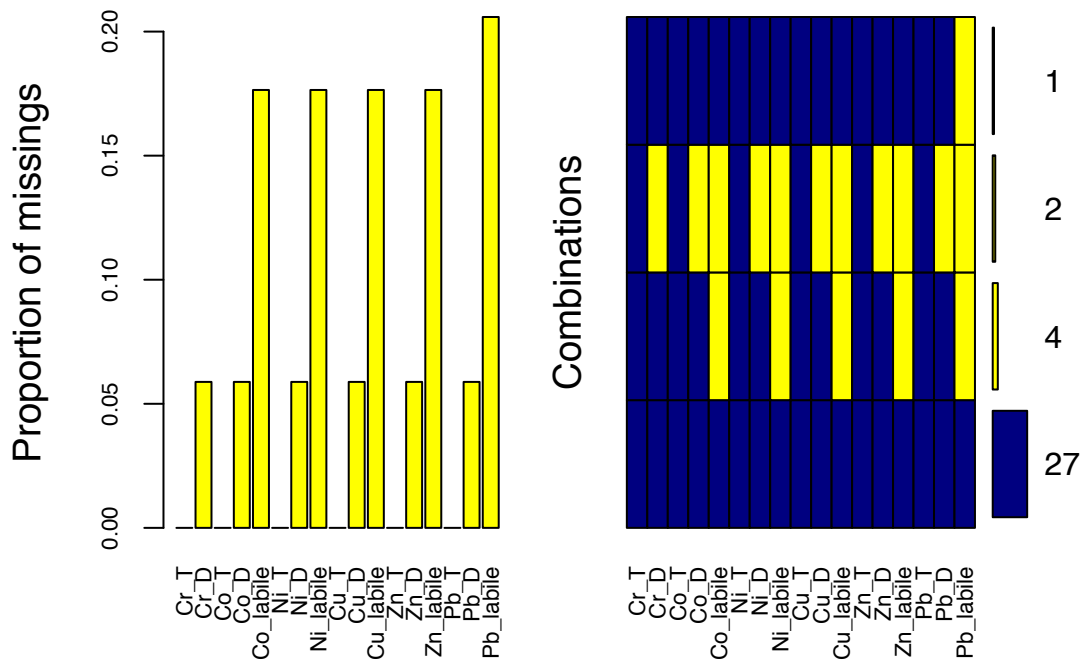


Figure 41 Proportion of missing values (left) and combination of metal and environmental data (right)

Table 37 Summary table of metal data

Metal	mean	sd	median	max	min	missing (%)
Cr_T	1.91	0.86	1.61	4.55	1.05	6
Cr_D	0.40	0.23	0.36	0.92	0.1	6
Co_T	0.76	0.27	0.64	1.62	0.35	6
Co_D	0.58	0.30	0.50	1.89	0.26	6
Co_labile	0.34	0.33	0.23	1.65	0.07	17
Ni_T	1.48	0.33	1.40	2.78	1.08	6
Ni_D	0.93	0.22	0.90	1.61	0.69	6
Ni_labile	0.49	0.17	0.47	1.03	0	17
Cu_T	2.06	0.84	1.94	4.4	0.69	6
Cu_D	0.73	0.37	0.67	1.42	0.12	6
Cu_labile	0.30	0.27	0.23	1.04	0	17
Zn_T	11.27	5.40	10.25	26.51	2.49	6
Zn_D	5.19	3.58	4.14	21.39	1.33	6
Zn_labile	4.06	3.76	3.04	20.45	0.64	17
Pb_T	0.51	0.53	0.32	2.512	0.053	6
Pb_D	0.12	0.15	0.05	0.753	0.012	6
Pb_labile	0.09	0.16	0.03	0.717	0	19

3.5.2. Missing value treatment

The Random Forest model does not work with missing values included in the dataset. Therefore, the missing values must be substituted or excluded before running the Random Forest model. There are many approaches to deal with the missing values (Acuña and Rodriguez, 2004):

- mean or median imputation
- knn imputation: affect the value of k nearest neighbor of the missing value
- imputation using a prediction model or a regression model
- imputation using decision trees

We decided to use the imputation algorithm included in the Random Forest model: `rfImpute` (randomForest R package <http://www.stat.ucl.ac.be/ISdidactique/Rhelp/library/randomForest/html/rfImpute.html>)

The algorithm developed by Liaw works as follows: All the missing values are omitted from the dataset. The RF model is run with this dataset. An output of the RF model is a proximity matrix that is used to substitute the missing values. In our case, we imputed continuous values computed as the weighted average of the non-missing observations, where the weights are the proximities. In Ishonoka (2013) and according to Brieman, the proximity is defined as follows: “the (i, j) element of the proximity matrix produced by a random forest model is the fraction of trees in which elements i and j fall in the same terminal node. This means that “similar” observations should be in the same terminal nodes more often than dissimilar ones.”

In our study site, additional information was used in the missing value treatment. Lake Pampulha presents some specific characteristics: a contrasted concentration of chlorophyll a at the surface and the bottom, a permanent oxygen depleted layer under 3.5m. Considering this pattern, we decided to treat separately the missing values in the upper and lower layers in order to take into account the vertical distribution of variables.

3.5.3. The final dataset

As discussed above, the environmental dataset presents a high missing value percent for some variables. We decided to include in the dataset only the variables with less than 35% of missing values. Therefore, ORP, chloride, bromide, sulfate, phosphate, nitrate were excluded from the dataset. The only exception is the oxygen because the missing values are principally in the bottom layer. We know that the oxygen concentration is nearly permanently very low in the bottom layer. Figure 42 shows the dissolved oxygen concentration after the substitution of the missing values. Its distribution at 3 depths corresponds to what we expected.

In addition, we included an additional variable: the average flow during 5 days preceding the monthly campaign. This variable will allow us to test if the metal bioavailability is impacted by the flow of the principal tributary. This variable is named “mflow5j”

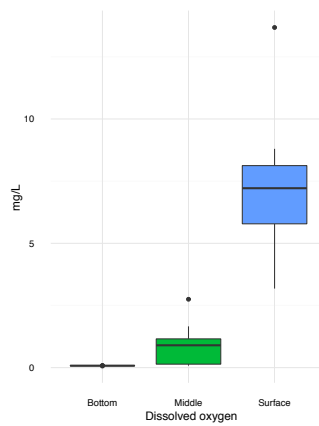


Figure 42 Dissolved oxygen after missing values substitution

The dataset used in the Random Forest modelling contains the following variables: Temperature, Chlorophyll a, conductivity, oxygen, pH, SM, NH₄, total phosphorus, mflow5j.

3.5.4. Parametrization of Random Forest model

Variable importance in the random forest model is estimated according to the methods explained in the chapter “Material and methods”.

The Table 38 shows the most important variables selected by the RF model for each metal labile fraction. Cobalt showed a dependence for the Chla and Oxygen concentration. It corresponds to the Spearman correlation coefficient of cobalt and these variables. Ni and Zn depend strongly on conductivity. Cu and Pb seem to be influenced by the previous day discharge of the tributaries.

Table 38 Selected variables based on variable importance - Pampulha

Labile(%)	Selected variables for final model classed by variable importance				
Co	Chla	Oxygen	pH	NH ₄	Ptot
Ni	Conductivity	Temp	SM	NH ₄	Ptot
Cu	SM	mflow5j	Conductivity	Chla	Temp
Zn	Conductivity	Oxygen	SM	Chla	Temp
Pb	Oxygen	mflow5j	Conductivity	Chla	NH ₄

3.5.5. Results of the Random Forest modelling

The shows the parameters used for the selected variables in the Random Forest model and the average R² of the model. The random forest model is applied for all metals using 85 % of dataset for training and 15% for validation. The model is applied for 1000 trees with different parameters (nvar, mtry, node size) depending on each metal. For the detailed explanation on the RF model parameters, see in the Material and Methods chapter. The cross validation is based on the Monte Carlo cross-validation method (Mercier et al., 2011): for each permutation, the subset of training and validation data is randomly generated.

The Random Forest model uses the selected variables (Table 39) to predict the labile fraction of metals. The accuracy of the model is best for cobalt with (R² = 0.86). It is similar for other metals (R² = 0.24 – 0.29). The model can explain 86% of the variance of cobalt labile fraction using the selected variables: Chla, Oxygen, pH, NH₄ and Ptot.

Table 39 Parametrization and results of random forest model on the labile fraction of metals

% labile	Training (%)	nvar	mtry	node size	ntree	n permutation	Rfit	mean R2
Co	85	9	3	2	1000	1000	0.97	0.86
Ni	85	9	2	2	1000	1000	0.91	0.29
Cu	85	9	5	4	1000	1000	0.89	0.25
Zn	85	9	4	2	1000	1000	0.90	0.27
Pb	85	9	5	4	1000	1000	0.91	0.24

The relationship between the selected variables and the predicted variable (the fraction of labile metal) is illustrated using the partial dependence plot (Figure 43). Among the selected variables, the marginal effect of chlorophyll a and oxygen shows a threshold effect.

The percent of labile Co decreases with the chlorophyll a concentration. For chlorophyll a concentration higher than 40 µg/L, the percent of labile Co decreases strongly (~20%). We can suggest that at the bottom of the lake where Chlorophyll concentration are lower, the cobalt is more bioavailable contrary to the surface, where Co is less bioavailable due to an active phytoplankton development.

For oxygen, the threshold is more pronounced. The percent of labile Co decreases strongly when oxygen become more available. We can suggest that under the anoxic condition, cobalt is more labile at the lake bottom. This trend is consistent with the marginal effect of Chla on cobalt.

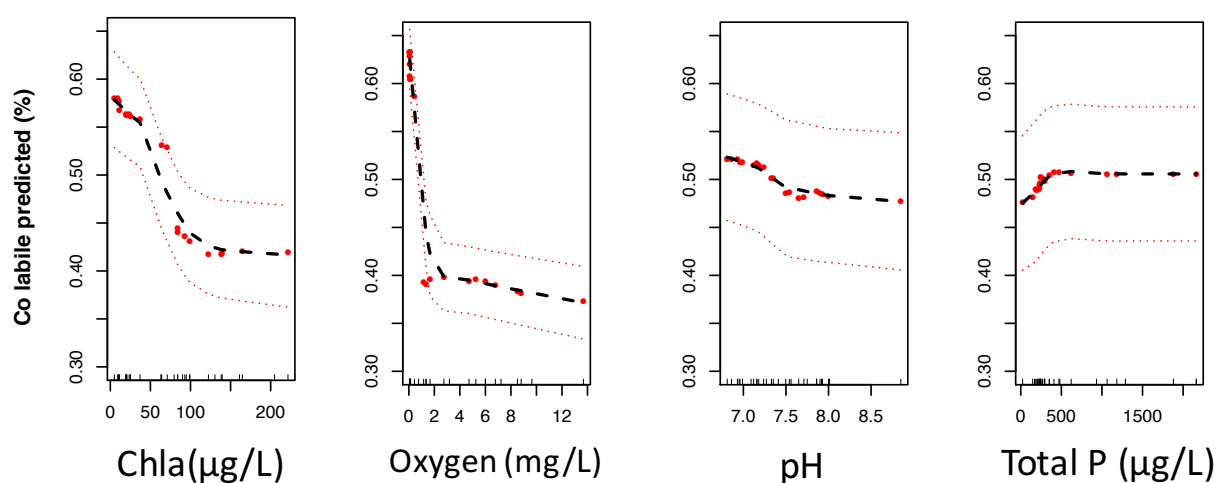


Figure 43 The marginal effect of the variables on the percent of labile cobalt

3.6. Conclusion

In this section, we investigated the speciation of trace metals in the water column of Lake Pampulha, Brazil. We also tried to understand the longitudinal transfer of trace metals within the lake and to assess the contribution of trace metals by the lake tributaries during the dry period by punctual sampling and during a 24h automatic sampling during. The speciation of trace metals gives information on the potential bioavailability of metals. Our results showed that trace metal speciation and the pattern of distribution of each metal in the water column are influenced by various

environmental factors. Under anoxic conditions and high Fe and Mn concentrations, chromium is more particulate than dissolved and thus less bioavailable. Total concentration of cadmium is low in the water column, often under quantification limit. At 7m depth, we found some high concentrations for the campaign 21/11/2012 (0.032µg/L) and the campaign 31/01/2013 (0.025µg/L). Cobalt may be adsorbed by carbonate, hydroxide or oxide minerals, humic substances, and organic matter present in water. An acid pH favors cobalt in form of free ions. On 26/02/2013, high free cobalt ion can be explained by the high chlorophyll-a concentration, which indicates an active photosynthesis activity with a consequence of an increasing pH (8,85). Nickel is the most stable and seems not to be influenced by any environmental factors in the water column. The ratio of dissolved to total metal of copper and zinc have similar values. Copper is more inert at the surface and at the bottom of the point P2. Zinc is less inert than copper. Regarding the metal concentrations in the lake, they are higher in the inlet area of the lake and the concentrations decreased toward the outlet. During the dry period, the same order of magnitude of the concentrations is measured in the tributaries and in the lake. The 24h sampling showed that during some periods of the day, the concentrations are highest. Trace metals have been largely studied in Lake Pampulha but mainly in sediment. And no information about the speciation of trace metals in the water column was available until now. Our speciation results constitute interesting information for the water authorities to maintain or improve the water quality of the lake.

4. Results on Lake Créteil

Lake Créteil is the reference site of the PULSE project aimed at assessing the ecological and sanitary state of a representative panel of urban lakes in the Ile-de-France region. An innovative aspect of the 3-year survey of Lake Créteil to perform an intense monitoring of a reference lake to better understand the signification of inter-lake variability at the regional level, regarding physical, chemical and biological parameters.

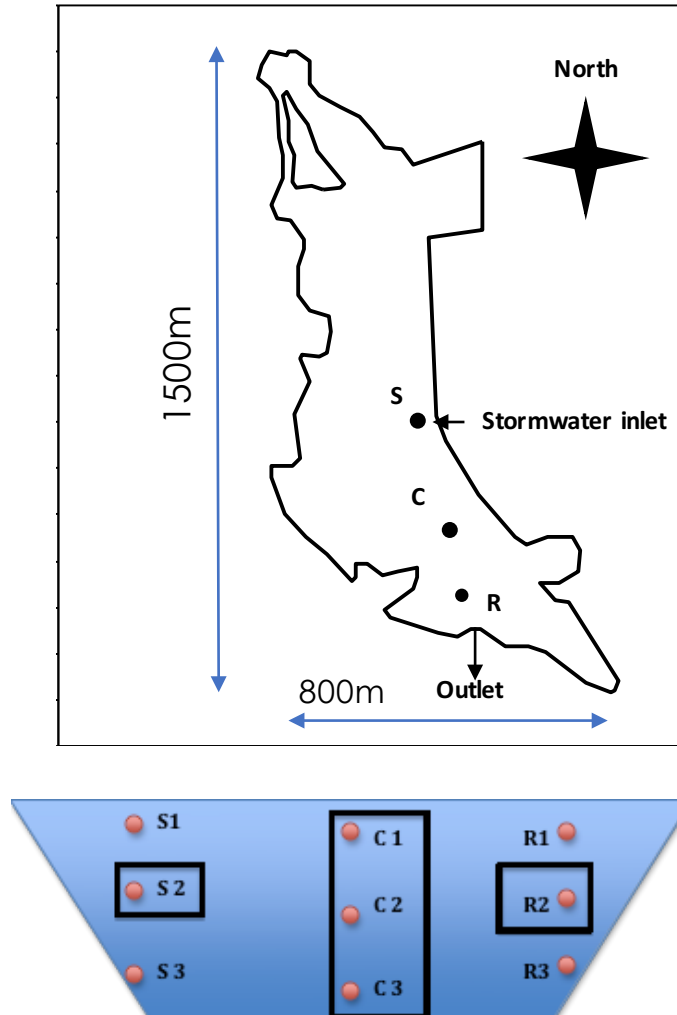


Figure 44 Map of Lake Créteil (redrawn from Soullignac et al., 2017) and location of monitoring points

4.1. Seasonal lake functioning

Firstly, before looking at the trace metal concentrations and their speciation in the water column, it is primordial to present a descriptive analysis of the limnological functioning because it will help us to better understand the behavior of these metals in the water column.

4.1.1. The dataset of Lake Créteil

The monitoring was carried out from 2011 to 2013. As the data collection was performed in the framework of different workpackages of the project, data are missing for some dates: campaigns of August 2011, 2012 and 2013³. The results of the laboratory analysis of organic carbon from July 2013 to December 2013 were lost.

4.1.2. Water temperature evolution

In the next paragraphs, two types of plots of the monitoring parameters will be presented :

- Vertical profile at the central point C at 3 depths : C1 (surface), C2 (middle) and C3 (bottom)
- Horizontal transect at the middle of the water column: S2 (stormwater inlet), C2 (centre) and R2 (Reedbed)

The evolution of the water temperature at the point C from December 2011 to November 2013 is shown in Figure 45. The water temperature varies from 1.41°C to 23.85 °C.. The thermal stratification lasts from March to October in 2012 and 2013. During the stratification period, the difference of water temperature between the surface (C1) and the bottom (C3) can be up to 2.26 °C in 2012 and 4.61 °C in 2013.

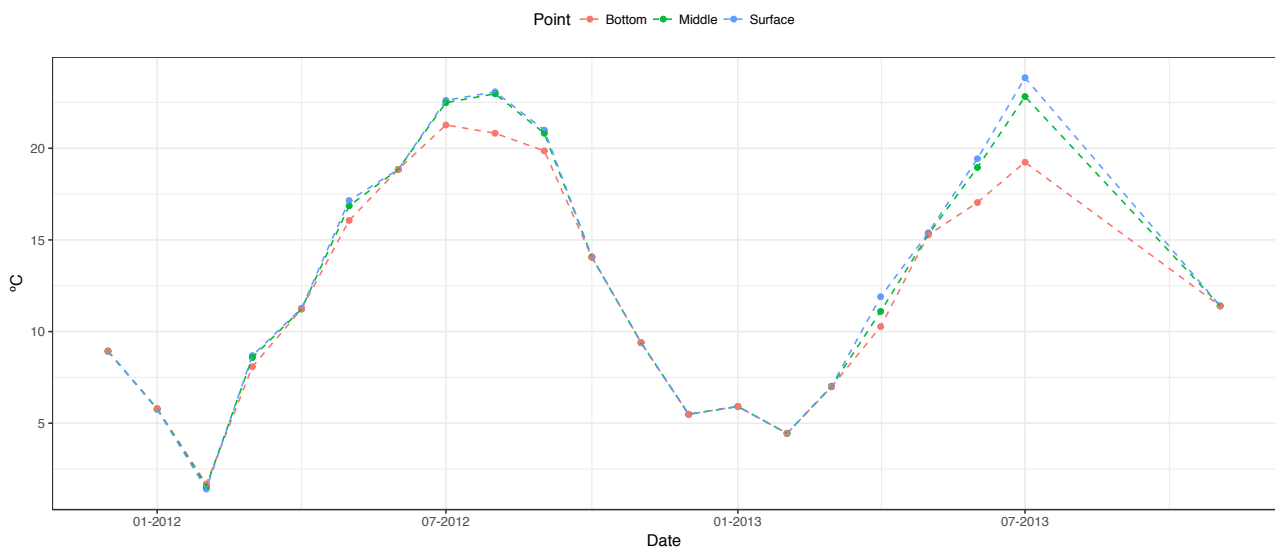


Figure 45 Evolution of the water temperature at 3 depths (surface, middle and bottom) of the point C

The horizontal evolution of the water temperature at the points S2, C2 and R2 from December 2011 to November 2013 is shown in Figure 46. At the time scale of the observations, there is almost no difference of the water temperature in the middle of water column except for March – April and

³ The monthly monitoring campaigns of August 2011-2013 took place at the same time of the campaigns for PULSE 49 lakes. The BBE probe's measurements were carried out by the MNHN research group. These data are still missing.

August – September 2012 and from March to November 2013. However, the temperature difference is very small: lower than 1 °C in 2012 and 2013.

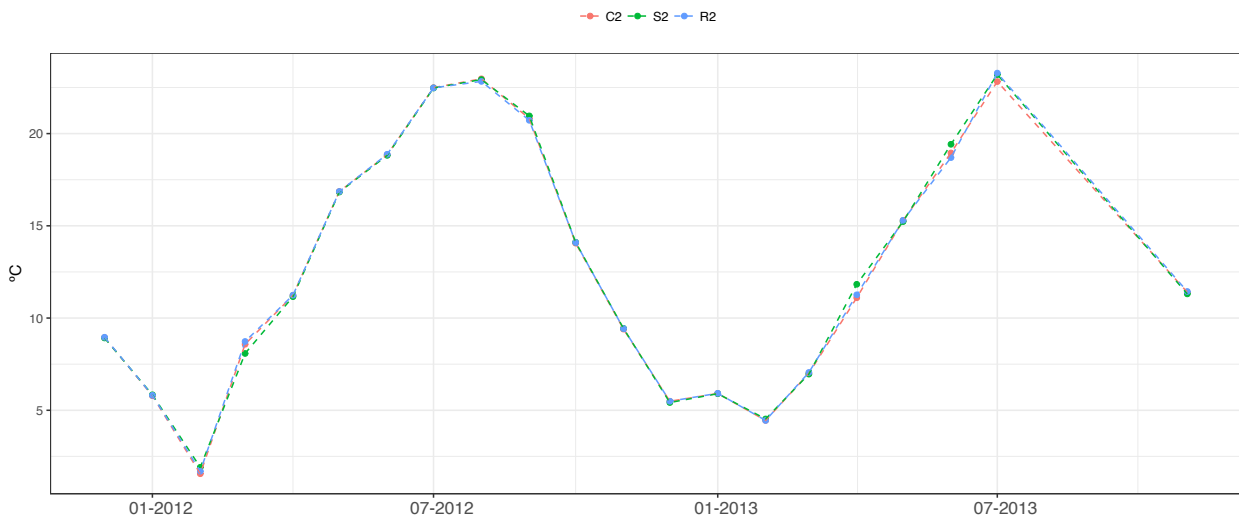


Figure 46 Evolution of water temperature at the middle of the water column S2, C2, R2

4.1.3. Chlorophyll-a concentration

The chlorophyll-a concentrations in 2011-2013 are presented in Figure 47 for the vertical profiles and in Figure 48 for the horizontal variations. The total chlorophyll-a concentrations vary from 1.1 µg/L to 22.5 µg/L.

The chlorophyll-a concentrations fluctuate with time and vary with the depth. The maximum concentration, 22.5 µg/L, is observed in February 2013. The difference of chlorophyll-a concentration can be up to 6 µg/L between the surface and the bottom.

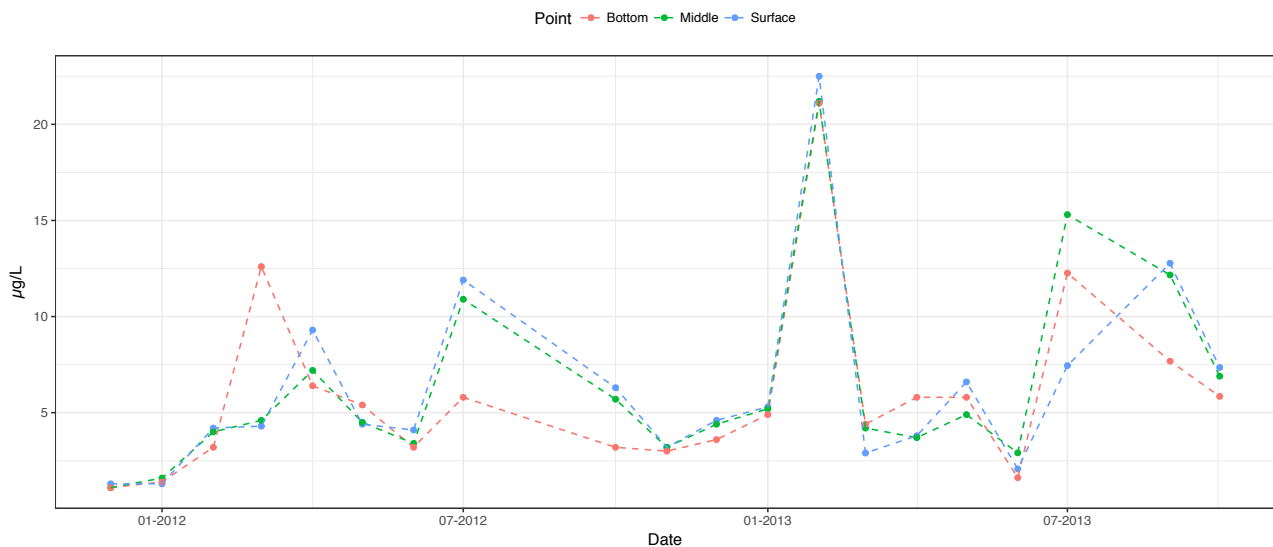


Figure 47 Evolution of chlorophyll-a concentration at surface, middle and bottom of the point C

The horizontal variations of the chlorophyll-a concentrations are very low at points S2 and C2. At point R2, chlorophyll-a concentrations are slightly different than at points S2 and C2. The 2013 February maximum of chlorophyll-a is also observed at the points S2 and R2.

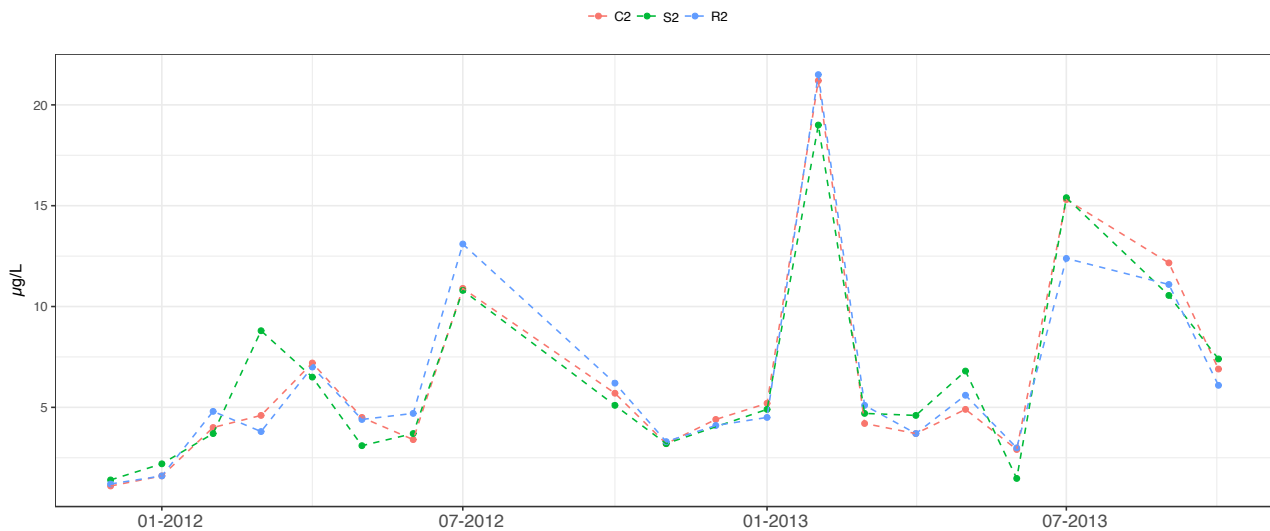


Figure 48 Evolution of chlorophyll-a concentration at the points S2, C2, R2

4.1.4. Other physical chemical parameters

The distribution of other physical chemical parameters such as Oxygen, pH, Conductivity, suspended matter (SM)... are presented in Figure 49, Figure 50.

Oxygen concentration, at the point C, varies strongly at the bottom (C3) from 0.32 mg/L to 17.19 mg/L with a mean concentration at 7.50 mg/L. The mean oxygen concentrations are 9.31 mg/L at C2 and 9.11 mg/L at C1. The highest oxygen concentrations are found during the winter months (December to March). However, the difference of oxygen concentrations at C1, C2 and C3 are not statistically significant ($p > 0.05$). At the points S2, C2, R2, the spatial variation is very low. No statistical difference is observed.

At the point C, pH remains unchanged between 3 depths with a mean values around 7.9.

The conductivity is very high in Lake Créteil, median value of $1100 \mu\text{S}/\text{cm}$, due to the geological background. Conductivity variation appears to be stronger at the surface. The suspended matter variation is stronger at the surface, but the mean values at the three depths are not significantly different. At points S2, C2 and R2, pH variation is less important at point S2 with 1st percentile at 7.7 and 3rd percentile at 8.4 while 1st percentile is around 7.0 and 3rd percentile is around 8.3 at C2 and R2. The suspended matter is higher at point C2 in comparison of S2 and R2. There are no significant difference for these variables ($p > 0.05$)

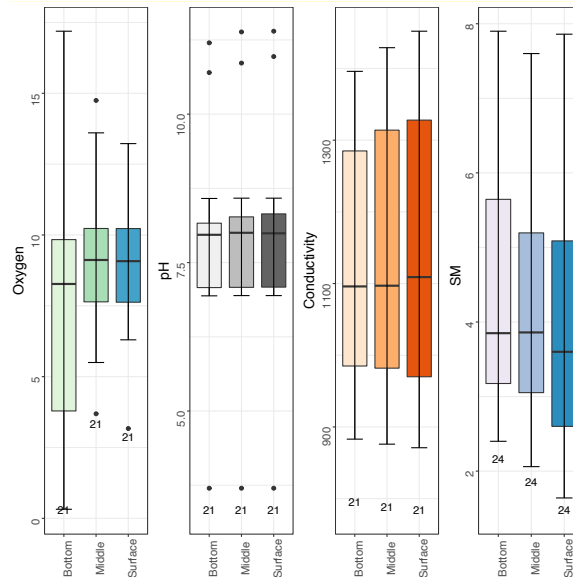


Figure 49 Boxplot of Oxygen, pH, Conductivity and SM at the point C1, C2, C3

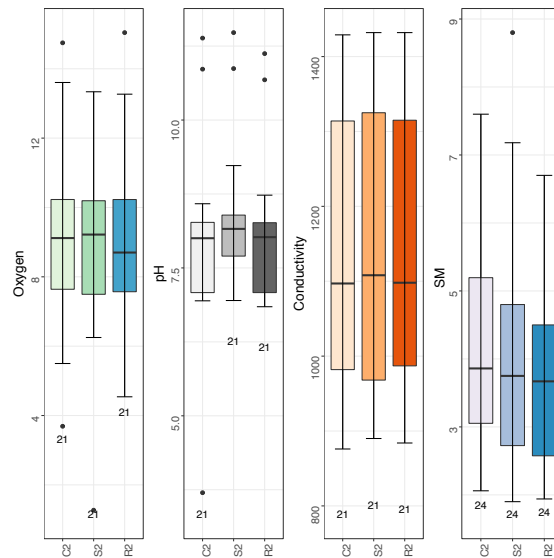


Figure 50 Boxplot of Oxygen, pH, Conductivity and SM at the point S2, C2, R2

4.2. Trace metals speciation in Lake Créteil

In this paragraph, we present the trace metals concentrations and their speciation in Lake Créteil. At first, we present the results of the Wilcoxon Mann Whitney test for the comparison of the average values of the vertical profile (C1,C2,C3) and between the points (S2,C2,R2)

The p-values of the Wilcoxon Mann Whitney test for the vertical profiles are indicated in Table 40 and for the three points in Table 41. For the whole period, no significant differences were observed between depths at point C neither between points S2, C2 and R2. Only the labile Cu concentration is statistically different between S2, C2 and R2.

Table 40 p-values for the comparison of mean metal concentrations (total, dissolved and labile) at point C1, C2 and C3 (threshold 5%)

	Total		Dissolved		Labile	
	C1 vs C2	C2 vs C3	C1 vs C2	C2 vs C3	C1 vs C2	C2 vs C3
Cr	0.63	0.72	0.56	0.34	0.39	-
Co	0.86	0.5	0.83	0.75	0.28	0.71
Ni	0.87	0.9	0.39	0.57	0.4	0.29
Cu	0.60	0.72	0.8	0.30	0.78	0.17
Zn	0.45	0.84	0.86	0.78	0.69	0.38
Pb	0.91	0.41	0.75	0.21	0.89	0.2

Table 41 p-values for the comparison of mean metal concentrations (total, dissolved and labile) at point S2, C2 and R2 (threshold 5%)

	Total		Dissolved		Labile	
	S2 vs C2	C2 vs R2	S2 vs C2	C2 vs R2	S2 vs C2	C2 vs R2
Cr	0.82	0.88	0.81	0.55	-	-
Co	0.99	0.79	0.97	0.57	0.18	0.89
Ni	0.56	0.89	0.39	0.53	0.8	0.32
Cu	0.59	0.75	0.47	0.49	0.05	0.09
Zn	0.38	0.05	0.22	0.56	0.21	0.48
Pb	0.79	0.33	0.73	0.18	0.69	0.14

According to the variation of the physical-chemical and biological parameters, we decided to separate the dataset into 2 periods: Period 1, Summer-Autumn, from May to October and Period 2, Winter-Spring, from November to April. The p-values are indicated for the points C1, C2, C3 during period 1 in Table 42 and during period 2 in Table 44, for the points S2, C2, R2 during period 1 in Table 43, for the point C2, S2, R2 during period2 in Table 45.

By separating into 2 periods, total and labile Cu and total Zn concentrations are statistically different between P2 and C2 in Summer-Autumn period(Period 1). We also found total Zn concentrations are statistically different between respectively C1 and C2 ; C2 and R2.

Table 42 p-values for the comparison of mean metal concentrations (total, dissolved and labile) at point C1, C2 and C3 during period 1 (threshold 5%)

	Total		Dissolved		Labile	
	C1 vs C2	C2 vs C3	C1 vs C2	C2 vs C3	C1 vs C2	C2 vs C3
Cr	0.98	0.62	0.59	0.65	-	-
Co	0.9	0.33	0.83	0.64	0.63	0.61
Ni	0.73	0.88	0.39	0.61	0.37	0.4
Cu	0.25	0.51	0.98	0.56	0.78	0.39
Zn	0.2	0.55	0.66	0.6	0.73	0.15
Pb	0.76	0.4	0.61	0.32	0.96	0.29

Table 43 p-values for the comparison of mean metal concentrations (total, dissolved and labile) at point S2, C2 and R2 during period 1 (threshold 5%)

	Total		Dissolved		Labile	
	S2 vs C2	C2 vs R2	S2 vs C2	C2 vs R2	S2 vs C2	C2 vs R2
Cr	0.76	0.87	0.89	0.64	-	-
Co	0.73	0.81	0.92	0.51	0.15	0.51
Ni	0.83	0.86	0.4	0.4	0.74	0.23
Cu	0.03	0.94	0.59	0.67	0.06	0.18
Zn	0.01	0.99	0.26	0.98	0.32	0.95
Pb	0.84	0.67	0.62	0.2	0.46	0.28

Table 44 p-values for the comparison of mean metal concentrations (total, dissolved and labile) at point C1, C2 and C3 during period 2 (threshold 5%)

	Total		Dissolved		Labile	
	C1 vs C2	C2 vs C3	C1 vs C2	C2 vs C3	C1 vs C2	C2 vs C3
Cr	0.5	1	0.54	0.08	-	-
Co	0.68	0.96	0.97	0.94	0.3	0.94
Ni	0.55	1	0.68	0.75	0.98	0.46
Cu	0.55	0.33	0.34	0.32	0.82	0.31
Zn	0.09	0.52	0.67	0.8	0.29	0.84
Pb	0.47	0.93	0.79	0.46	0.92	0.51

Table 45 p-values for the comparison of mean metal concentrations (total, dissolved and labile) at point S2, C2 and R2 during period 2 (threshold 5%)

	Total		Dissolved		Labile	
	S2 vs C2	C2 vs R2	S2 vs C2	C2 vs R2	S2 vs C2	C2 vs R2
Cr	1	0.96	0.53	0.34	-	-
Co	0.77	0.53	0.81	0.99	0.73	0.64
Ni	0.55	0.69	0.79	0.75	0.75	0.73
Cu	0.51	0.75	0.19	0.19	0.41	0.36
Zn	0.56	0.03	0.58	0.21	0.47	0.24
Pb	0.47	0.26	0.93	0.65	0.83	0.34

4.2.1. Total, dissolved and labile concentrations of trace metals in Lake Créteil

In this paragraph, we will present the distribution of metal concentrations (total, dissolved and labile) and compare these ranges at points C1, C2, C3, S2 and R2.

The total and dissolved Cr concentrations are presented in Figure 51. Cr is found in the water column principally in particulate forms. The median of total Cr concentration is higher at C1 than at other points.

As mentioned in the precedent chapter Results on Lake Pampulha, we compare the metal concentrations with the European environmental quality standards (EQS) of the Water Framework Directive 2008/105/CE, EU WFD which is presented in Table 29.

The total and dissolved Cr concentrations are presented in Figure 51. Cr is mainly particulate in the water column. The median of Cr total concentration is higher at C1 than at other points

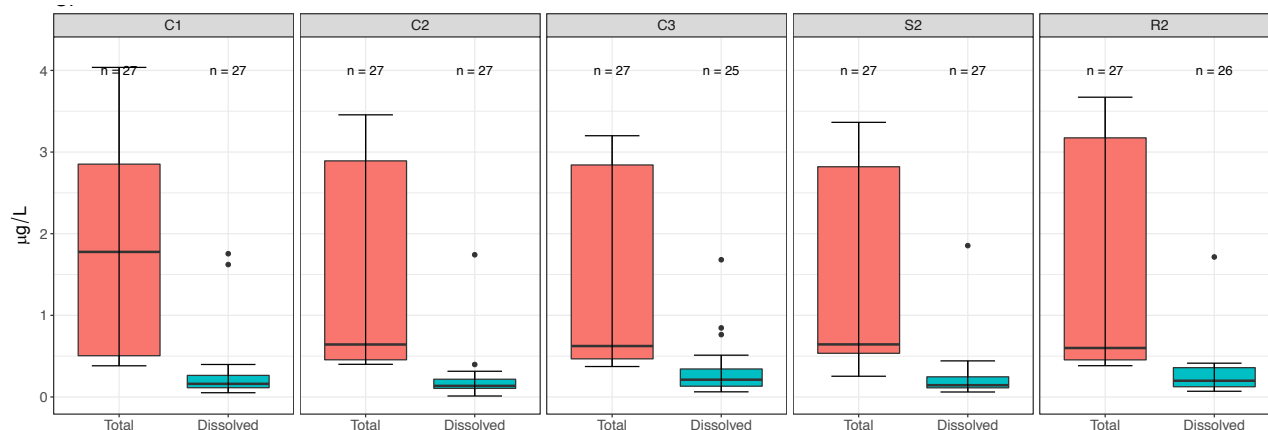


Figure 51 Boxplot of total and dissolved Cr concentrations at points C1, C2, C3, S2 and R2

The total, dissolved and labile Co concentrations are presented in Figure 52. Co is highly dissolved in the water column. Its total concentration variation seems to be stronger at the point C1 and S2. Its dissolved concentrations are lower at points S2 and R2. The median values remain the same at all points.

Regarding the environmental quality standards (EQS), no value exceeds the standard value which is 3.4 µg/L.

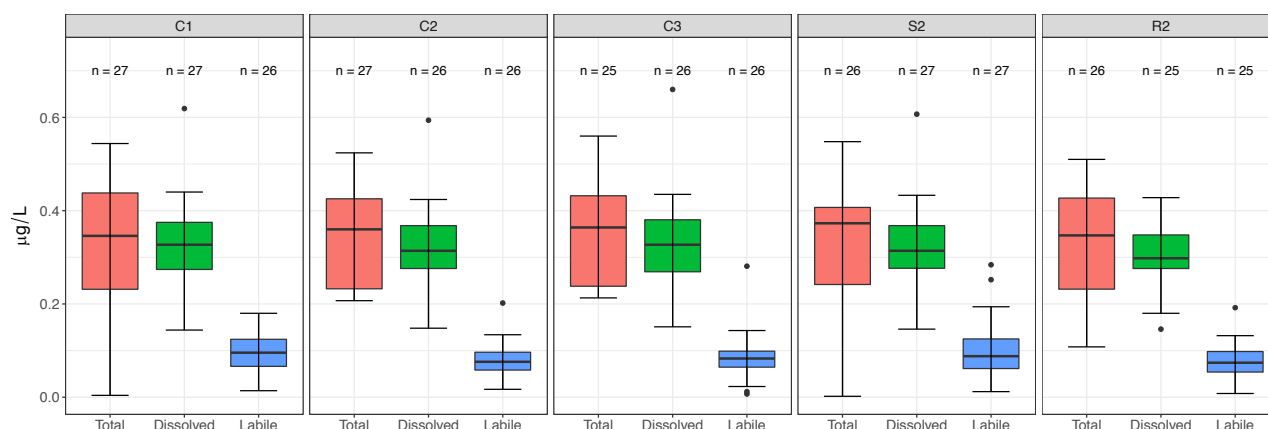


Figure 52 Boxplot of total, dissolved and labile Co concentrations at points C1, C2, C3, S2 and R2

The total, dissolved and labile Ni concentrations are presented in Figure 53. Ni is highly dissolved in the water column. The variation of the concentrations of total Ni is more important at the surface at point C (C1). For the other points, these variations are weak. The concentrations of dissolved and labile Ni remain similar at points C1, C2, C3, S2 and R2. There is no statistical difference of mean values between these points.

Comparing to the EQS, over the total 27 measured concentrations, 22 values for the point C1 and 24 values for the other points of dissolved Co concentrations exceed the EQS which is 4µg/L. It represents respectively 82% and 88% of total values.

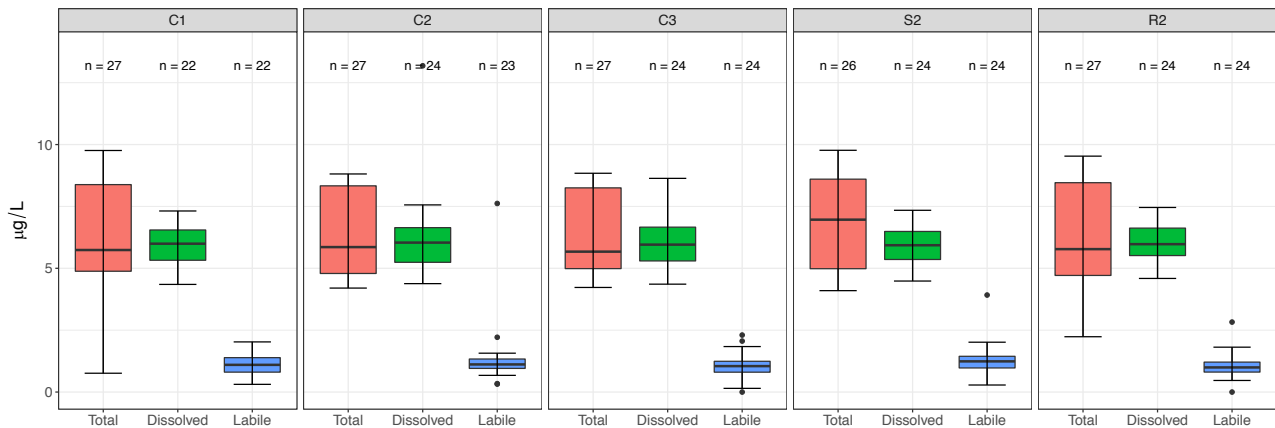


Figure 53 Boxplot of total, dissolved and labile Co concentrations at points C1, C2, C3, S2 and R2

The total, dissolved and labile Cu concentrations are presented in Figure 54. Cu has the same distribution comparing to Ni. It is highly dissolved. The variation of the concentrations of total Cu is important at point C1. The differences comparing to Ni are as follows: the labile Ni varies widely at point S2 and many outliers points are found at points C3 and S2.

Comparing to the EQS, which is 1.4µg/L for Cu, over the total 27 measured concentrations, the points C1, C2, C3 have similar exceedance of EQS which ranges between 77 and 85%. At point S2 only 2 values are lower than the EQS (95% exceedance). At point R2 67% of the values exceed the EQS.

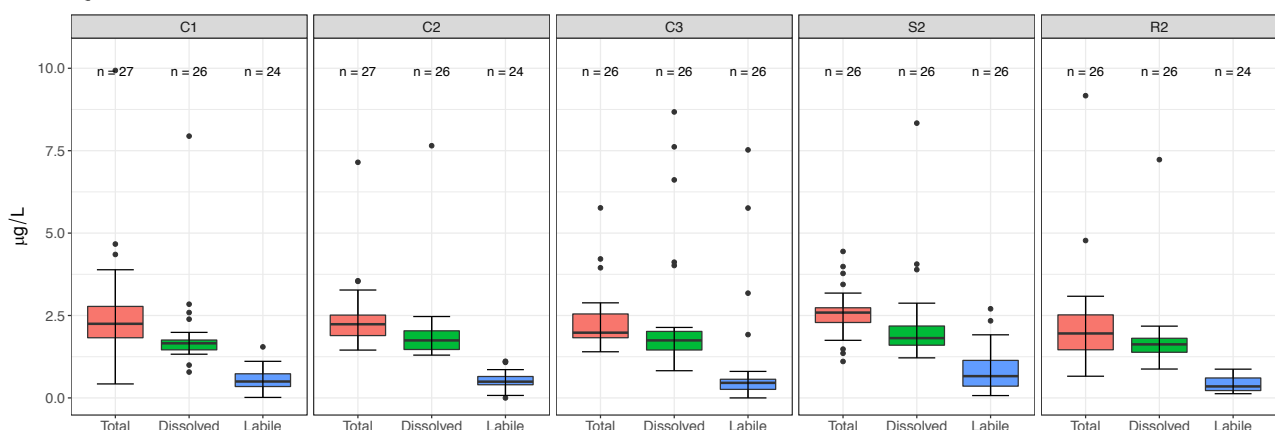


Figure 54 Boxplot of total, dissolved and labile Cu concentrations at points C1, C2, C3, S2 and R2

The total, dissolved and labile Zn concentrations are presented in Figure 55. Zn is highly dissolved in the water column. The variation of the concentration of dissolved Zn is higher than its total concentration at point C1. The dissolved concentrations higher than the total concentrations correspond to campaigns where the total concentrations are missing.

The EQS value for Zn is 7.8 µg/L. Most of the 27 measured values are lower than EQS. Between 7 and 22% of the values exceed the EQS. Point S2 has more values exceeding the EQS (22%).

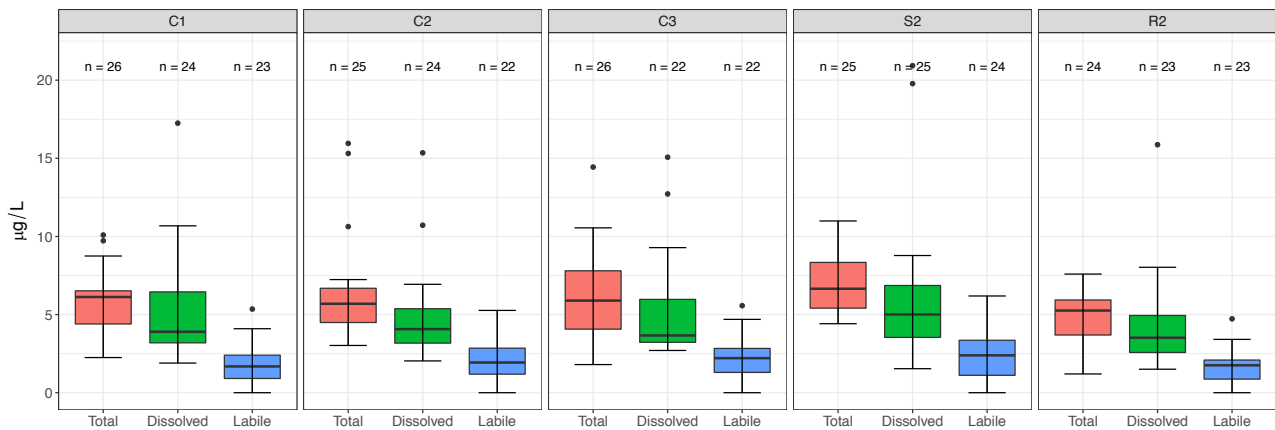


Figure 55 Boxplot of total, dissolved and labile Zn concentrations at points C1, C2, C3, S2 and R2

The total, dissolved and labile Pb concentrations are presented in Figure 56. Pb has the same distribution as Cr. It is highly particulate, thus its labile concentrations are weak. There are no statistical difference between the points.

Regarding the EQS, only one value at point C3 exceeded the norm .

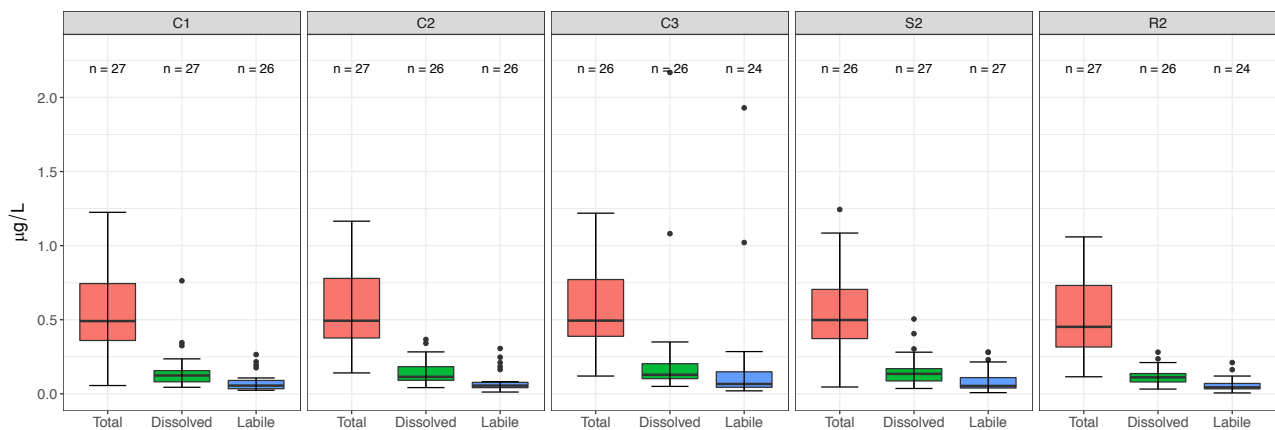


Figure 56 Boxplot of total, dissolved and labile Pb concentrations at points C1, C2, C3, S2 and R2

4.2.2. Trace metal speciation in the water column

In this paragraph, we will present the distribution of total, dissolved and labile concentrations in the water column at three depths at point C and in the middle of the water column of points S, C and R.

The average ratios of the dissolved to total fractions at point C at the three depths during 27 monthly campaigns from 2011 to 2013 are presented in Table 46 and Figure 57 (left). The average

ratios of the dissolved to total fractions in the middle of the water column at points S, C, R are presented in Table 47 and Figure 58 (left).

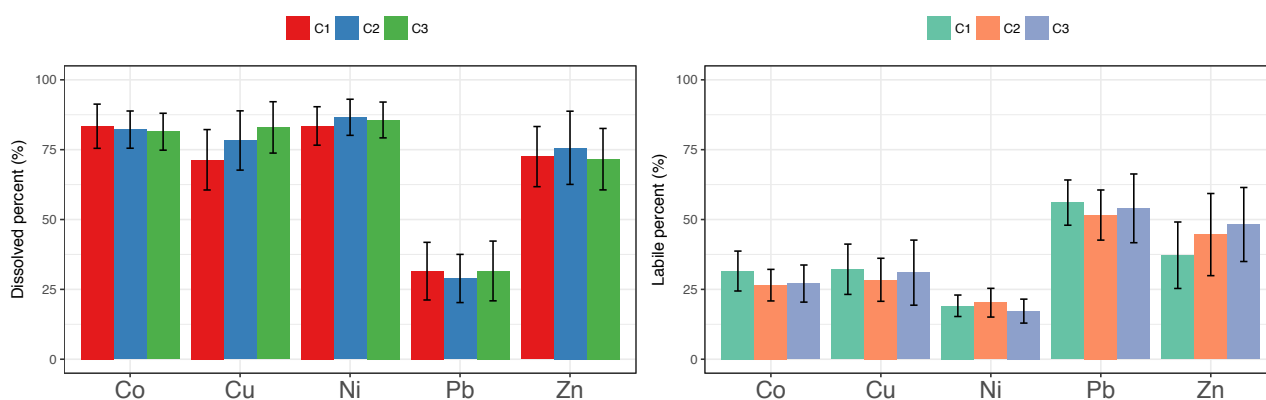


Figure 57(Left) Dissolved percent and (Right) labile percent of metal concentrations at C1, C2,C3

Table 46 Mean ratio of dissolved to total metals at three depths at the point C

Mean ratio Dissolved/Total	Cr (%)	Co (%)	Ni (%)	Cu (%)	Zn (%)	Pb (%)
C1 (0.5m)	24.8 ± 24.0	83.4 ± 15.8	83.5 ± 13.8	71.4 ± 21.6	72.5 ± 21.5	31.5 ± 20.6
C2 (2.5m)	25.5 ± 26.2	82.2 ± 13.3	86.6 ± 12.9	78.3 ± 21.2	75.7 ± 26.2	28.9 ± 17.3
C3 (4.5m)	32.4 ± 27.9	81.4 ± 13.2	85.6 ± 12.8	83.0 ± 18.4	71.6 ± 22.0	31.6 ± 21.4

Table 47 Mean ratio of dissolved to total metals in the middle of the water column at points S, C and R

Mean ratio Dissolved/Total	Cr (%)	Co (%)	Ni (%)	Cu (%)	Zn (%)	Pb (%)
C2	25.5 ± 26.2	82.2 ± 13.3	86.6 ± 12.9	78.3 ± 21.2	75.7 ± 26.2	28.9 ± 17.3
S2	30.4 ± 29.3	80.7 ± 14.9	81.8 ± 14.0	77.8 ± 17.4	72.5 ± 22.6	30.9 ± 20.0
R2	28.4 ± 25.6	81.6 ± 13.5	85.6 ± 14.2	75.1 ± 25.0	74.3 ± 23.5	28.5 ± 16.0

In the water column of Lake Créteil, the average ratios of dissolved to total concentration are high for Co, Ni, Cu and Zn. They are respectively around 80%, 85%, 70% and 75% for Co, Ni, Cu, and Zn. There is no significant difference of this ratio for both horizontal and vertical distribution (pvalue > 0.05). Pb is more particulate in the water column with the dissolved fraction around 30%. The standard deviation of these ratios is lower for Co and Ni, around 10-15% and higher for Cu, Zn and Pb, around 20-25%. The dissolved fraction is higher for Ni, Cu and Zn in Lake Créteil than in Lake Pampulha where it is respectively 60%, 35% and 40%.

In order to estimate the metal fraction that is potentially bioavailable, we calculated the ratio of labile to dissolved fraction. These average ratios at point C at the three depths during 27 monthly campaigns from 2011 to 2013 are presented in Table 48 and Figure 57 (right). The average ratios of labile to dissolved fractions in the middle of the water column at points S, C, R are presented in Table 49 and Figure 58 (right).

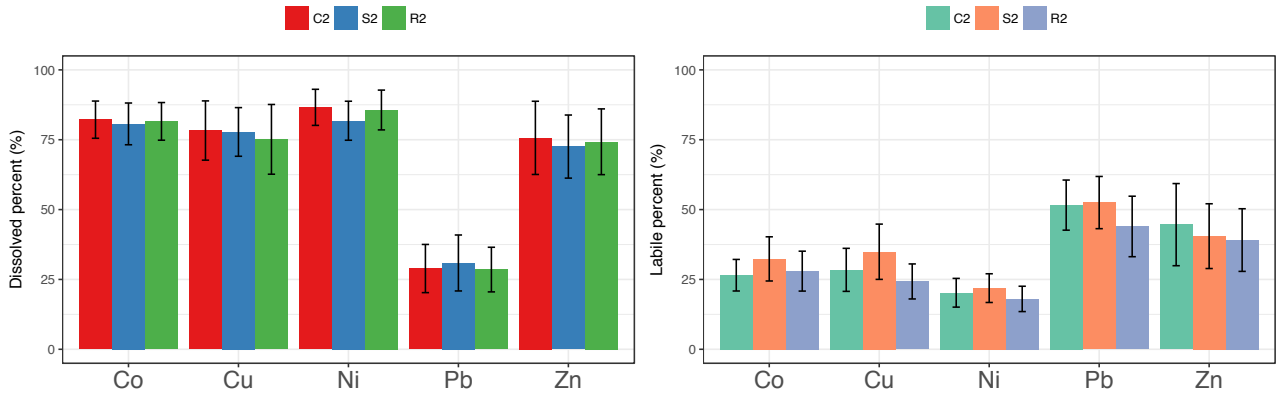


Figure 58 (Left) Dissolved percent and (Right) labile percent of metal concentrations at C2, S2,R2

Table 48 Mean ratio of labile to dissolved metals at three depths of the point C

Mean ratio Labile/Dissolved	Cr (%)	Co (%)	Ni (%)	Cu (%)	Zn (%)	Pb (%)
C1 (0.5m)	NA	31.6 ± 14.3	19.1 ± 7.7	32.1 ± 18.1	37.2 ± 23.9	56.1 ± 16.2
C2 (2.5m)	NA	26.5 ± 11.3	20.2 ± 10.3	28.4 ± 15.4	44.6 ± 29.4	51.6 ± 17.9
C3 (4.5m)	NA	27.1 ± 13.3	17.2 ± 8.6	31.0 ± 23.3	47.8 ± 27.4	54.0 ± 24.7

Table 49 Mean ratio of labile to dissolved metals in the middle of the water column at points S, C and R

Mean ratio Labile/Dissolved	Cr (%)	Co (%)	Ni (%)	Cu (%)	Zn (%)	Pb (%)
S2	NA	32.3 ± 15.8	21.9 ± 10.3	34.9 ± 19.8	40.5 ± 23.2	52.5 ± 18.7
C2	NA	26.5 ± 11.3	20.2 ± 10.3	28.4 ± 15.4	44.6 ± 29.4	51.6 ± 17.9
R2	NA	28.0 ± 14.3	18.0 ± 9.2	24.3 ± 12.6	39.1 ± 22.4	44.0 ± 21.7

The labile fraction is relatively low for Co, Ni and Cu, between 17 and 35%. It is slightly higher for Zn, around 40 % and higher for Pb, around 50%. There is no significant difference in both vertical and horizontal distribution. However, it seems that Co is more labile at the surface and Zn more labile at the middle and bottom of the water column. The labile fraction remains similar for Ni, Cu and Pb. Zn has a strong standard deviation in both horizontal and vertical distribution. Pb has more variation at the bottom. Its variation remains similar at the middle of water column.

4.2.3. Seasonal variation of trace metal

In this paragraph, we present the evolution of the concentrations of total, dissolved and labile metals along the horizontal transect S2, C2, R2 and the vertical profile C1, C2, C3. The evolution of these concentrations is presented as bar chart figures.

We will comment whether the metal concentrations present a seasonal variation in their total, dissolved and labile concentration and the differences between 2012 and 2013. In this paragraph, we do not compare the concentrations between the points.

4.2.3.1. Chromium

For Chromium, we only present the temporal evolution of total and dissolved concentrations of Cr at the vertical profile C1, C2 and C3 in Figure 59 and at the horizontal transect S2, C2 and R2 in Figure 60.

At the vertical profile C1, C2 and C3, the total Cr is under 1 µg/L during the 2012 while its concentration is higher up to 3.5µg/L during the 2013. The dissolved concentration is weak during all period. Except the difference between the 2012 and 2013, no seasonal variation is observed.

At the horizontal transect S2, C2, and R2, the same observation was noted as at the vertical profile.



Figure 59 Total and dissolved concentration of Cr at the points C1, C2, C3 of Lake Créteil. The dissolved concentration is in red. The total concentration corresponds to the red + blue bar.



Figure 60 Total and dissolved concentration of Cr at the points S2, C2, R2 of Lake Créteil

4.2.3.2. Cadmium

The temporal evolution of total, dissolved and labile concentrations of Cd at the vertical profile C1, C2 and C3 is presented in Figure 61 and at the horizontal transect S2, C2 and R2 in Figure 62. Total concentration of cadmium is lower than 0.05 µg/L in the water column except in August 2013. It seems that Cd concentrations are higher in 2013 than 2012.



Figure 61 Total, dissolved and labile concentration of Cd at the points C1, C2, C3 of Lake Créteil. The labile concentration is in green. The dissolved concentration is the sum of green and red bars and the total concentration is the sum of the green, red and blue bars

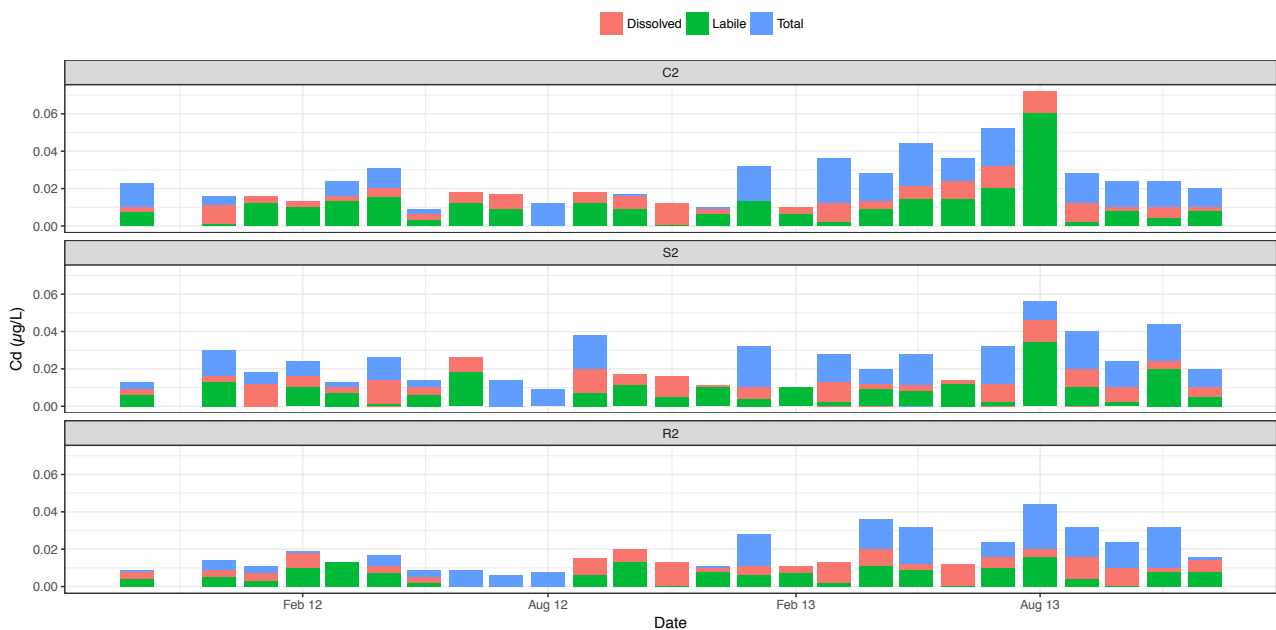


Figure 62 Total, dissolved and labile concentration of Cd at the points C2, S2, R2 of Lake Créteil. The labile concentration is in green. The dissolved concentration is the sum of green and red bars and the total concentration is the sum of the green, red and blue bars.

4.2.3.3. Cobalt

The temporal evolution of total, dissolved and labile concentrations of Co at the vertical profile C1, C2 and C3 is presented in Figure 63 and at the horizontal transect S2, C2 and R2 in Figure 64. At points C1, C2 and C3, the concentrations of total Co were often not validated for the campaigns from June 2012 to February 2013. The concentrations of Co seem to be higher during the spring – summer period.



Figure 63 Total, dissolved and labile concentration of Co at the points C1, C2, C3 of Lake Créteil. The labile concentration is in green. The dissolved concentration is the sum of green and red bars and the total concentration is the sum of the green, red and blue bars.



Figure 64 Total, dissolved and labile concentration of Co at the points S2, C2, R2 of Lake Créteil. The labile concentration is in green. The dissolved concentration is the sum of green and red bars and the total concentration is the sum of the green, red and blue bars.

4.2.3.4. Nickel

The temporal evolution of total, dissolved and labile concentrations of Co at the vertical profile C1, C2 and C3 is presented in Figure 65 and at the horizontal transect S2, C2 and R2 in Figure 66.

The concentration of total Ni is stable. Its concentration is slightly higher in 2013 comparing to 2012. The concentrations of dissolved Ni is high and vary weakly with time. The concentrations of labile Ni remain low except at point C2 in September 2013.

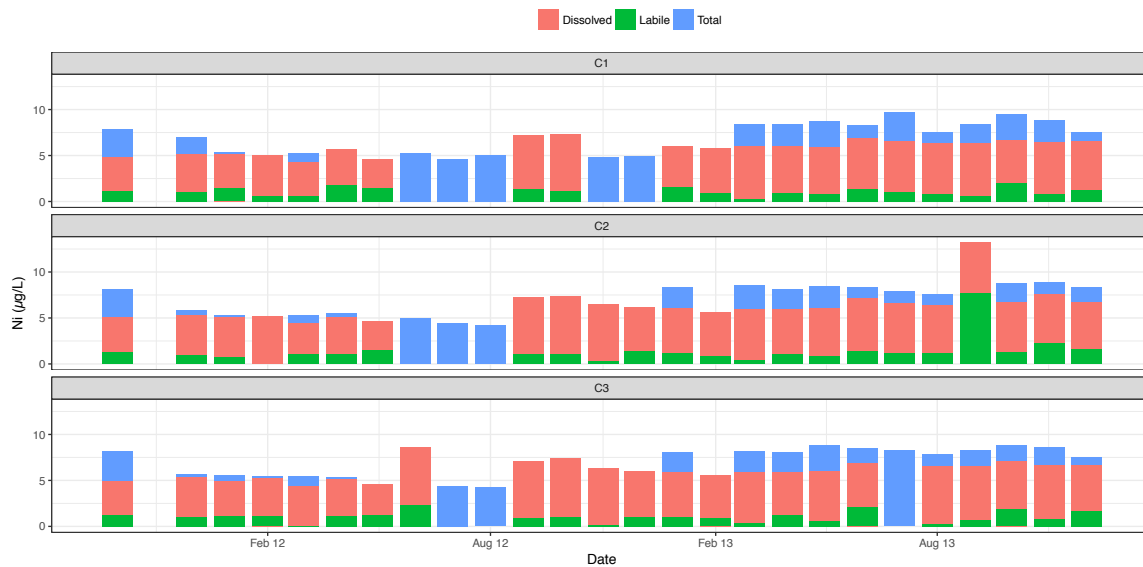


Figure 65 Total, dissolved and labile concentration of Ni at the points C1, C2, C3 of Lake Créteil. . The labile concentration is in green. The dissolved concentration is the sum of green and red bars and the total concentration is the sum of the green, red and blue bars

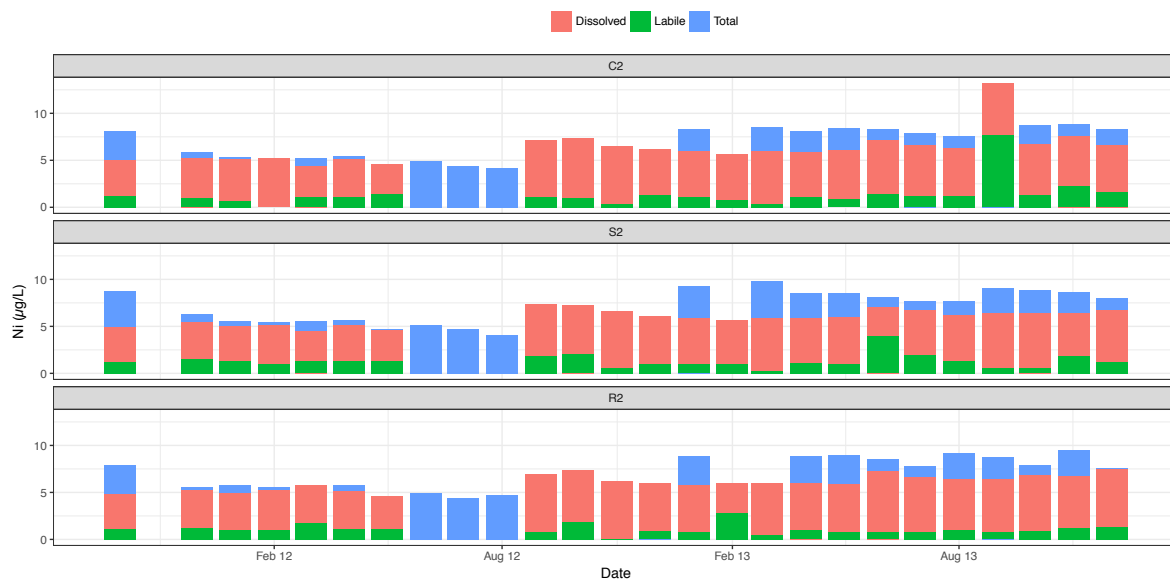


Figure 66 Total, dissolved and labile concentration of Ni at the points S2, C2, R2 of Lake Créteil. . The labile concentration is in green. The dissolved concentration is the sum of green and red bars and the total concentration is the sum of the green, red and blue bars.

4.2.3.5. Copper

The temporal evolution of total, dissolved and labile concentrations of Cu at the vertical profile C1, C2 and C3 is presented in Figure 67 and at the horizontal transect S2, C2 and R2 in Figure 68. For the vertical profile and horizontal transect, the concentrations of total Cu were often not validated for the campaigns from June 2012 to February 2013. The total, dissolved and labile concentrations of Cu do not present any trend except for the peaks of total concentration in March 2012 and April 2013 and the peaks of dissolved concentration at point C3 from October to December 2013.



Figure 67 Total, dissolved and labile concentration of Cu at the points C1, C2, C3 of Lake Créteil. The labile concentration is in green. The dissolved concentration is the sum of green and red bars and the total concentration is the sum of the green, red and blue bars.



Figure 68 Total, dissolved and labile concentration of Cu at the points S2, C2, R2 of Lake Créteil. The labile concentration is in green. The dissolved concentration is the sum of green and red bars and the total concentration is the sum of the green, red and blue bars

4.2.3.6. Zinc

The temporal evolution of total, dissolved and labile concentrations of Zn at the vertical profile C1, C2 and C3 is presented in Figure 69 and at the horizontal transect S2, C2 and R2 in Figure 70. The variation of Zn concentrations is slightly different between the points. However, we observed no seasonal variation of Zn concentrations.

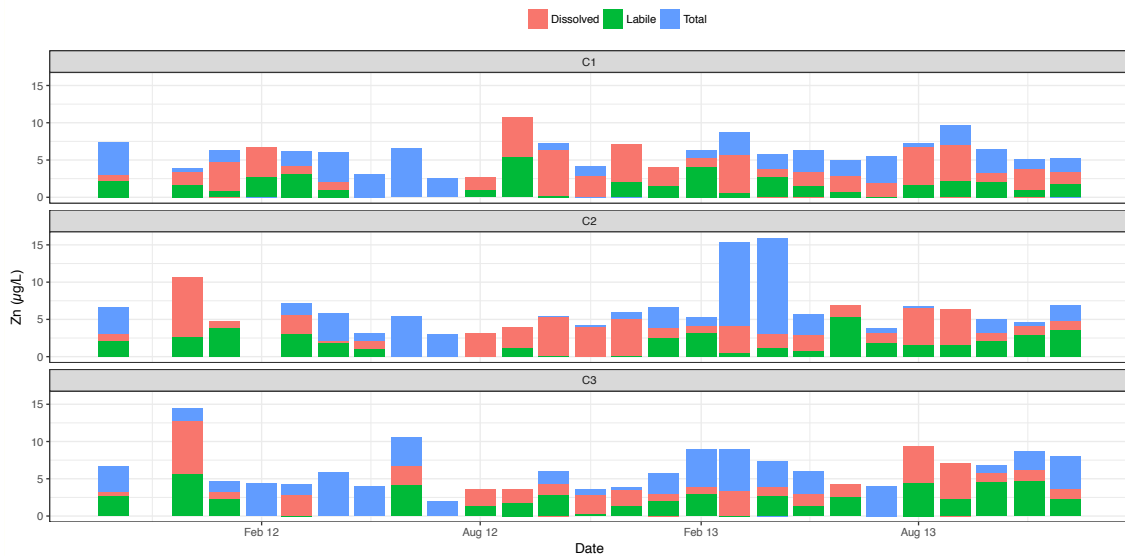


Figure 69 Total, dissolved and labile concentration of Zn at the points C1, C2, C3 of Lake Créteil. The labile concentration is in green. The dissolved concentration is the sum of green and red bars and the total concentration is the sum of the green, red and blue bars.

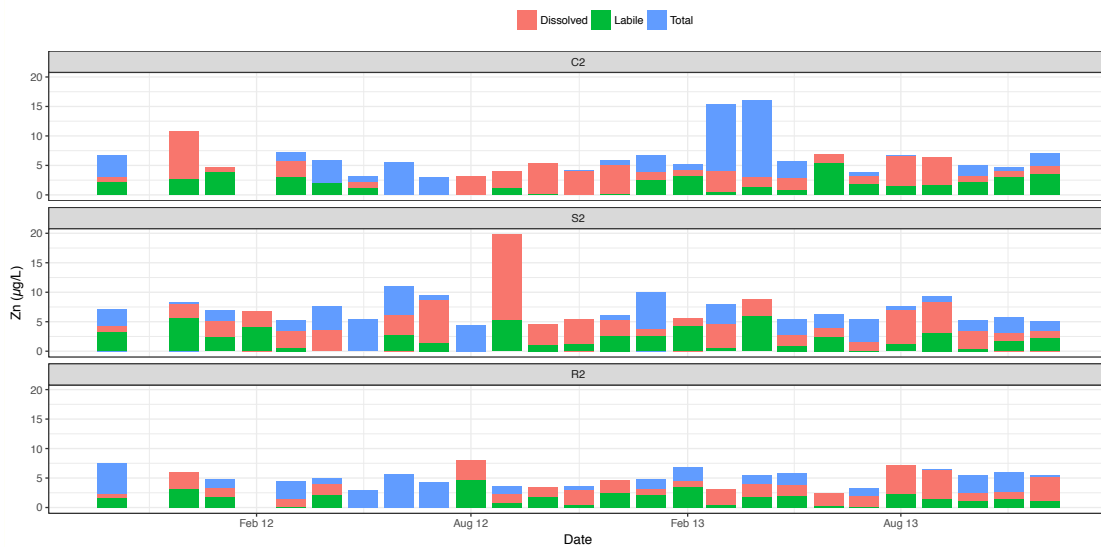


Figure 70 Total, dissolved and labile concentration of Zn at the points S2, C2, R2 of Lake Créteil. The labile concentration is in green. The dissolved concentration is the sum of green and red bars and the total concentration is the sum of the green, red and blue bars.

4.2.3.7. Lead

The temporal evolution of total, dissolved and labile concentrations of Zn at the vertical profile C1, C2 and C3 is presented in Figure 71 and at the horizontal transect S2, C2 and R2 in Figure 72. The concentrations of Pb total vary similarly between the points except for the peak of total Pb up to

6 $\mu\text{g/L}$ in June 2012 at point C3. From October 2013 to December 2013, the Pb concentrations seem to be higher and decrease gradually comparing to the other months and the same period in 2012.

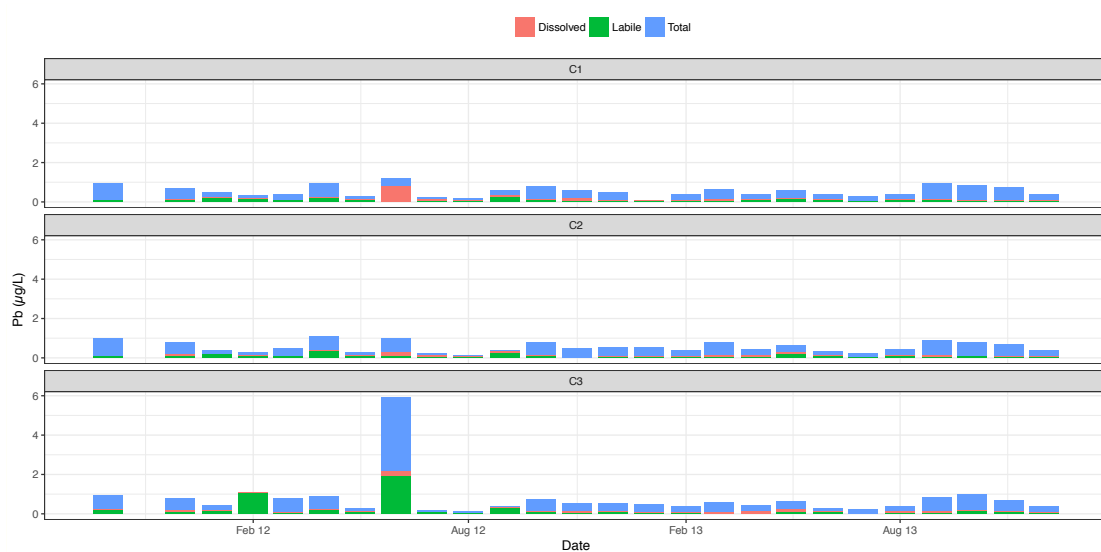


Figure 71 Total, dissolved and labile concentration of Pb at the points C1, C2, C3 of Lake Créteil. The labile concentration is in green. The dissolved concentration is the sum of green and red bars and the total concentration is the sum of the green, red and blue bars.

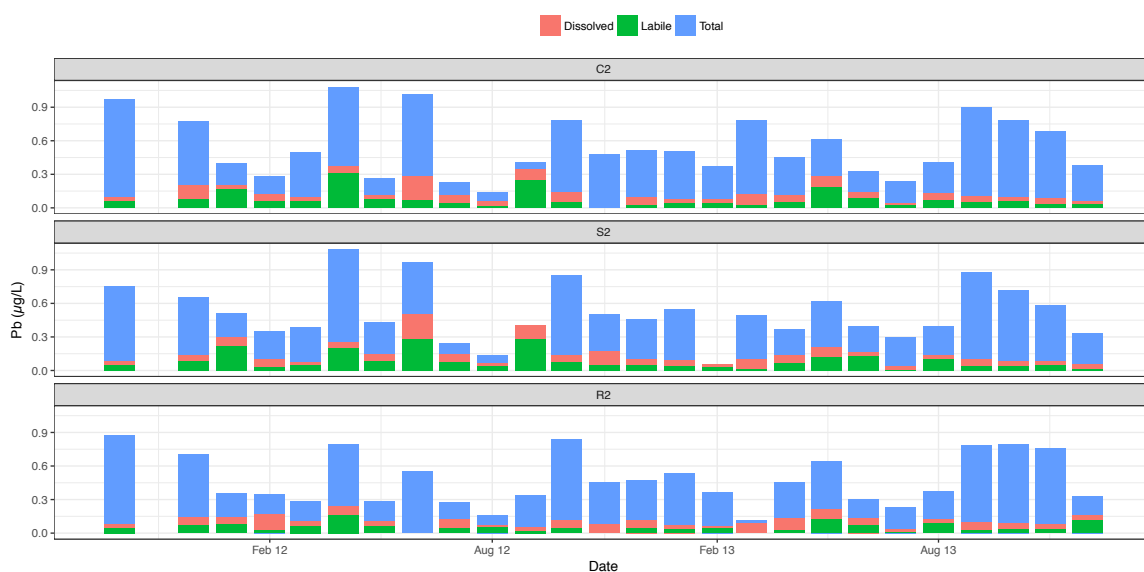


Figure 72 Total, dissolved and labile concentration of Pb at the points S2, C2, R2 of Lake Créteil. The labile concentration is in green. The dissolved concentration is the sum of green and red bars and the total concentration is the sum of the green, red and blue bars.

4.3. Metal bioavailability in Lake Pampulha and environmental variables

In this section, we present the correlation of metal bioavailability with the environmental variables. In the next figures, the linear Spearman correlations of the labile to dissolved ratios with the environmental variables are depicted as a panel of coloured circles. All the insignificant correlations with p value <0.05 are omitted. The degree of correlation corresponds to the color gradient and size of symbol.

4.3.1. At point C1

The correlation of the labile metal fraction and the environmental variables at point C1 is presented in Figure 73. The labile Co fraction presents a significant correlation with most of environmental variables. However the correlations are weak except for a negative correlation (around 0.7) with POC concentration and a positive correlation (around 0.6) with the total phosphorus concentration. The labile Cu fraction presents positive correlations with oxygen, total phosphorus. The labile Zn fraction correlates positively with oxygen (around 0.7) and DOC (around 0.6). All the labile metal fractions correlate positively with the oxygen.

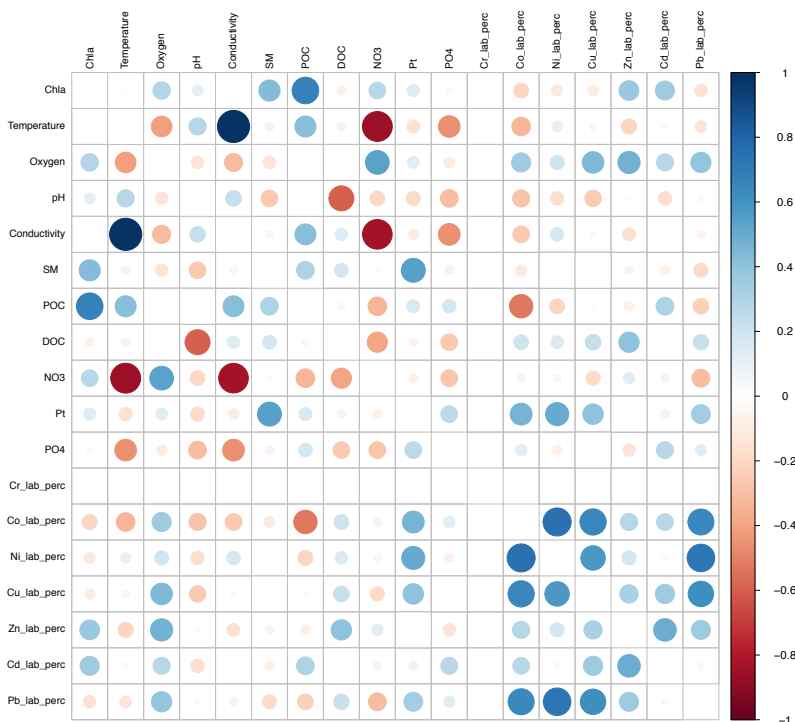


Figure 73 Correlation of labile metal fraction and environmental variables at the point C1

4.3.2. At point C2

The correlation of the labile metal fraction and the environmental variables at the point C2 is presented in Figure 74. In general, we did not find a strong correlation at this depth comparing to the surface. The correlation of labile metal fraction with oxygen is significant for all the elements. The correlations of Cd and Pb labile fraction with oxygen are stronger between 0.6 and 0.7. Some negative correlations appear: Cu with pH (~0.5), Cd with SM (~0.5) and Pb with Nitrate (~0.5)

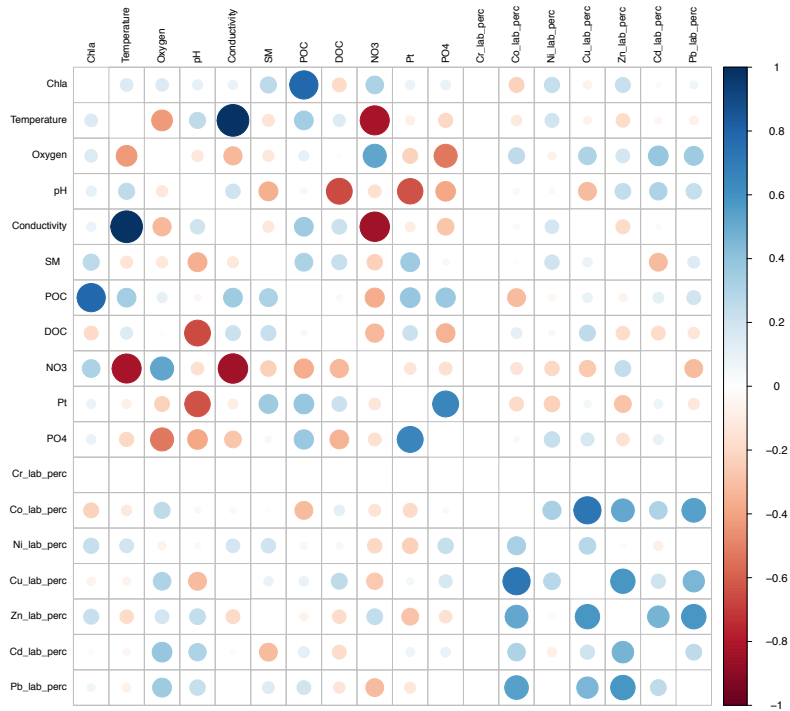


Figure 74 Correlation of labile metal fraction and environmental variables at the point C2

4.3.3. At point C3

The correlation of the labile metal fraction and the environmental variables at the point C3 is presented in Figure 75. In general, we did not find a strong correlation at this depth comparing to the surface. The correlation of labile metal fraction with oxygen is significant for all the elements. The

correlations of Cd and Pb labile fraction with oxygen are stronger between 0.6 and 0.7. Some negative correlations appear: Cu with pH (~0.5), Cd with SM (~0.5) and Pb with Nitrate (~0.5).

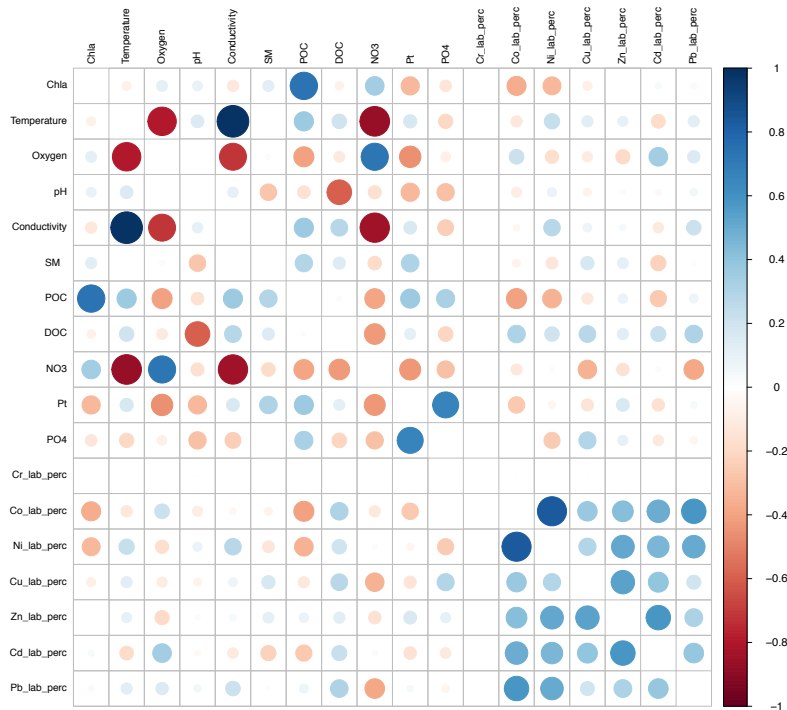


Figure 75 Correlation of labile metal fraction and environmental variables at the point C3

4.3.4. At point S2

The correlation of the labile metal fraction and the environmental variables at the point S2 is presented in Figure 76. In general, Ni, Cu and Zn present significant correlation with most of environmental variables. For instance, temperature correlates positively with Ni (~0.7) and Cu (~0.6) and negatively with Zn (~0.7). Conductivity has similar correlations with Ni, Cu and Zn. Particularly,

labile Cu fraction presents significant correlation with all environmental variables except for Chla concentrations. Point S2, located near the stormwater inlet, might be impacted by raining events.

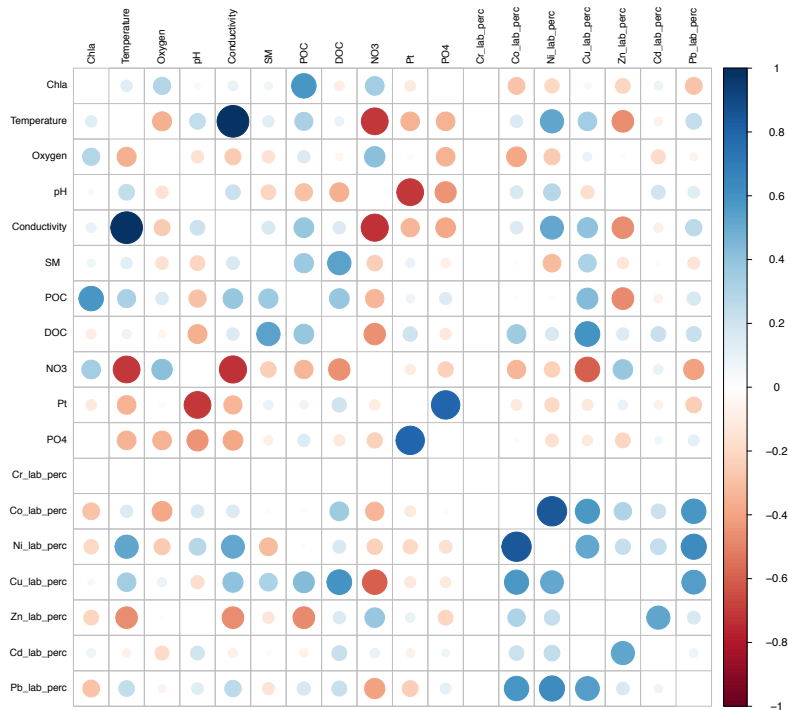


Figure 76 Correlation of labile metal fraction and environmental variables at the point S2

4.3.5. At point R2

The correlation of the labile metal fraction and the environmental variables at point R2 is presented in Figure 77. In general, strong correlations are mainly observed for chla concentrations, temperature and oxygen. Co and Ni have strong correlation with the three environmental variables mentioned above. Chla and Oxygen correlate positively with Co and Ni while temperature correlates negatively with them.

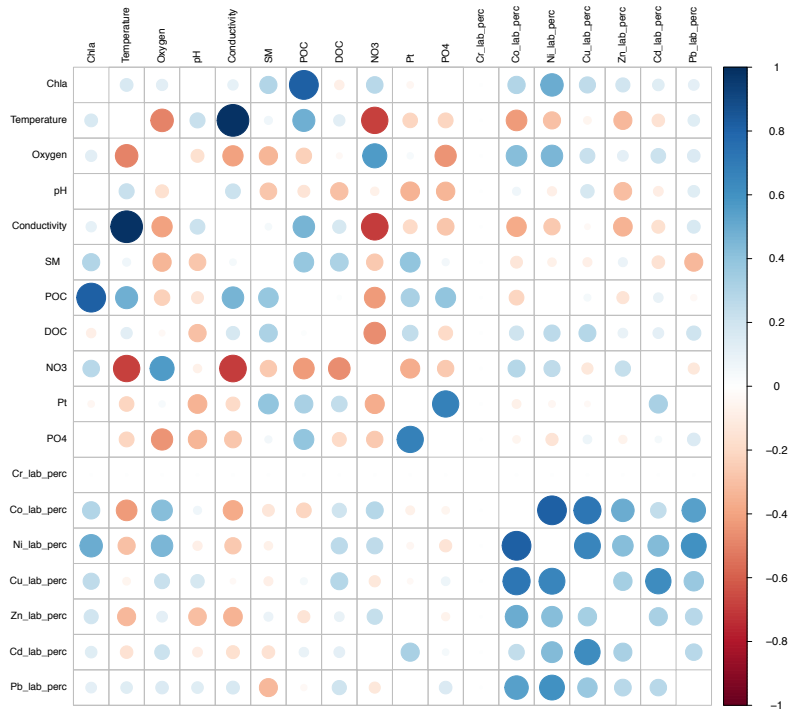


Figure 77 Correlation of labile metal fraction and environmental variables at the point R2

Conclusion

The correlation analysis indicates different patterns depending on the monitoring points. At point C, Co presents a significant correlation with most of environmental variables at the surface while this is not observed at the middle and bottom of the water column. However, all the labile metal fractions correlate positively with oxygen concentration at all depths at point C.

Point S2 presents a different correlation pattern comparing to point C. Ni, Cu and Zn show significant correlation with most of environmental variables. Temperature and conductivity have a strong correlation with Ni, Cu and Zn. Especially, Cu presents a significant correlation with all environmental variables.

Point R2 presents some similarities with point C. Strong correlations are mainly observed between Co, Ni and chla concentrations, temperature and oxygen.

4.4. Statistical analysis

The objectives of this section are as follows: (1) to present the different steps to constitute the data set that will be analyzed with the statistical model Random Forest (RF); (2) to present the parameterization of the RF model and (3) to present the modelling results.

4.4.1. Missing values

The missing values of the dataset at the point C1, C2, C3, S2 and R2 are presented in Figure 78. The left zone of the figure corresponds to the proportion of missing values for each variable. The right zone corresponds to the proportion of missing values for a combination of variables (yellow = missing, and blue = not missing). The variation of the environmental variables and the percent of missing values for each variable are presented in Table 50.

The environmental dataset is relatively complete except for nitrate with the 40% of missing values. Other variables such as total phosphorus, phosphate, POC and Chla concentration have less than 20% of missing values. Temperature, Oxygen, pH, Conductivity and DOC are 100% complete.

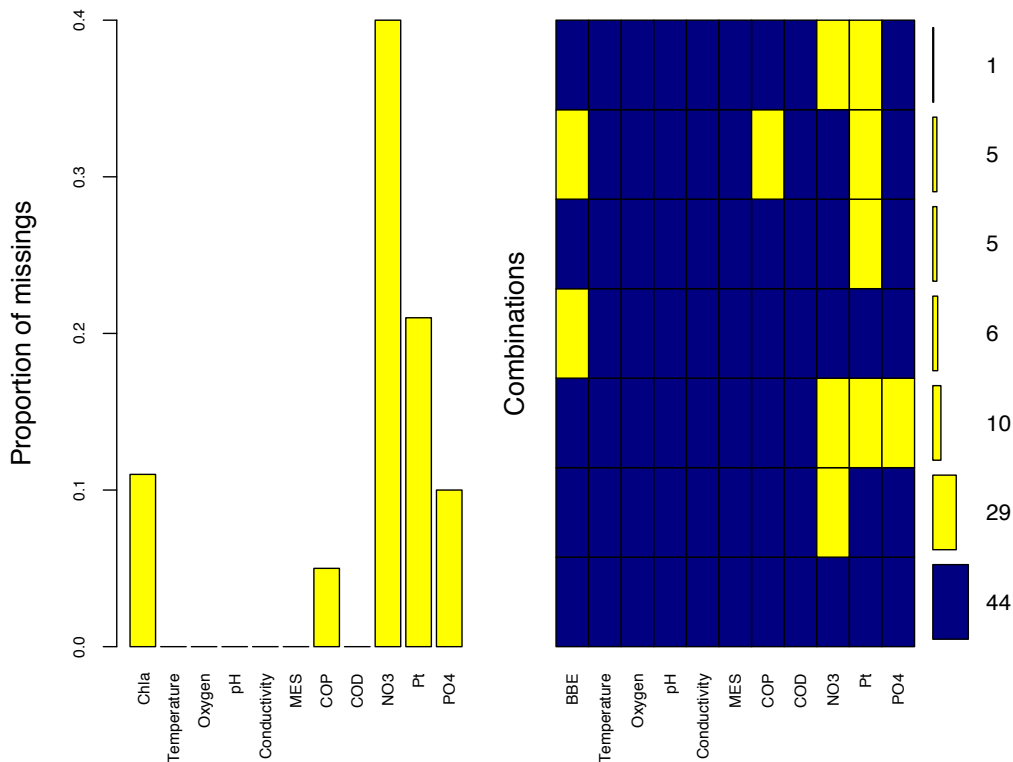


Figure 78 Proportion of missing values (left) and combination of environmental variables (right)

Table 50 Summary table of environmental data of Lake Créteil

Parameters	mean	sd	max	min	missing (%)
Chla	6.0	4.8	22.5	1.1	11
Temperature	12.0	6.2	23.9	1.4	0
Oxygen	9.0	2.9	17.2	0.3	0
pH	8.0	1.4	11.5	3.7	0
Conductivity	1133.8	176.4	1452.0	871.0	0
MES	4.0	1.5	8.8	1.9	0
COP	0.7	0.3	1.8	0.3	5
COD	6.0	0.5	7.9	5.0	0
NO3	0.5	0.2	0.8	0.1	40

The metal dataset presents more missing values however their proportion remains lower than 13 % except for dissolved and labile Zn. Comparing to the dataset of Lake Pampulha, the proportion of missing values is relatively low except for the dissolved and labile Zn. The right zone of the Figure 79 indicates that all metal concentrations are available for 71 samples..

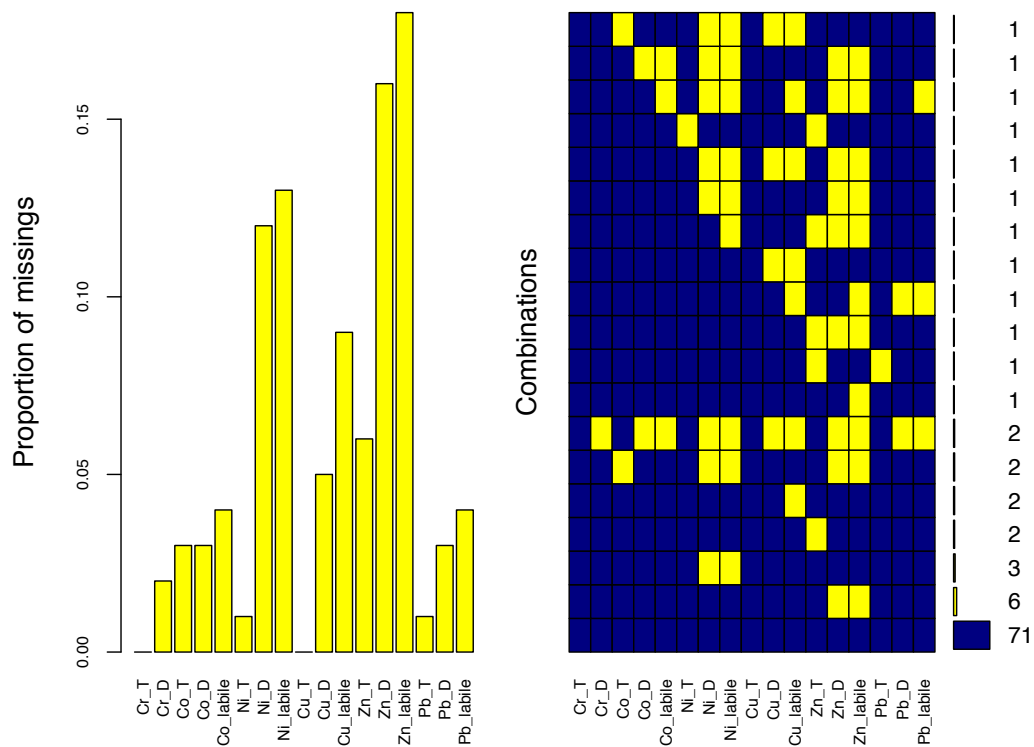


Figure 79 Proportion of missing values (left) and combination of metal and environmental data (right) of the dataset of Lake Créteil

Table 51 Summary table of metal data

Metal	mean	sd	max	min	missing (%)
Cr_T	1.35	1.22	4.04	0.25	0
Cr_D	0.20	0.12	0.76	0.01	2
Co_T	0.32	0.12	0.56	0.00	3
Co_D	0.31	0.10	0.66	0.15	3
Co_labile	0.09	0.05	0.28	0.01	4
Ni_T	6.15	1.86	9.77	0.76	1
Ni_D	5.96	0.89	8.63	4.35	12
Ni_labile	1.12	0.58	3.92	0.00	13
Cu_T	2.32	1.16	9.17	0.42	0
Cu_D	1.87	0.89	8.68	0.79	5
Cu_labile	0.64	0.88	7.52	-0.03	9
Zn_T	5.84	2.62	15.96	1.20	6
Zn_D	4.58	2.65	19.78	1.50	16
Zn_labile	1.98	1.53	5.86	-0.04	18
Pb_T	0.56	0.59	5.91	0.05	1
Pb_D	0.18	0.25	2.17	0.03	3
Pb_labile	0.11	0.22	1.93	-0.03	4

4.4.2. Missing value treatment

We applied the same treatment of the missing values as we applied for the dataset of Lake Pampulha (see section 3.5.2). Although environmental variables present a tiny difference between the points, the imputation of the missing values is performed considering the points and the depths, in order to take into account the spatial distribution, in the horizontal and vertical dimensions. The variables with more than 35% of missing values are automatically eliminated.

4.4.3. The final dataset

Only NO₃ with 40% of missing values was excluded from the final dataset. Other parameters are imputed and included into the final dataset.

The dataset used in the Random Forest modelling contains the following variables: Temperature, Chlorophyll a, Conductivity, Oxygen, pH, SM, POC, DOC, NH₄, total phosphorus, phosphate.

4.4.4. Parametrization of the Random Forest model

Variable importance in the random forest model is estimated according to the methods explained in the chapter “Material and methods”.

Table 52 shows the most important variables selected by the RF model for each labile metal fraction. Oxygen appears to be an important explanatory variable for metal labile fraction. This agrees with the results of the correlation analysis.

Table 52 Selected variables base on its importance score – Lake Créteil

Labile(%)	Selected variables for final model classed by variable importance				
Co	POC	Oxygen	Conductivity	Chla	pH
Ni	Conductivity	Temperature	SM	PO4	pH
Cu	DOC	Pt	pH	PO4	Oxygen
Zn	pH	Oxygen	Temperature	Pt	PO4
Pb	Oxygen	Conductivity	DOC	Temperature	SM

4.4.5. Results of the Random Forest modelling

Table 53 shows the parameters used in the final Random Forest model, the R² obtained on the training data, the R² of the model validation on the testing data and its standard deviation. The Random Forest model is applied for all metals using 80 % of dataset for training and 20% for validation. The model is applied for 1000 trees with different parameters (nvar, mtry, node size) depending on each metal. For the detailed explanation on the RF model parameters, see in the Material and Methods chapter (chapter 2). The cross validation is based on the Monte Carlo cross-validation method.

The performance score of the RF model on the dataset of Lake Créteil is lower than in Lake Pampulha. The maximal R² values that we obtained are 48% for Co and 42% for Pb. Co obtained the better R² values. After Co, the RF model can explain until 42% of its variance. We obtained similar R² values for Ni and Cu while a low R² value was obtained for Zn.

Table 53 Results of the random forest model on the labile fraction of metals

% labile	Training (%)	mtry	node size	ntree	n permutation	R2 fitting	mean R2 (val)	sd R2
Co	80	3	3	1000	1000	0.95	0.48	0.22
Ni	80	3	3	1000	1000	0.93	0.32	0.22
Cu	80	3	3	1000	1000	0.93	0.31	0.19
Zn	80	3	3	1000	1000	0.90	0.18	0.17
Pb	80	3	3	1000	1000	0.93	0.42	0.21

To highlight the relationships between the selected variables and the predicted variables (the fraction of labile metal) the partial dependence plots are used as illustrated on Figure 80.

The relationships between the labile Co fraction and the environmental variables are presented in Figure 80. The labile Co fraction decreases significantly with the POC concentration. From 0.5 mg/L to 1.5 mg/L of POC, the labile Co fraction changes from 35% to under 25%. For other parameters, we observed no threshold effect and the variation of labile Co fraction remains relatively low.

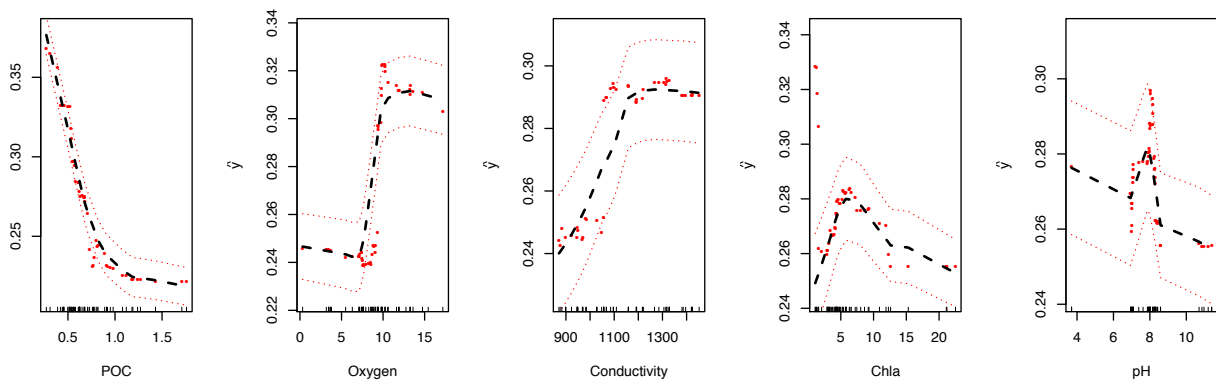


Figure 80 The marginal effect of the variables on the percent of labile cobalt

The relationships between the labile Pb fraction and the environmental variables are illustrated in Figure 81. The oxygen concentration presents a threshold effect for the labile Pb fraction. Oxygen concentration in Lake Créteil is higher than in Lake Pampulha. During the winter, the oxygen concentration can be up to 17.2 mg/L. The RF model shows that the labile Pb fraction increases with the oxygen concentration. This is an opposite result than the one obtained on Lake Pampulha. However, the environmental conditions of these two lakes are different. Lake Créteil does not present a permanent anoxic layer and its oxygen concentration is higher. Moreover, Pb is mostly in particulate form. Thus, the labile lead fraction is relatively low.

Based on these results, all the conclusions need to be made with prudence because the standard deviation of R^2 values is relatively high.

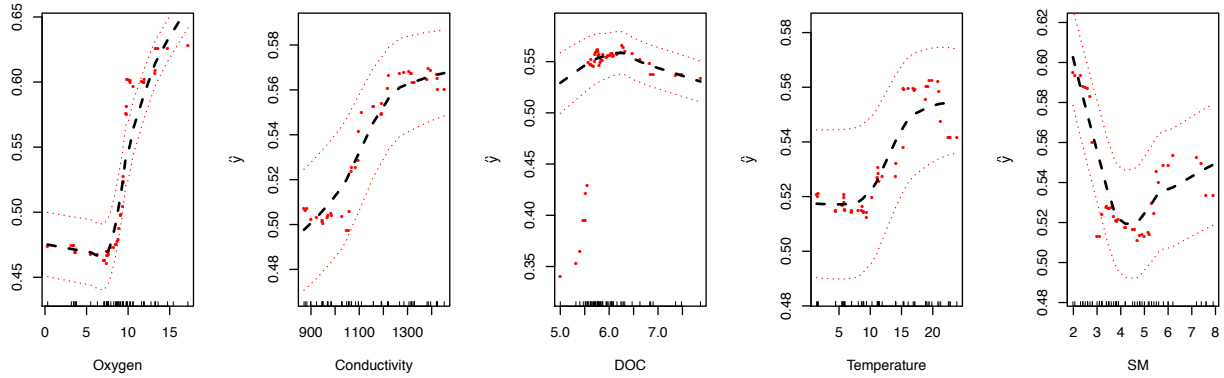


Figure 81 The marginal effect of the variables on the percent of labile lead

4.5. Impact of raining events

As mentioned in the chapter Material and Methods (section 2.1.1.8), a stormwater outlet discharges into Lake Créteil. Therefore, the impact of raining events on trace metal concentrations in the lake was studied from June to December 2013. During this period, we calculated the daily sum of precipitation. 6 raining events were monitored. The green points correspond to the day of the raining campaigns (Figure 82). In the lake, the sampling campaigns were performed the day after the raining event.

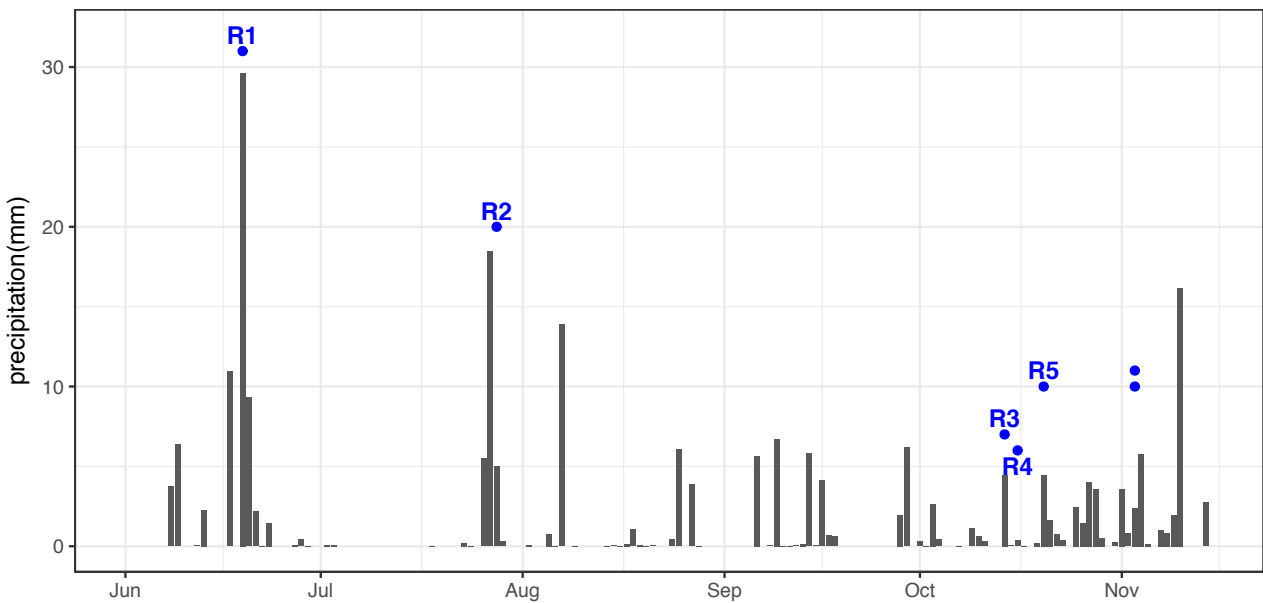


Figure 82 Precipitation during raining campaigns

For the campaigns performed on 19/09/2013 and 17/10/2013, the rainfall was weak, inferior to 1mm per day. For the campaigns performed on 15/10/2013 and 21/10/2013, the rainfall was stronger, about 5 mm per day. The characteristics of the rain events are presented in Table 54.

Table 54 Main characteristics of the rain events

	Event 1	Event 2	Event 3	Event 4	Event 5	Event 6
Date	19/06/13	28/07/13	14/10/13	16/10/13	20/10/13	03 and 04/11/2013
Raining events						
Max intensity (mm/h)	88.2	34.4	31.4	4.6	52.3	16.7
Cumulative rainfall (mm)	22.7	5.0	4.5	0.4	4.2	4.2
Duration (h)	9.9	0.6	0.6	1.1	0.3	4.7
Return period	5 ans	6 mois	6 mois	15 jours	6 mois	3 mois
Max flow rate (l/s)	435.2	413.9	761.5	279.8	694.7	248.3
Previous days						
Cumulative rainfall j ⁻¹ (mm)	6.6	0.0	0.0	0.0	0.3	0.8
Cumulative volume j ⁻¹ (m ³)	1121.7	37.2	97.0	168.8	84.1	624.2
Cumulative rainfall j ⁻⁷ (mm)	19.9	24.2	2.0	6.5	5.4	9.9
Cumulative volume j ⁻⁷ (m ³)	3940.8	3452.0	1317.7	2743.8	3319.4	7957.0
Concentrations						
[Pt] (µgP/L)	1389.06	1000.5	2720.22	562.25	2834.42	439.87
[PO ₄] (µgP/L)	50.67	194.8	102.44	89.88	118.66	75.48
[NO ₃] (mgN/L)	0.33	0.37	0.33	0.34	0.19	0.17
[DOC] (mg/L)	4.18	11.57	9.26	6.56	9.09	3.94
[SM] (mg/L)	275.96	134.4	544.8	85.1	380.1	43.2
[POC] (mgC/L)	44.19	25.3	97.82	17.32	58.95	9.3
[POC] (gC/gMES)	16.01	18.83	17.95	20.36	15.51	21.52

In order to provide information on the lake context, key limnological variables measured at high frequency in the water column at point C from June to December 2013 are presented on Figure 83. The chlorophyll-a concentration, which is a proxy of the phytoplankton biomass, shows two high value periods (~50µg/L) the first one in mid-July and the second one in September. The surface water temperature decreases during the period, from 25 °C to 14 °C. The lake water column was thermally stratified from June to end of July. Between the end of July and the end of September, an alternation of mixing and stratification periods occurs. A long stratification period occurs during the second half of September. From the beginning of October to the end of December, the water column was fully mixed.

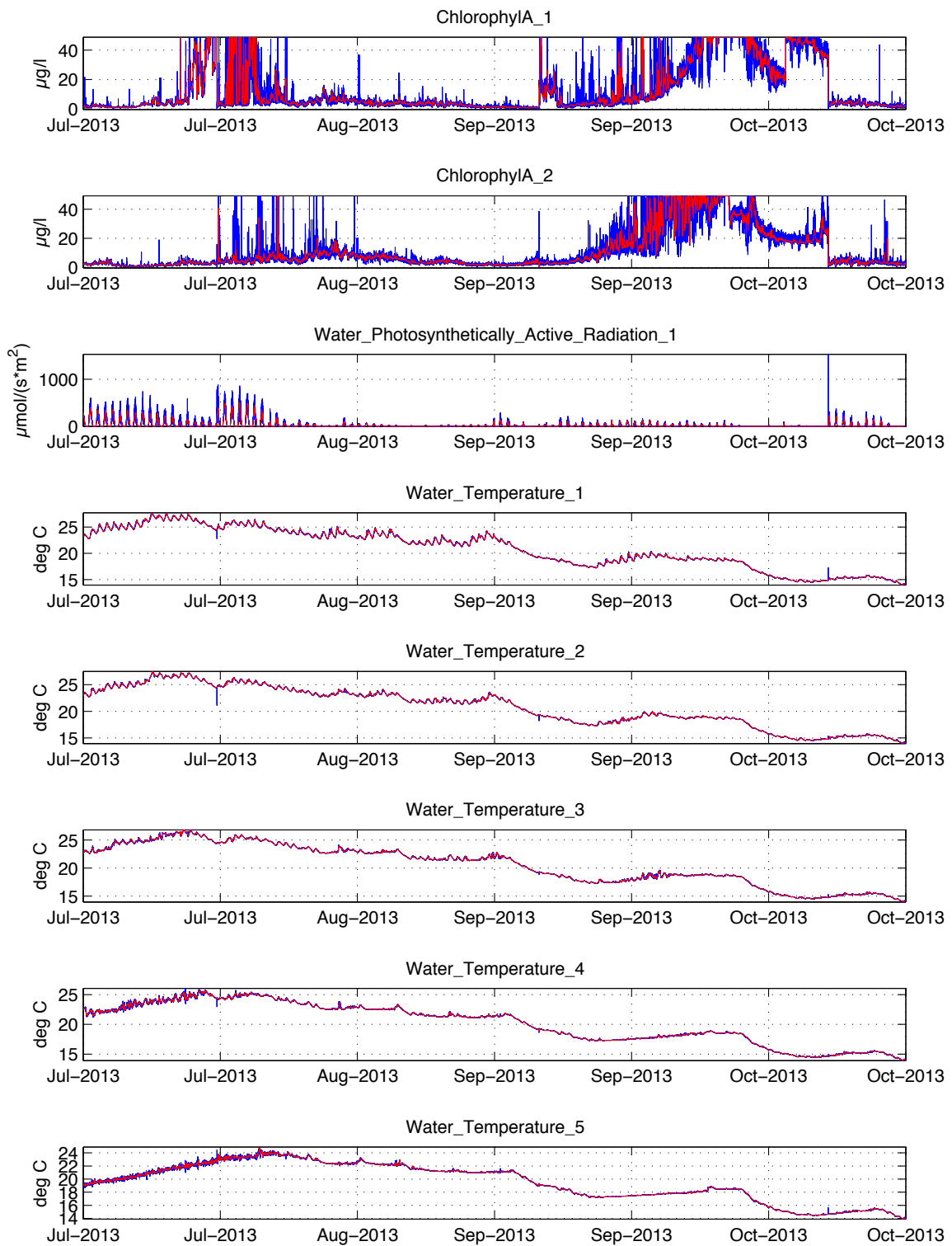


Figure 83 Measurements of limnological variables from 13/07/2013 to 31/10/2013 in Lake Créteil

On Figure 84, we present the total Ni, Cu, Zn and Pb concentrations measured in the drainage network outlet. The Ni concentration is around 15 $\mu\text{g/L}$. The Cu concentration range is high, between 50 and 300 $\mu\text{g/L}$. The Zn concentration range is even higher, between 200 and 800 $\mu\text{g/L}$ and the Pb concentrations are between 15 and 140 $\mu\text{g/L}$.

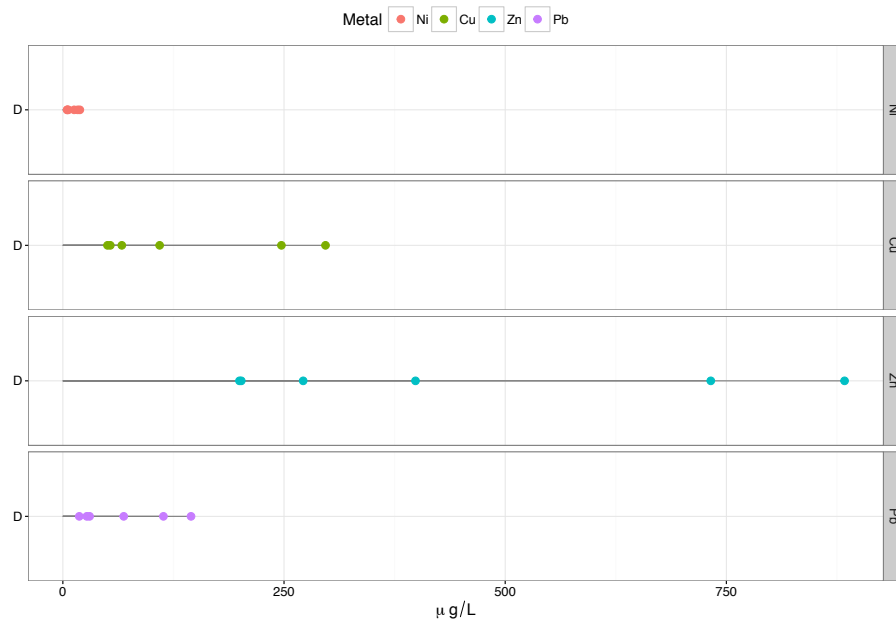
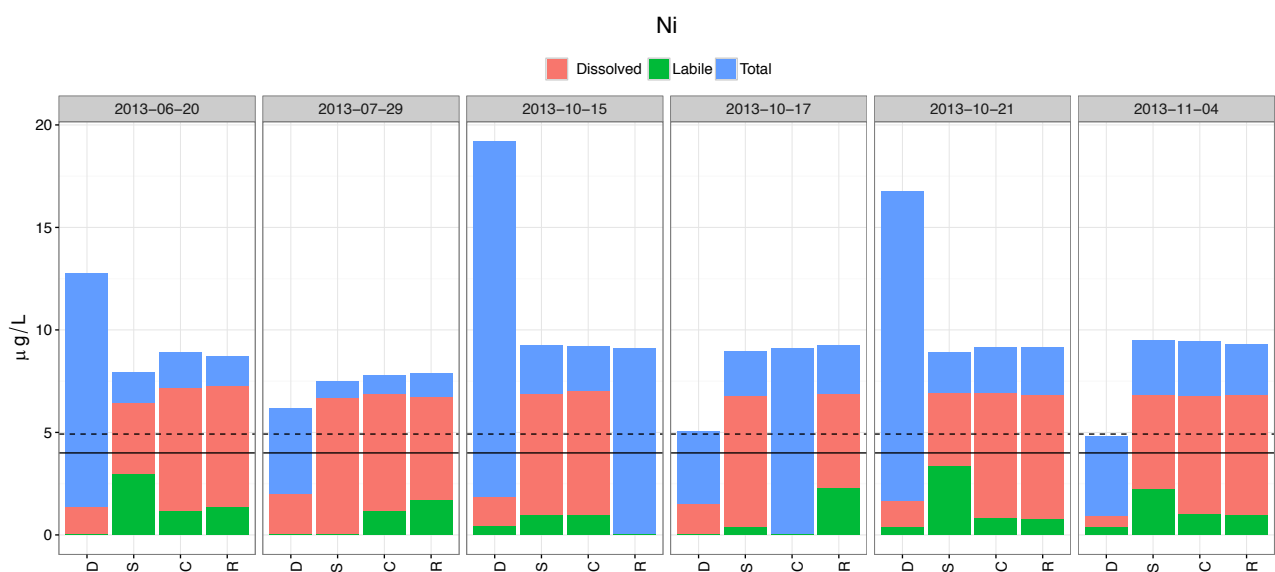


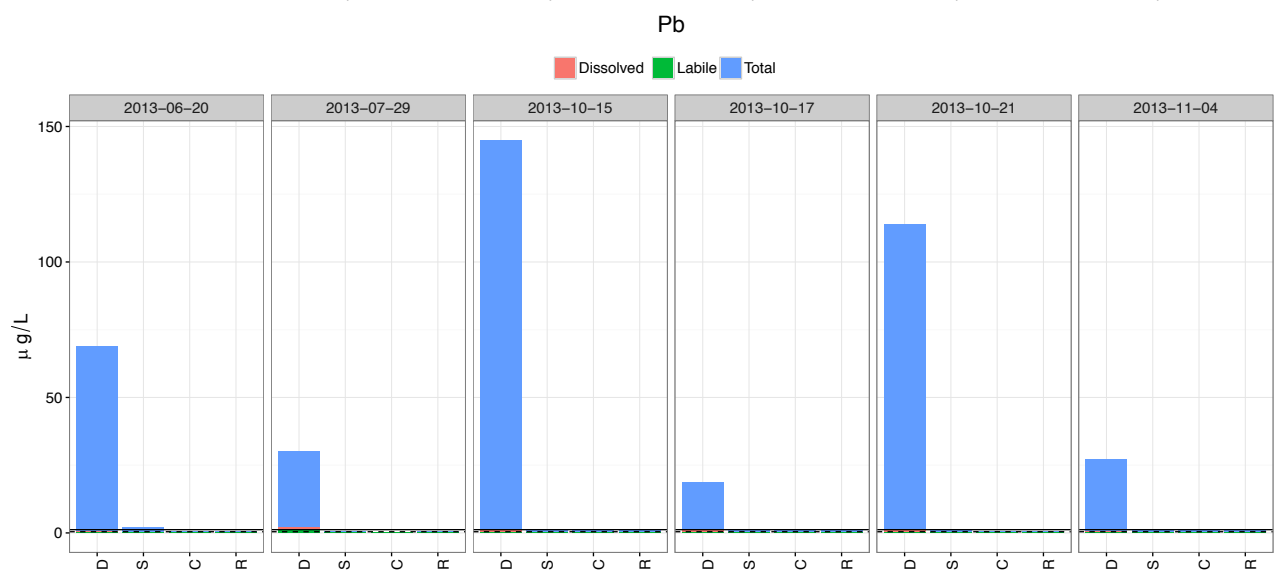
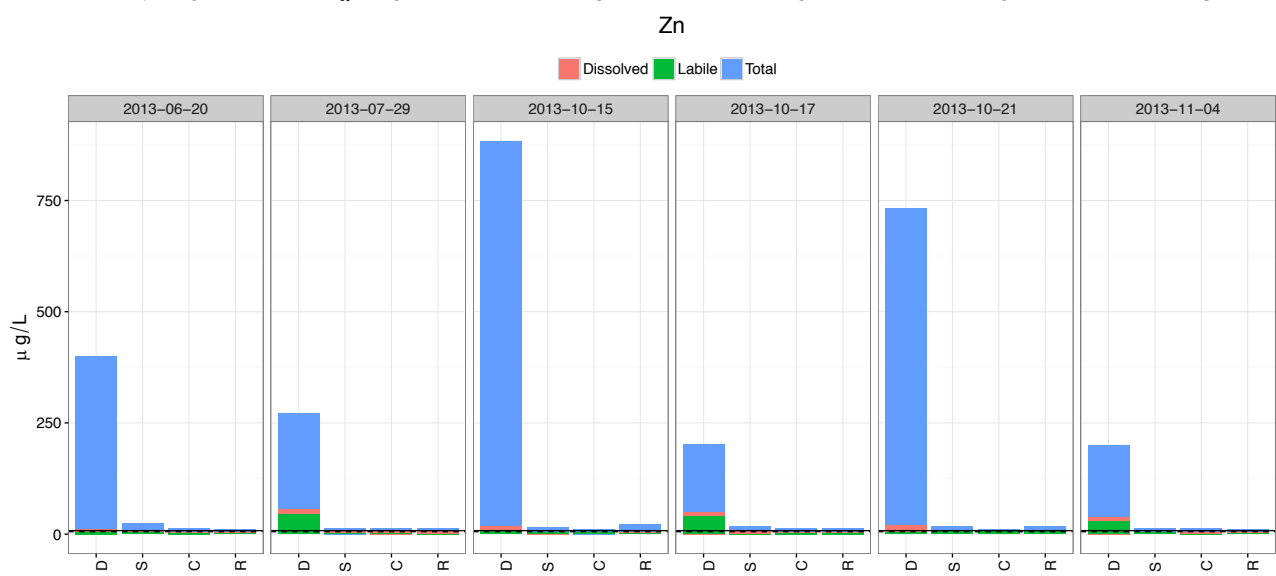
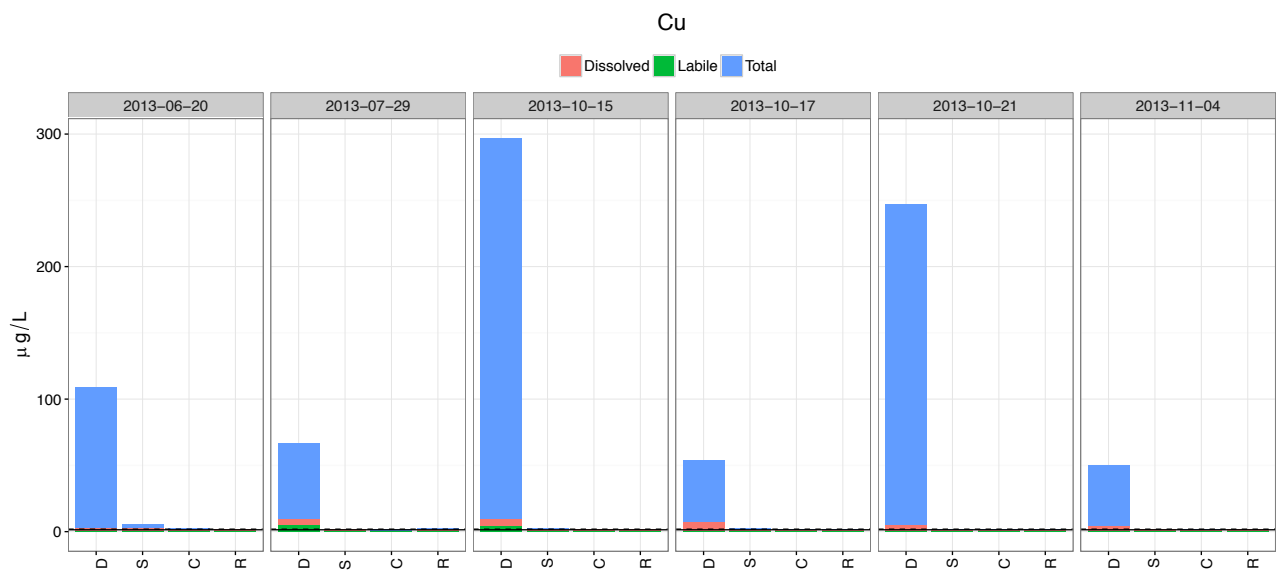
Figure 84 Total Ni, Cu, Zn, Pb concentrations in the stormwater outlet

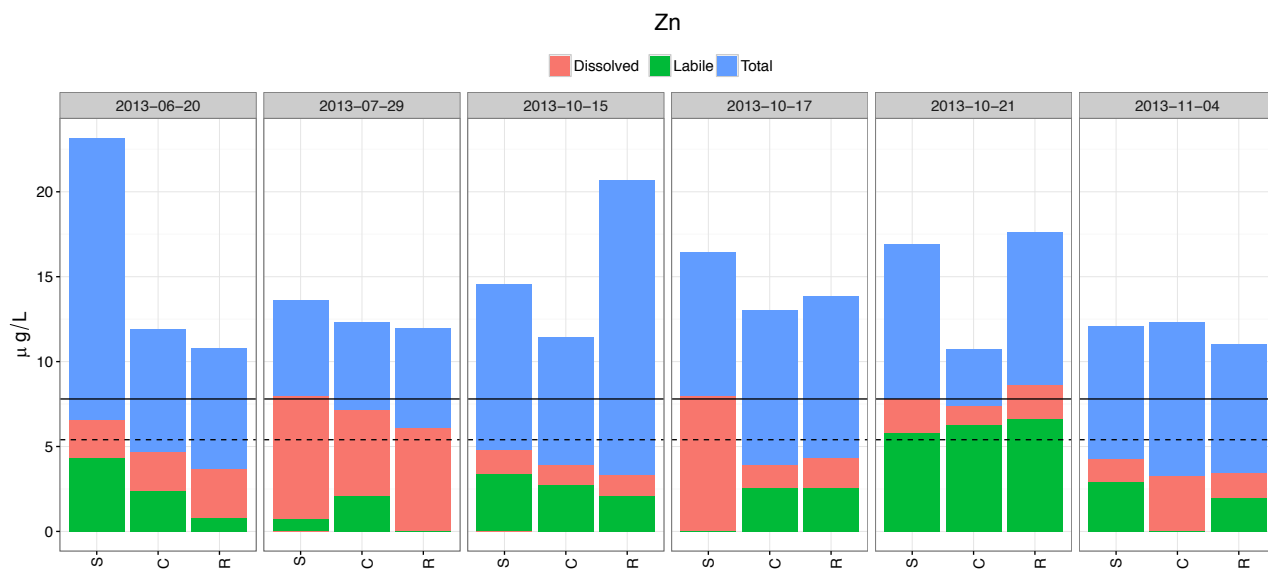
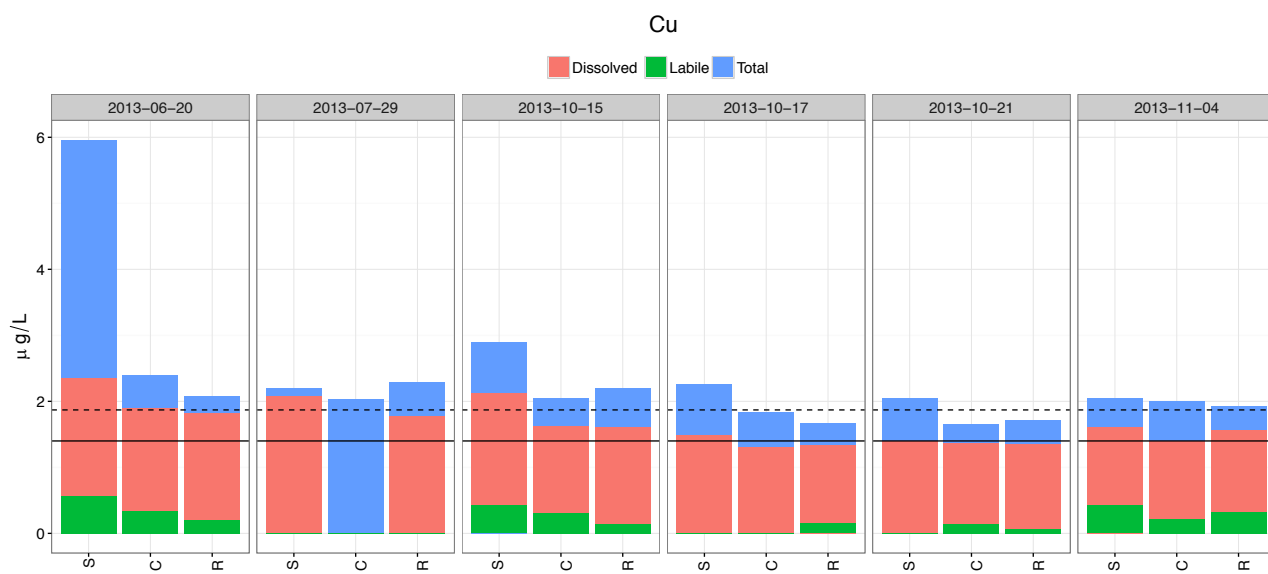
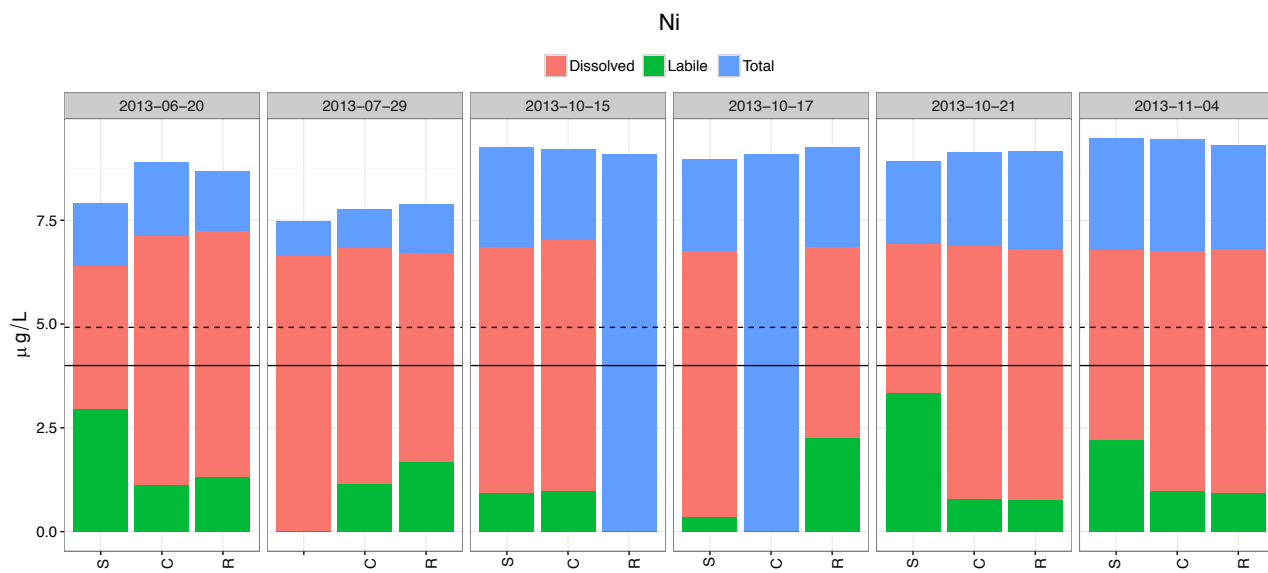
The concentrations of total, dissolved and labile trace metals in the stormwater inlet (D) and at points S, C and R in the lake are plotted on Figure 85.

Ni concentrations in the stormwater outlet and in the lake are of the same magnitude, excepted during 3 days where they are around 50% higher.

Cu, Zn and Pb concentrations in the stormwater outlet are several orders of magnitude higher than in the lake.







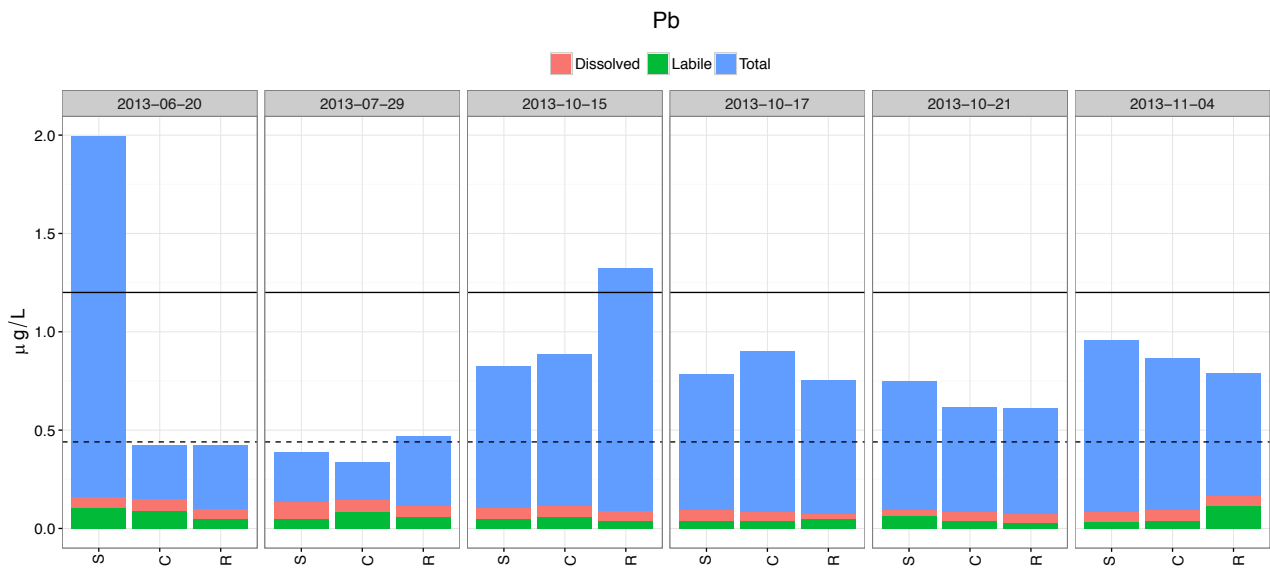


Figure 85 Metal concentrations in the stormwater outlet and in the lake

To highlight the impact of the raining events on the distribution of the dissolved and labile fractions in the lake, the concentrations of total, dissolved and labile trace metals in the lake at points S, C and R are plotted on Figure 53.

The total Ni concentration is rather similar at the 3 sampling points for all the dates. The Ni dissolved concentration remains around $6\mu\text{g/L}$, this represents around 60% of the total concentration at all dates and depths. The labile fraction is between 5 and 30% of the dissolved metal. The labile fraction seems higher at point S, near the stormwater outlet.

The total Cu concentration is rather similar at the 3 sampling points for all the dates, excepted at the point S for the first campaign. The Cu dissolved concentration remains around $2\mu\text{g/L}$, this represents around 80% of the total concentration at all dates and depths. The labile fraction is between 5 and 30% of the dissolved metal.

The total Zn concentration is generally higher at point S. The Zn dissolved concentration varies between 4 and $8\mu\text{g/L}$, this represents around 60% of the total concentration. The labile fraction can be high, around 80% of the dissolved metal.

4.6. Conclusion

In this chapter, we investigated the environmental variables and the trace metal speciation in the water column of Lake Créteil in France. The water samples correspond to a vertical profile at point C (C1, C2, C3) and a horizontal transect from stormwater inlet to reedbed (S2, C2 and R2).

The water temperature measurements indicated that the lake was stratified from March to October. The difference of water temperature between the surface C1 and the bottom C3 can be up to $2.26\text{ }^{\circ}\text{C}$ in 2012 and $4.61\text{ }^{\circ}\text{C}$ in 2013. The horizontal evolution of the water temperature presented no difference except for March – April and August – September 2012 and from March to November 2013 with a difference lower than $1\text{ }^{\circ}\text{C}$ in 2012 and 2013

The chlorophyll-a concentration varies from $1.1\mu\text{g/L}$ to $22.5\mu\text{g/L}$ from 2011 to 2013. Its vertical difference can reach up to $6\mu\text{g/L}$ between the surface and the bottom of the water column. Its horizontal variation showed that the point R2 was slightly different than the points C2 and S2. However, both the vertical and horizontal differences are non statistically significant.

The other physical chemical parameters presented no spatial significant variation. The lake can be poorly oxygenated at the bottom of the water column at point C3 in August 2012 with 0.48mg/L and in July 2013 with 0.32mg/L. Otherwise, the lake is oxic during the year. Lake Créteil has a stable pH around 7.9 and a high conductivity around 1100 μ S/cm due to its geological background.

In the water column of Lake Créteil, the average ratios of dissolved to total metal concentration are high for Co (80%) , Ni (85%) , Cu (70%) and Zn (75%). For Pb, as it is highly particulate, the ratio dissolved to total concentration is low. The labile fraction is relatively low for Co, Ni and Cu, between 17 and 35%, slightly higher for Zn, around 40 %. The labile fraction of Pb represents around 50% of the low amount of dissolved Pb. There is no statistical difference in both vertical and horizontal distribution of the dissolved and labile fractions.

The concentrations of dissolved Ni, Cu, Zn and Pb measured in the water column at three depths were compared with European Quality Standards (EQS). The median of dissolved concentrations of Ni in the lake water column is 6 μ g/L, higher than the european standard (4 μ g/L). All Ni concentrations overpass the EQS. The median of Cu concentrations is 2 μ g/L, equal to the EQS value. Nearly 50% of Cu concentrations overpass the EQS. All Zn concentrations are lower than the EQS value (8 μ g/L) and the Pb concentrations are very low, much lower than the EQS value (1 μ g/L).

The correlation analysis indicated that Co presents a significant correlation with most of environmental variables only at the surface; all the labile metal fractions correlated positively with oxygen at all depths of the water column at point C. At point S2, Ni, Cu and Zn present significant correlation with most of environmental variables. At point R2 some strong correlations are mainly observed between Co, Ni and Chla concentrations, temperature and oxygen.

During the raining events, the concentrations of Cu, Zn and Pb are much higher in the stormwater outlet than in the lake. The Cu, Zn and Pb total concentrations in the lake increased after the raining events. However, the Pb dissolved concentration remains much lower than the EQS. The Cu and Zn dissolved concentrations reach nearly the EQS.

For Ni, no significant difference is observed between the concentrations in the stormwater outlet and in the lake. In the lake, Ni dissolved concentrations remain similar at all points and dates and higher than the EQS.

5. Results on peri-urban lakes in Ile-de-France region

One of the main objectives of the project PULSE is to determine the impacts of global changes and other anthropogenic pressures on peri-urban lakes. Besides the monthly monitoring conducted on Lake Créteil, environmental impacts on biodiversity, phytoplankton community structure and functional indicators were investigated on 49 peri-urban lakes in region Ile de France by estimating both anthropogenic pressures and physical and chemical parameters (Figure 86).

During 3 summers between 2011 and 2013, three teams from the laboratory MCAM Muséum national d'Histoire naturelle, BIOEMCO and Leesu Université Paris-Est have participated in monitoring physical, chemical and biological parameters in 49 peri-urban lakes. The area investigated is covering 12,011 km² in north-central France, in the center of the Paris basin. The region contains many large industrial towns and residential suburbs, and some agricultural production, mostly sugar beet and wheat (Catherine et al., 2008).

In this chapter, firstly, we present a general overview of trace metal concentrations of the 49 lakes: their distribution, their concentration in comparison to the Environmental Quality Standards (EQS) and their regional cartography. Secondly, we present the meteorological context for the sampling period during these 3 years. We present afterwards our choice to consider in our statistical analysis the landuse in a buffer zone around the lakes. Finally, we present the statistical approach with the Random Forest model and its results.

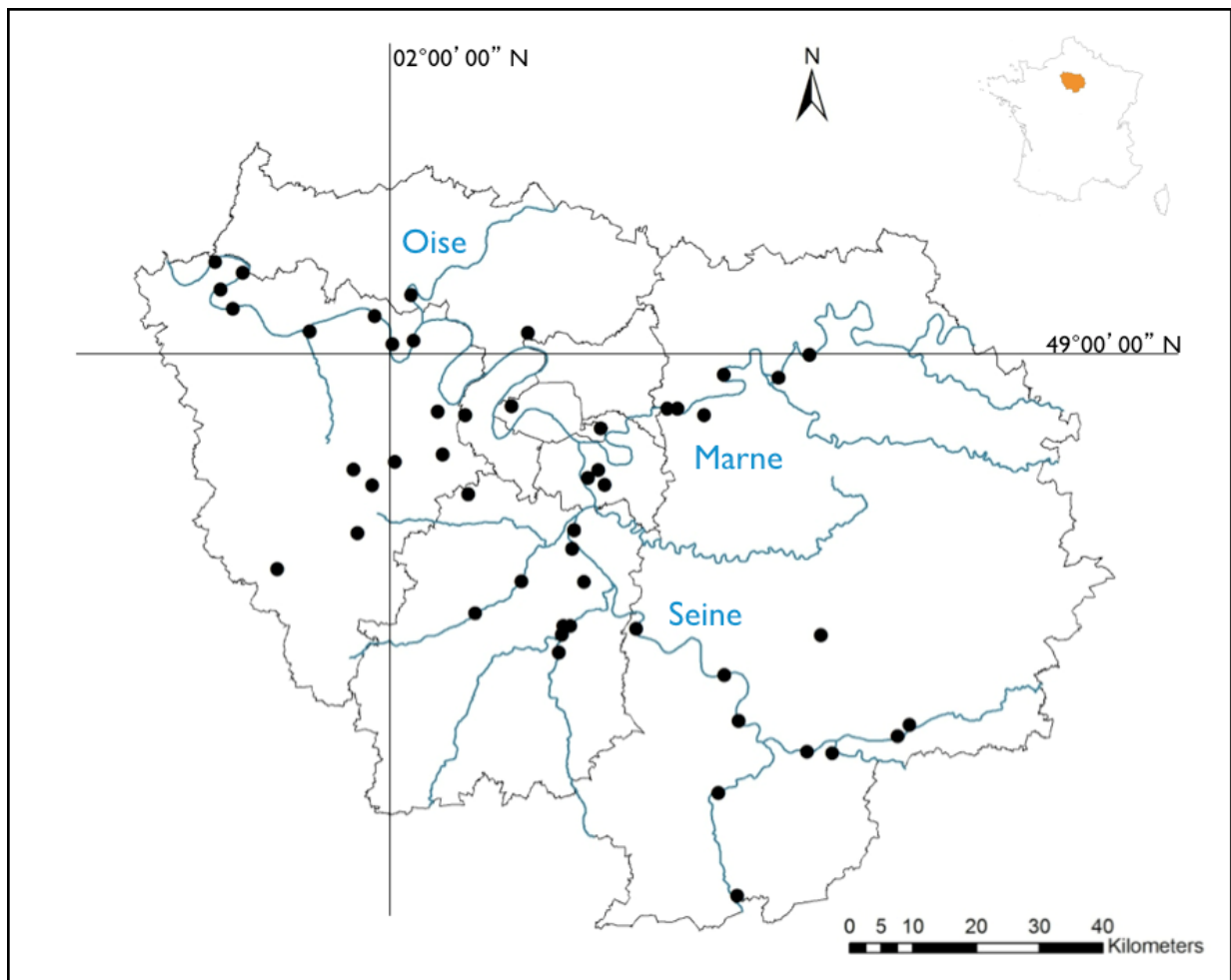


Figure 86 Location of 49 peri-urban lakes in region Ile de France (Catherine et al., 2008)

5.1. Distribution of the metal concentrations for the 3 years

The distribution of the total metal concentrations for the three pooled years is presented in Figure 87. We observe on the boxplots a wide distribution of the Zinc, Nickel and Copper concentrations and a compact distribution of Chromium, Cobalt, Lead and Cadmium. Additionally, we observe various outliers for the wide distribution elements, especially for Nickel. For information, the red line indicates the maximum allowance concentration according to the environmental quality standards (MAC-EQS) which is applied for the dissolved metal concentration.

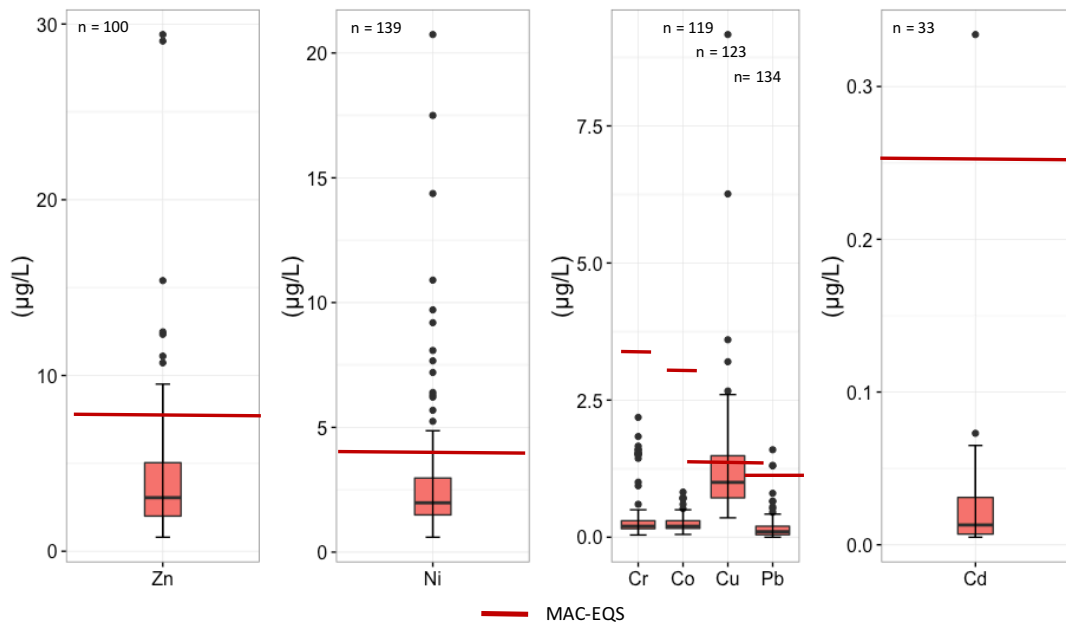


Figure 87 Distribution of the total metal concentrations for 3 years pooled

The distribution of the dissolved metal concentrations for the 3 pooled years is presented in Figure 88. The boxplots show a wide distribution of the nickel and copper concentrations. The dissolved nickel has a wide variation in comparison to its total concentration. Comparing to the Environmental Quality Standards, the dissolved concentrations of Zn, Cu and Pb exceeded the maximum allowance concentration (MAC-EQS).

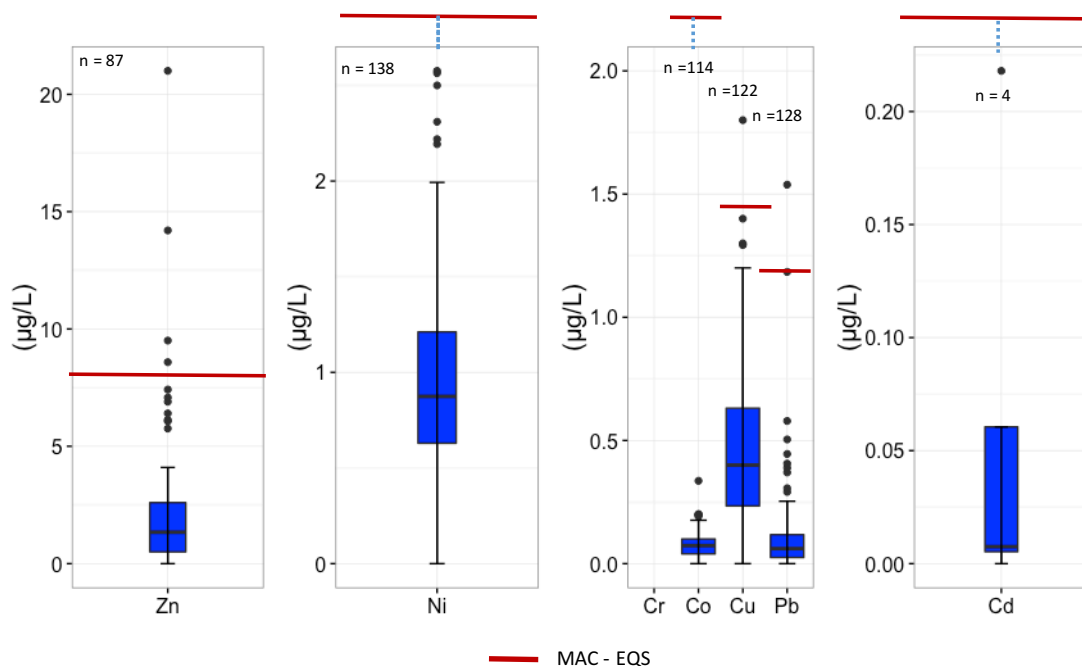


Figure 88 Distribution of the dissolved metal concentrations for 3 years pooled

The distribution of the total metal concentrations in the 3 years, 2011, 2012, 2013 is presented in Figure 89. For these 3 years, Zn and Ni show many outlier values. The concentrations remain similar during the 3 years, except Zn higher in 2013 and Pb higher in 2011.

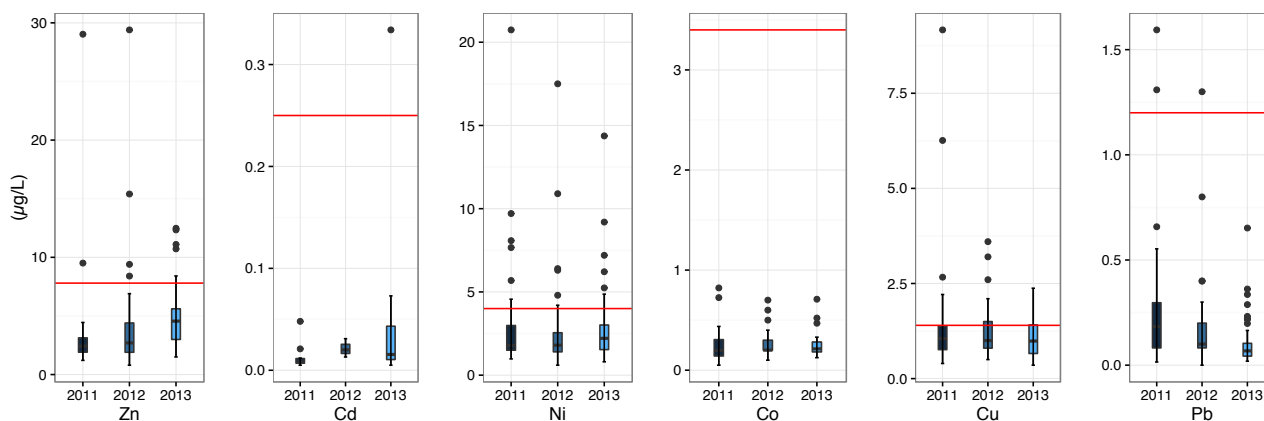


Figure 89 Distribution of the total metal concentrations in 2011, 2012, 2013

5.2. Meteorological context of the 49 lake survey

In order to obtain an overview of the regional meteorological context of the 49 lake survey during the 3 consecutive summers, we used as an integrated indicator of the meteorological forcing, the water temperature measured at 3 depths (0.5m, 3m and 5m) in Lake Créteil, from June to August. In order to perform the sampling campaigns in a similar meteorological condition, the sampling period for the 3 summers covered the last week of July and the first week of August (colored window in Figure 90).

The difference of water temperature during the 3 years is sharp. In 2011, during the first half of sampling period, the water column was not stratified. In 2012, the water stratification lasted the last two third of the survey period. In 2013, the water column was stratified during the whole sampling

period. In 2011, the weather was cooler and probably windier in the Ile de France region during the survey period. In 2012, it was cool and windy during the first days of the survey periods. 2013 was the warmer and less windy year.

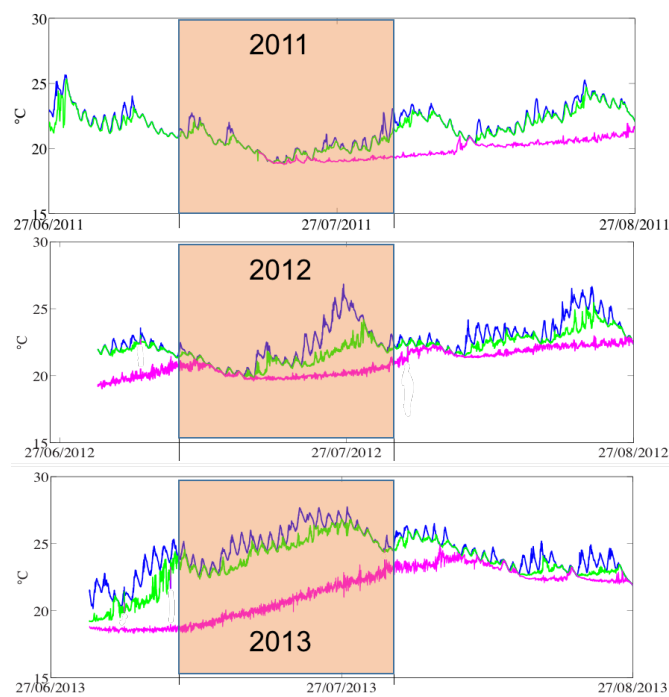


Figure 90 Water temperature in Lake Créteil during the 49 lake survey

5.3. Inter-lake variability

In the PULSE project, one of the questions is whether the variability between the 49 lakes is higher than the inter-annual variability of a single lake during the 3 years. In order to address this issue, we calculated the coefficient of variation of each variable for two cases:

- one coefficient of variation for 49 pooled lakes for each year 2011, 2012 and 2013
- one coefficient of variation for each lake with three pooled years

The coefficient of variation (CV), also known as relative standard deviation, indicates the relative variability of a variable to the mean. CV is unitless therefore we can compare different variables. It is just the ratio of the standard deviation divided by the mean. As an example, we present in the Figure 91 the coefficient of variation for the dissolved copper and the chlorophyll-a concentration.

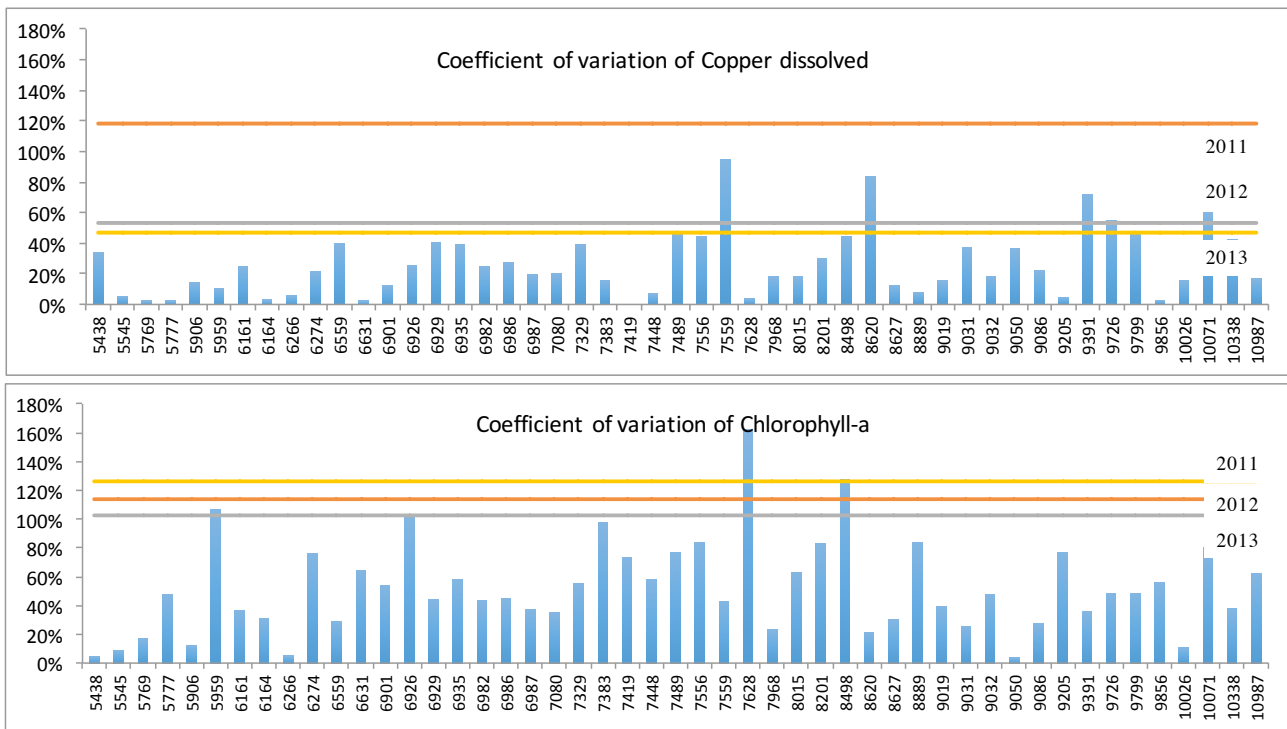


Figure 91 Coefficient of variation of the dissolved copper (above) and the chlorophyll-a concentration (below); the x-axis indicates the lake numbers, the blue bar indicates each lake CV and the colored horizontal lines indicate the 49 lake CV for each year

As we can observe in the Figure 57, CV shows that the variability between the lakes is much higher than the inter annual variability of a single lake except for certain lakes. In other words, the values of different lakes are representative of the quality state range of these lakes in the region. We also observe that the variability between the lakes is different for the dissolved copper and the chlorophyll-a concentration. For the same lake, CV of dissolved copper is lower than CV of chlorophyll-a.

5.4. Cartography of parameters

In this section, we present an overview of the dissolved metal concentrations of the 49 lakes in Ile-de-France region. The mapped concentration is the median concentration for the three years. Because of some outlier points for some metals, we supposed that the median value reflects better an overview of eco-sanitary status of the lakes than the average value. In the figures below (Figure 92 to Figure 96), we present the maps of chromium, nickel, copper, zinc, cadmium. Additionally, we compare the distribution of these concentrations with the standard EQS. All exceeded values are in red. The size of the circles is proportional to the concentration value.

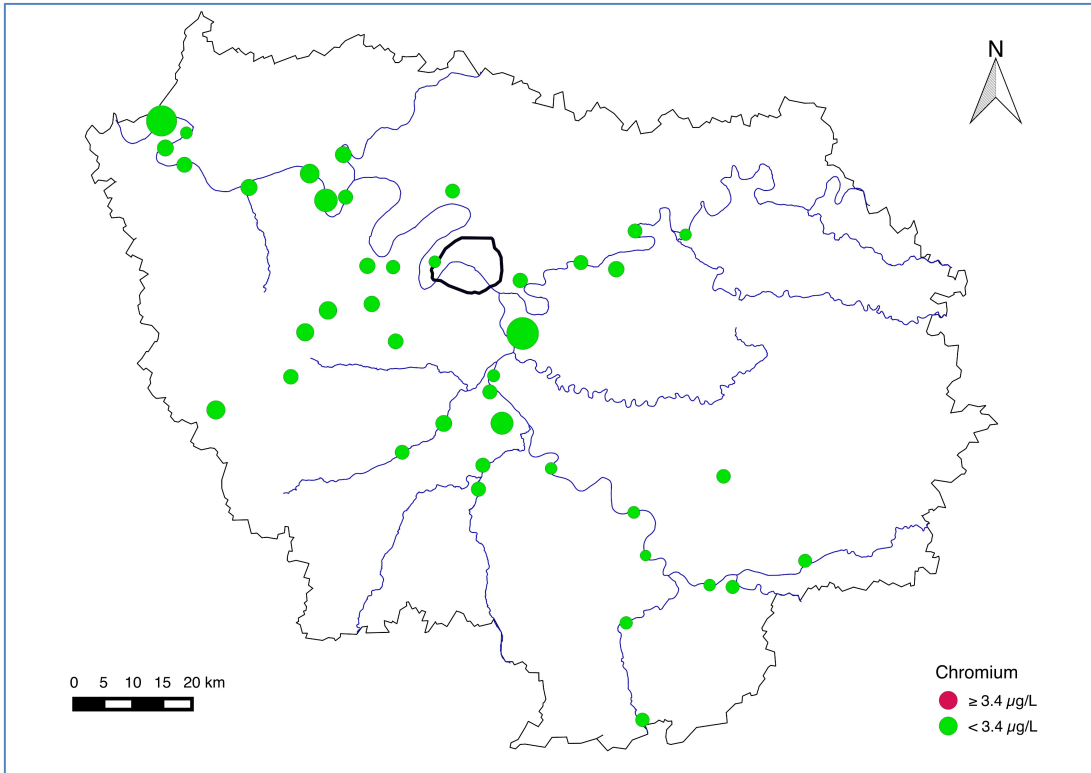


Figure 92 Dissolved chromium concentration in Ile-de-France region

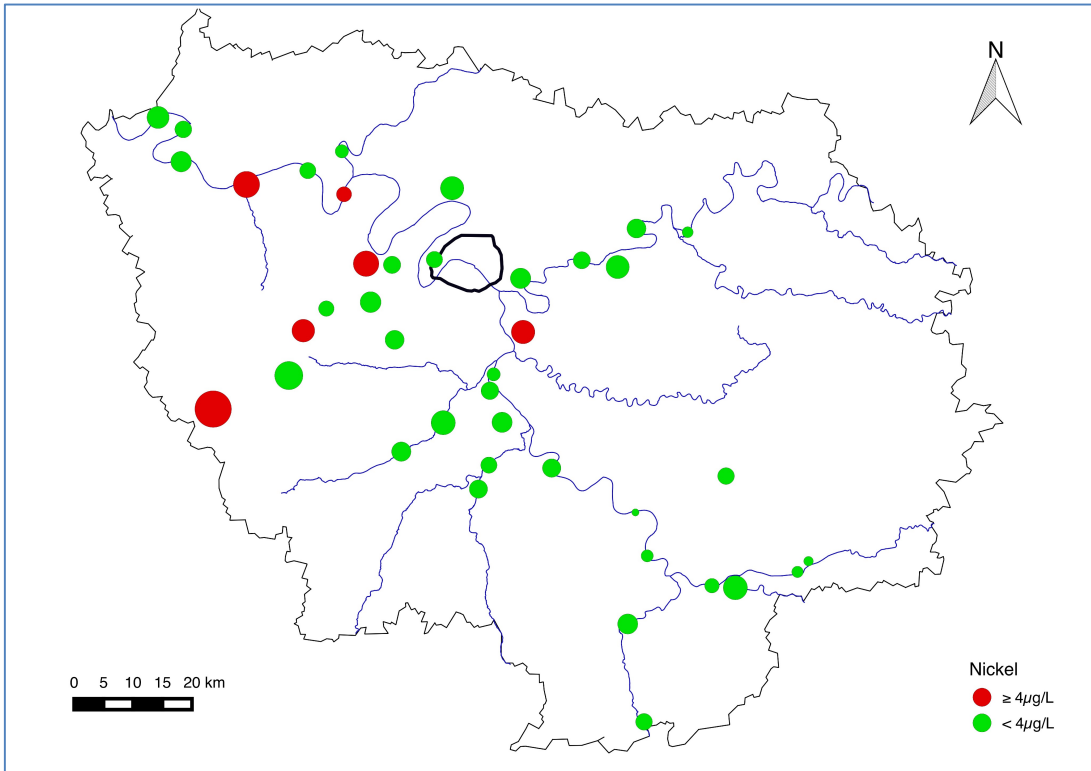


Figure 93 Dissolved nickel concentration in Ile-de-France region

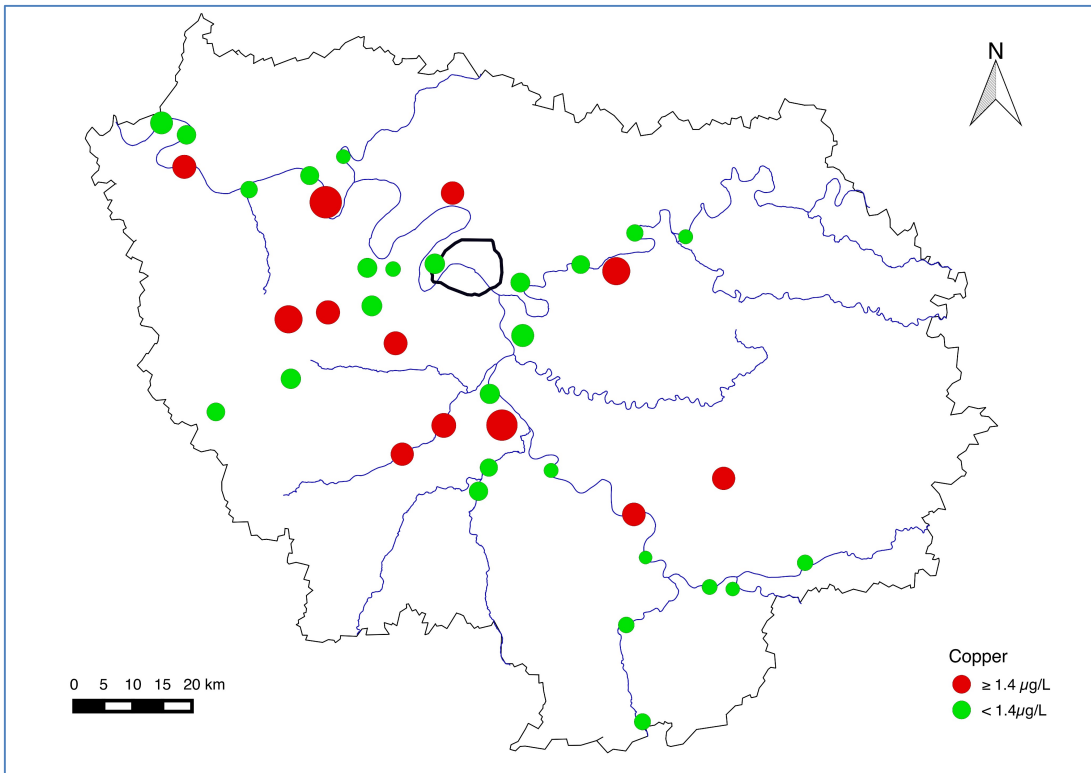


Figure 94 Dissolved copper concentration in Ile-de-France region

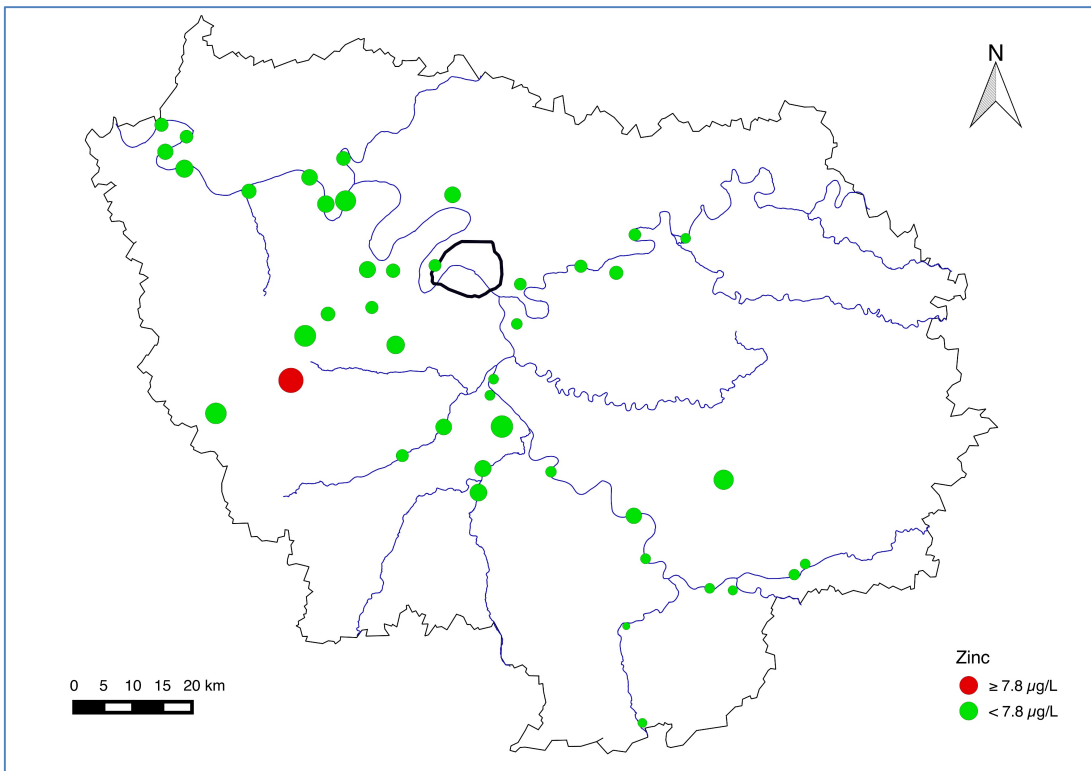


Figure 95 Dissolved zinc concentration in Ile-de-France region

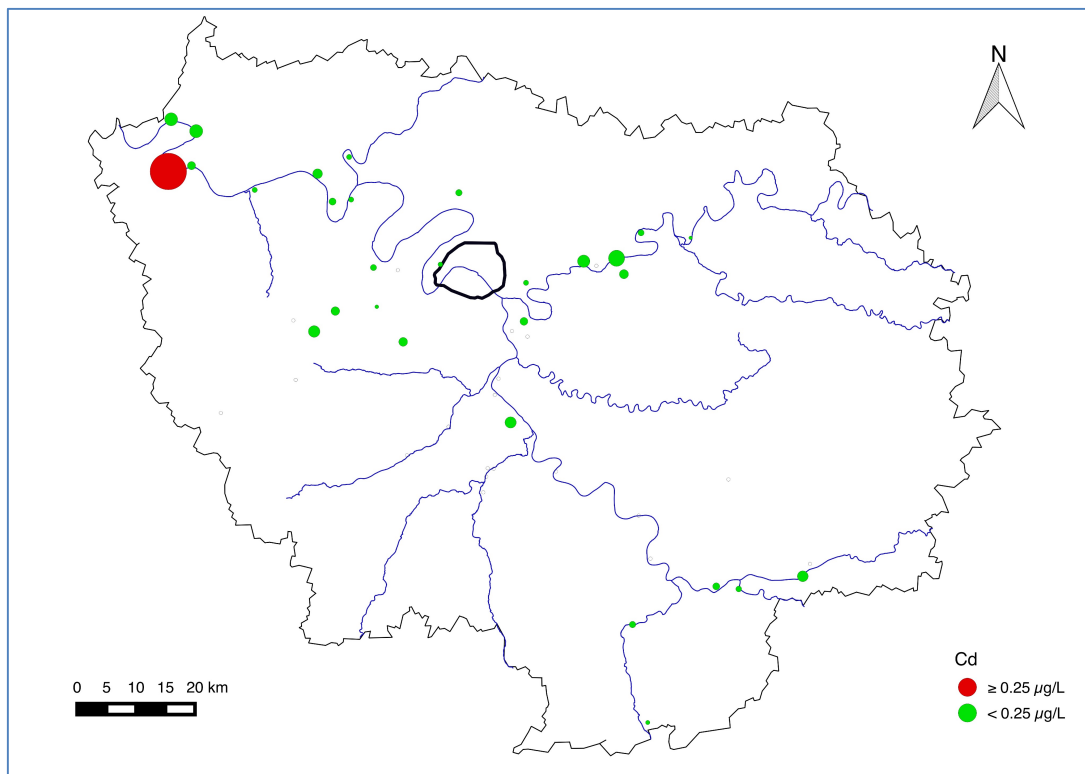


Figure 96 Dissolved cadmium concentration in Ile-de-France region

The dissolved Cr does not overpass the EQS value. The dissolved Ni overpasses the EQS value in 6 lakes, mainly in the Western part of the region. The dissolved Cu overpasses the EQS value in 12 lakes, without any specific geographical pattern. The dissolved Cd and Zn EQS are overpassed only in 1 lake

5.5. Land use of region Ile-de-France

As mentioned in the bibliography chapter, trace metals are naturally present in environment and have various anthropogenic sources. Thus, trace metals are strongly related to human activities. With an increasing urbanization, the water bodies are highly impacted by urban storm water discharge (Wash et al., 2005).

Many researches have showed the relation between land use and water quality. Reducing pressure in the catchment of seepage lakes might be expected to have a significant improvement of lake trophic status (Catherine et al., 2013). Zinc and copper concentrations are strongly impacted by suburban land use and imperviousness (Kuusisto-Hjort and Hjort 2013). Farm land and urban land correspond to higher metal levels in stream water than forest and green land (Shen et al., 2014). Land use should be considered as a driving parameter for trace metal loading of our 49 lakes of the Ile de France region.

Therefore, we included the land use of the 49 lakes into our statistical analysis. The land use database is provided by l'Institut d'aménagement et d'urbanisme de l'Ile de France (IAURIF). The database is detailed in the next paragraph.

Table 42 resumes all the datasets of land use in Ile de France region that IAURIF provided. IAURIF defines 4 land use datasets that go from 11 to 81 categories. The less detailed dataset with 11 land use categories is freely available at the website of IAURIF. IAURIF provided us with the

dataset that contains 11 to 47 land use categories. As shown below in Figure 64, the less detailed dataset of 11 categories contains geographical information about the following land use: Forests, Semi natural environments. Agricultural areas, water, artificial open spaces, individual housing, collective housing, activities, facilities, transportation and quarries, landfills and building sites. In each category, we can find more detailed information in the other datasets. As an example, agricultural areas include the semi-natural environments, field crops and other crops. Inside the field crops, we have ploughed lands and grasslands.

In this research, a detailed land use dataset helped us to get an overview of land use of the whole region, to understand the land use of each considered lake and to explain some anthropogenic impacts on the lakes.

In peri urban and urban areas, defining the water body watershed is not obvious: contribution of stormwater drainage network, modified river courses, contribution of underground water... Therefore, in order to take into account the land use impact on each lake, we suggest here two alternatives: using the land use of the watershed or using the land use of a buffer zone surrounding the lake. In the first approach, the watershed was delimited according to Catherine (2009) using a digital elevation model (e.g. BDAlti-IGN). In the second option, we consider that the impact of land use is related to an area directly surrounding the lake. We considered different buffer sizes from 500m to 5km diameters. Finally, we decided to consider a 2-km buffer zone.

5.6. The 2km buffer zone

In the 2km buffer zone around the lakes we considered the 11 landuse category dataset. As an example, the 11 landuse categories are presented in Figure 97 for Lake Créteil. For the 49 lakes, the land use in the 2km buffer zone is presented in Figure 98.

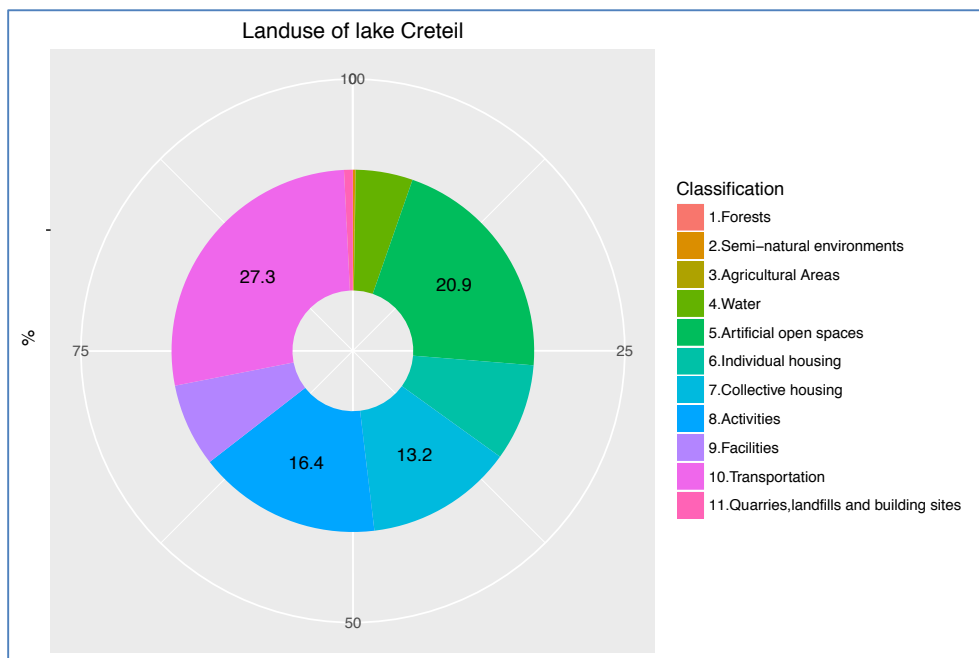


Figure 97 Example of the 11 landuse categories in the 2km buffer zone around Lake Créteil

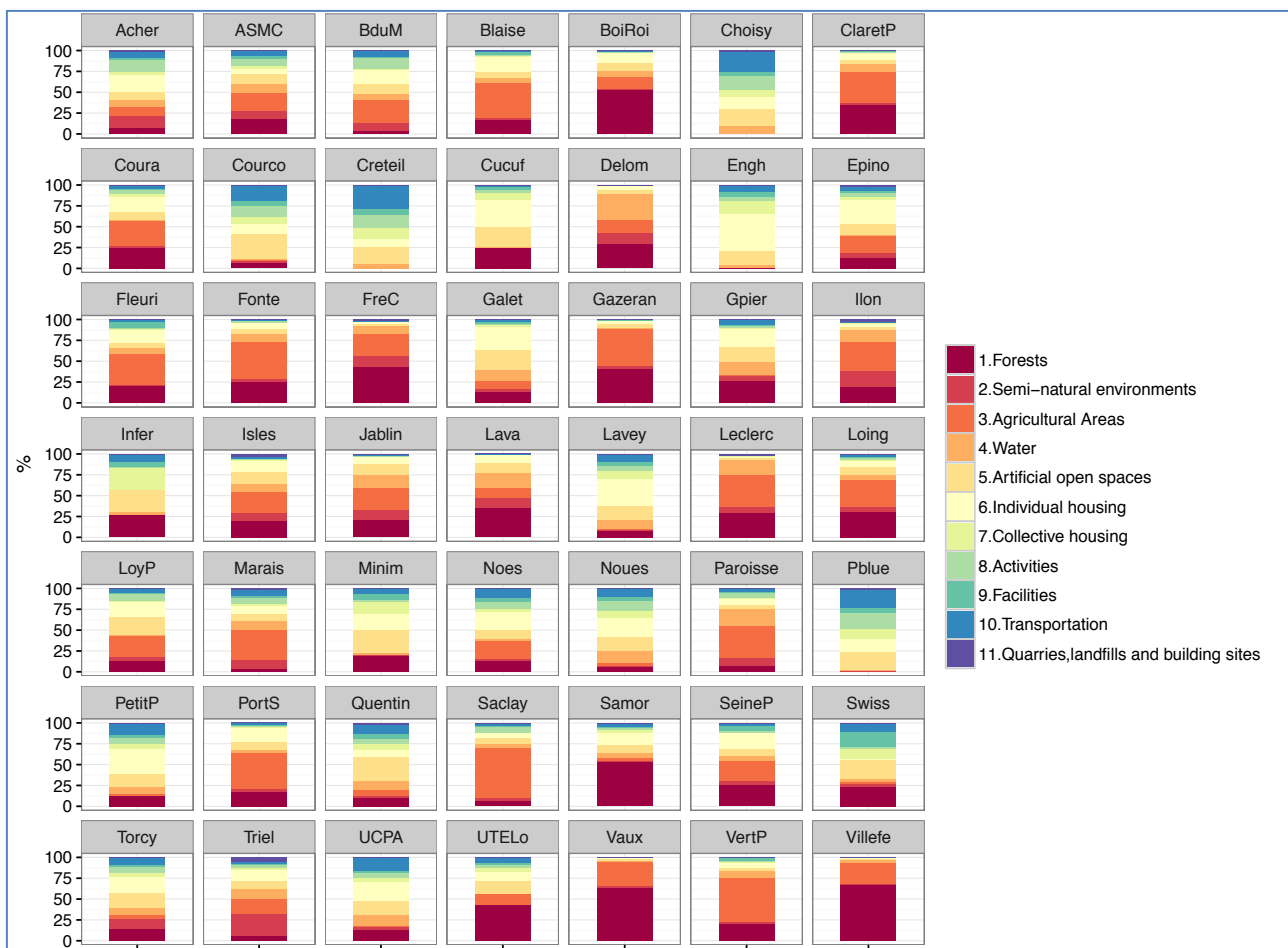


Figure 98 The 11 landuse categories in the 2km buffer zone around the lakes

5.7. Statistical Analysis

In order to explain the variation of the metal concentrations in the 49 lakes, the landuse around the lakes and the hydrological and morphological characteristics of the lakes must be considered. The hydrological and limnological variables are the following: lake volume, watershed surface (surface), altitude (alt), connection to the surface hydrological network (connection), drainage index (li)... Because of the regulatory context, the variables to explain are the dissolved metal concentrations.

In this section, we compare 3 different statistical approaches: Linear Regression (LM), single regression tree (CART) and Random Forest (RF) models.

The relationships between the trace metal concentrations and other environmental variables are complex. The descriptive statistics gave us very few information about these relationships. In order to better understand these relationships, we applied different statistical methods such as linear regression, decision tree regression and random forest models

The three models mentioned above shared a common point: each model is trained with 500 times bootstrap. It means that each model was trained 500 times on 500 subsets of the database.

5.7.1. Linear models

The most basic model is the linear regression. One of our first question is whether the dissolved metal concentration in the 49 lakes is linearly linked to the environmental variables. In order to answer this question, we elaborated a linear regression based on a stepwise variable selection.

Before using the statistical model, we performed a detailed exploratory study of the database. The correlation matrix between the metals and the environmental data has suggested that there was no high linear correlation between variables. We could expect that the linear model would give poor results.

5.7.2. Regression tree (Decision Tree)

The regression tree is a part of the Random Forest model. Instead of generating randomly a forest of regressions, we generated here only one regression tree to study the partition of the variables. The objective is to equitably divide the data into small groups with respect to the variable values.

As an example, the dissolved cobalt concentration can be divided according to environmental variables such as the landuse (Figure 99)

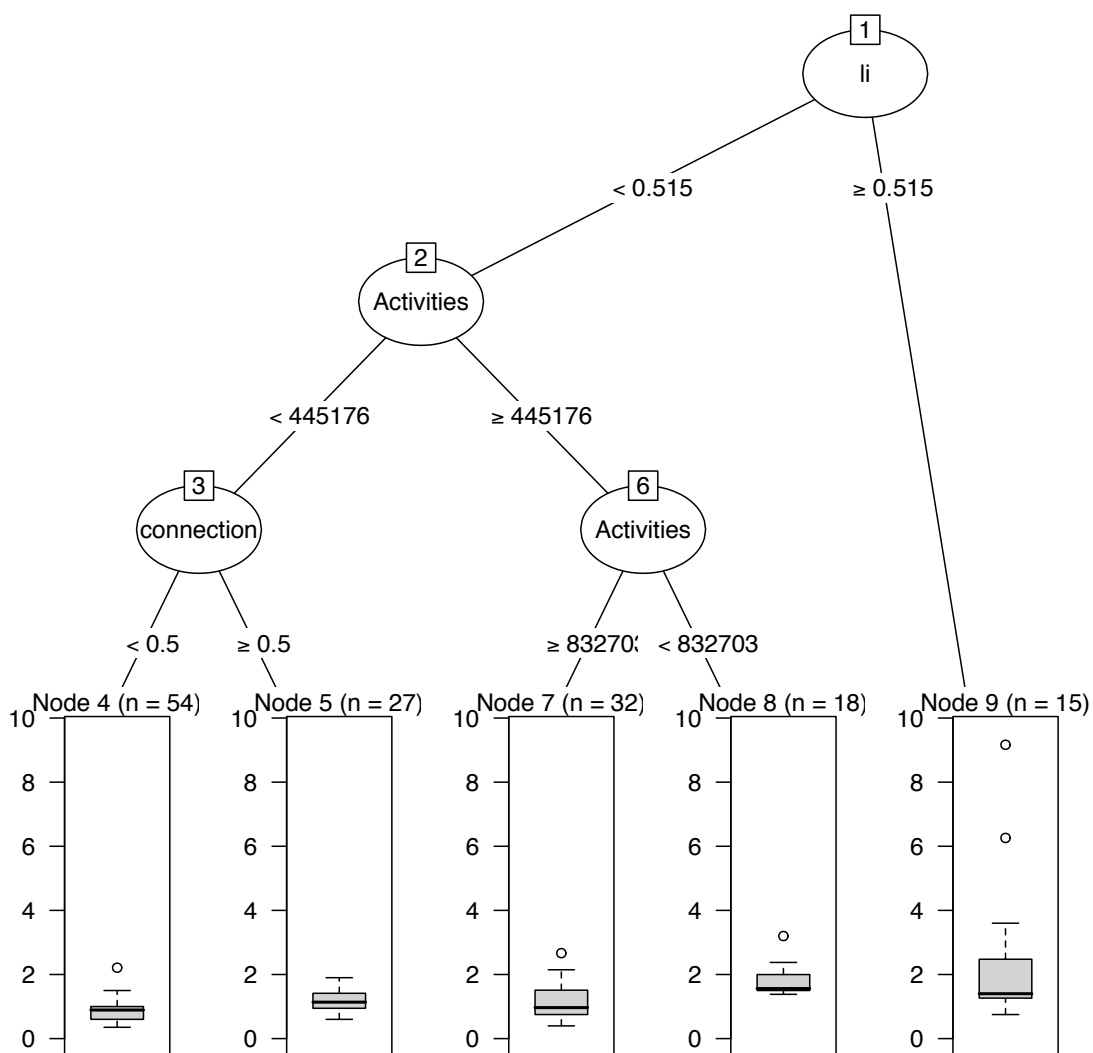


Figure 99 Regression tree for the dissolved copper concentration

5.7.3. Random Forest

As mentioned above, the Random Forest model generates randomly a forest of regression trees with the bootstrap. The Random Forest principles are discussed in the chapter Material and Methods.

5.7.4. Comparison between the three models

The performance of the three models was assessed by comparing the R squared values obtained with 500 bootstrap simulations of the dissolved metals, Cr (Figure 100), Co (Figure 101), Ni (Figure 102) Cu (Figure 103), Zn (Figure 104), Pb (Figure 105). The R squared values of the three models are indicated on the x-axis. The vertical blue line represents the average R squared of the three models. The summary of the R squared median values is presented in Table 55.

Table 55 Median of the R squared values for the three models

Metal	Median		
	RF	LM	CART
Cr	0.02	0.08	0.03
Co	0.65	0.32	0.29
Ni	0.85	0.45	0.35
Cu	0.25	0.30	0.15
Zn	0.40	0.22	0.20
Pb	0.19	0.25	0.17

For Cr, the performance of the three models are very low. For Co, Ni and Zn, the performance of the RF model is much better, particularly for Co and Ni. For Pb and Cu, the performance of the three models are similar and rather low.

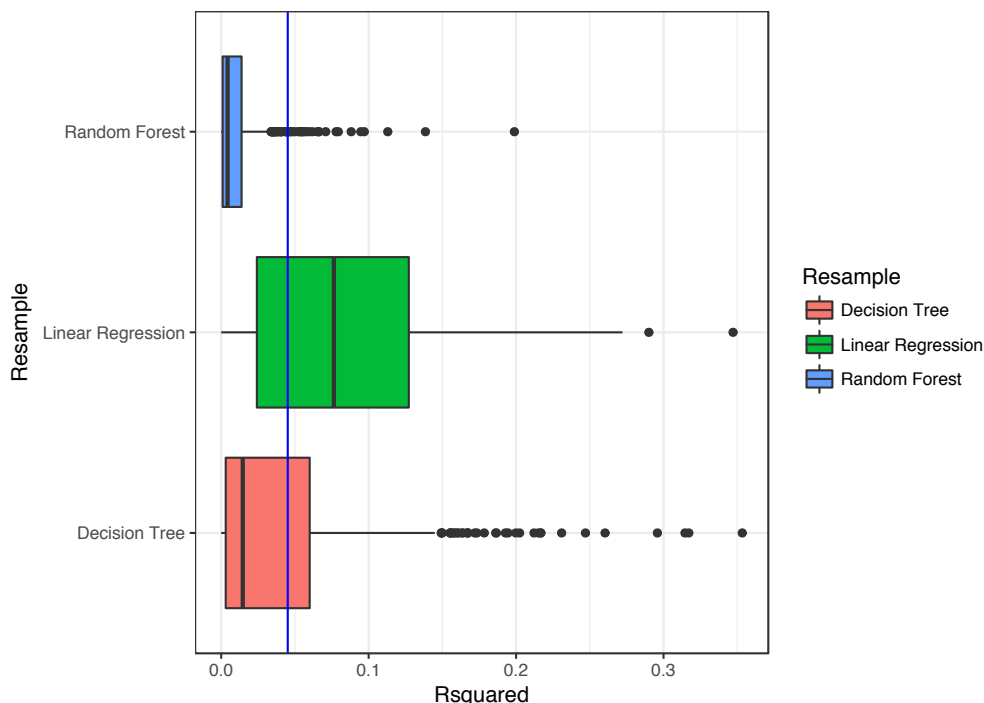


Figure 100 Comparison of three models performance for the dissolved chromium

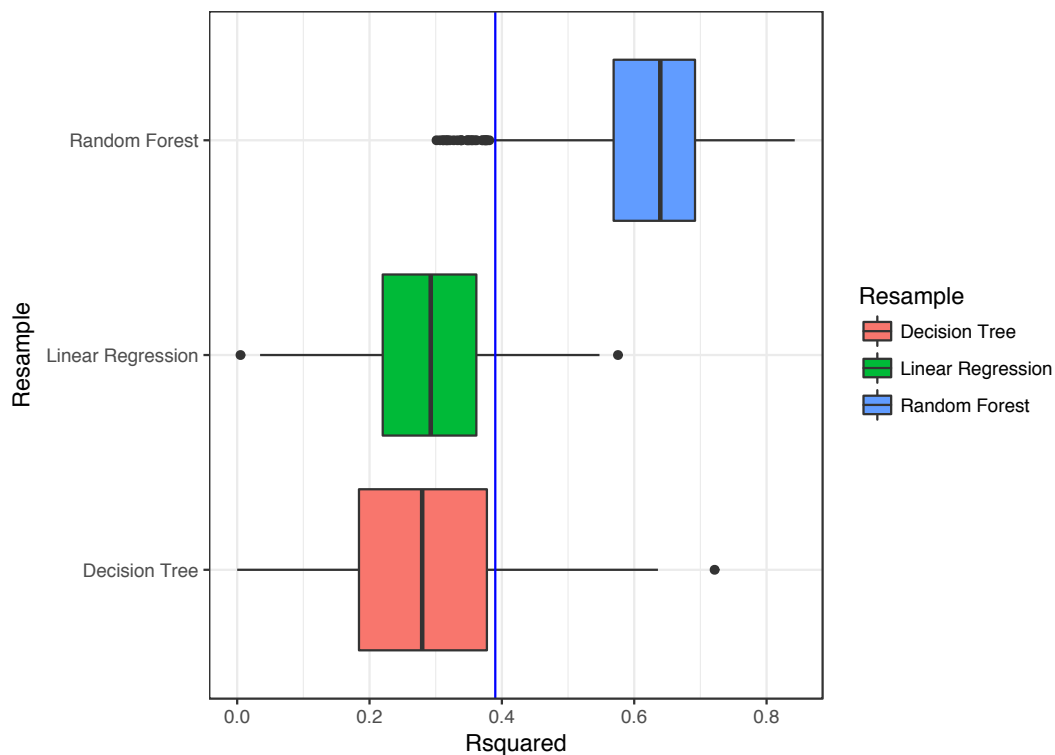


Figure 101 Comparison of three models performance for the dissolved Cobalt

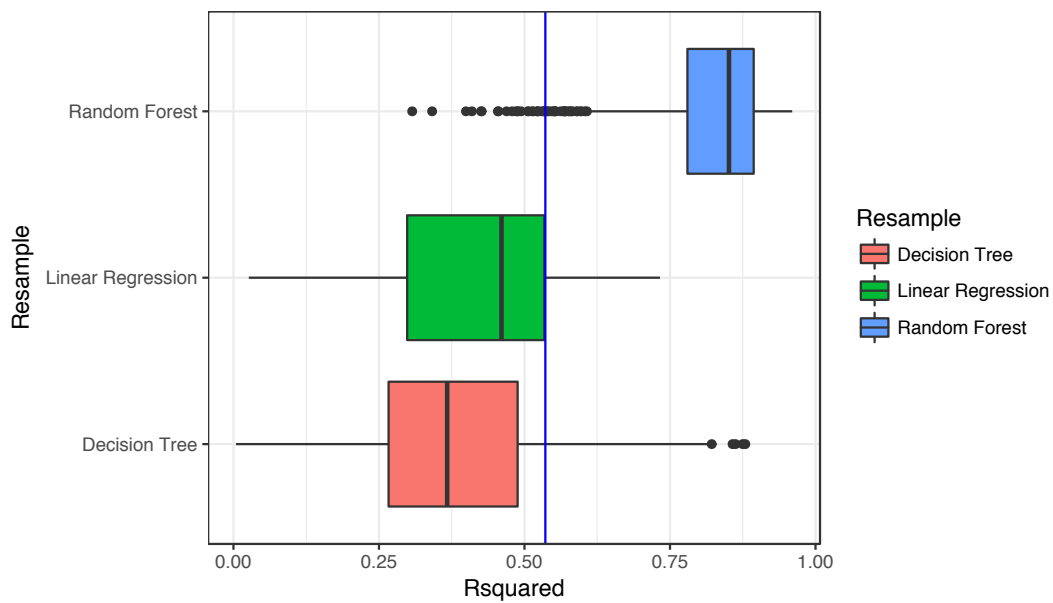


Figure 102 Comparison of three models performance for the dissolved Nickel

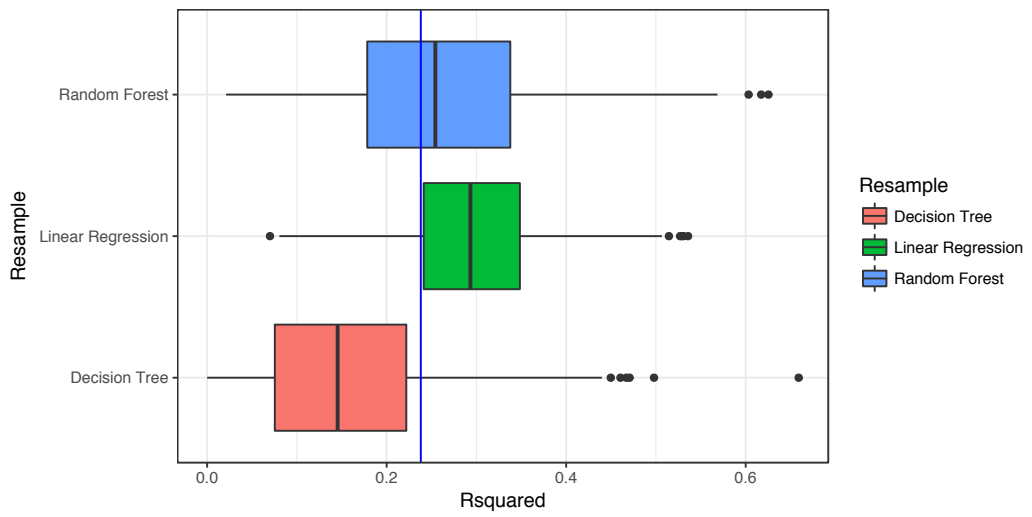


Figure 103 Comparison of three models performance for the dissolved Copper

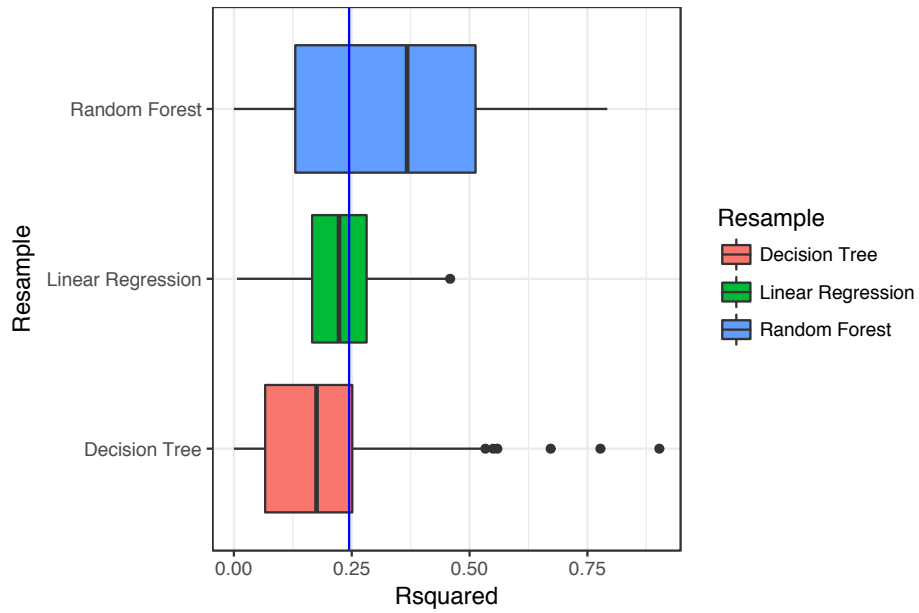


Figure 104 Comparison of three models performance for the dissolved Zinc

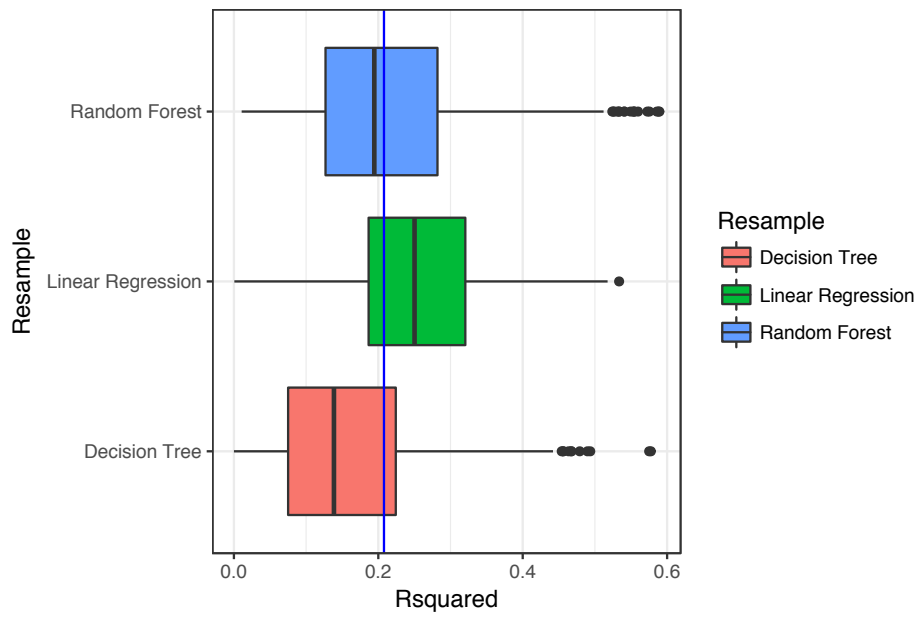


Figure 105 Comparison of three models performance for the dissolved Lead

Table 56 The landuse definition according to the Institut d'aménagement et d'urbanisme de la région Île-de-France (IAURIF)

11 categories	24 categories	47 categories
1 Forests	1 Forests	1 Wood or forests 2 Cutting or clearings in forests
2 Semi-natural environments	2 Semi-natural environments	3 Poplar plantations 4 Semi-natural environments
3 Agricultural Areas	3 Field crops 4 Other crops	5 Ploughed lands 6 Grasslands 7 Orchards, nurseries 8 Market gardening, horticulture 9 Intensive greenhouse cultivation
4 Water	5 Water	10 Water
5 Artificial open spaces	6 Urban green spaces	11 Parks or gardens 12 Family gardens 13 Gardens of housing
	7 Open spaces for sports	14 Outdoor sports grounds 15 Large surface sport facilities
	8 Open spaces for leisure and tourism	16 Camping, caravanning
	9 Cemeteries	17 Parks related to leisure activities except castles parks 18 Cemeteries
	10 Other open spaces	19 Sodded areas with or without shrubs 20 Empty site
6 Individual housing	11 Individual housing	21 Individual housing 22 Set of identical individual housing 23 Rural housing
7 Collective housing	12 Collective housing	24 Low continuous housing 25 High continuous collective housing 26 Discontinuous collective housing
	13 Other housing	27 Other housing
8 Activities	14 Economic and industrial activities 15 Logistical warehouses 16 Shops 17 Offices	28 Facilities for water, sanitation and energy 29 Zones or spaces allocated for activities 30 Logistical warehouses 31 Shops 32 Offices

11 categories	24 categories	47 categories
9 Facilities	18 Sport 19 Education facilities 20 Healthcare facilities 21 Cultural, touristic and recreational facilities 22 Other facilities	33 Sport premises or facilities 34 Education premises 35 Healthcare premises 36 Large conference and convention centers 37 Cultural and recreational facilities 38 Administrations, official organizations 39 Other public welcoming facilities
10 Transportation	23 Transportation	40 Transmission of rail transportation 41 Right-of-way 42 Parking areas Transmission of rail transportation 43 Bus stations, depots 44 Airport facilities
11 Quarries, landfills and building sites	24 Quarries, landfills and building sites	45 Materials Extraction 46 Landfills 47 Building sites

5.8. Random Forest model

According to the results obtained (see section 4.3.7.4), the performance of the Random Forest model is better than both other models.

Therefore, we decided to apply this model to study the relationship of the dissolved metal concentration and the environmental variables (limnological, hydrological and landuse). The objectives of this section are to present the different steps from the exploration of the dataset to the parametrization of the RF model. After the constitution of the final dataset, we will present the results of different tests:

- the performance of the RF model on the lake scale dataset and on the catchment scale dataset
- the performance of the RF model with the land use inside the watershed of the lakes or inside their buffer zone
- the performance of the RF model on the different size of the buffer zone

5.8.1. Missing values

As mentioned before, the RF model does not accept missing values. The missing values are presented in the following figures: for the limnological variables (Figure 106), for the hydrological and landuse variables (Figure 107) and for the dissolved metal concentrations (Figure 108).

The left zone of the graph corresponds to the proportion of missing values for each variable. The right zone corresponds to the proportion of missing values for a combination of variables (yellow = missing, and blue = not missing).

For the limnological data (Figure 106 and Table 57), the maximal percent of the missing values is more than 30% for O₂ and NO₃ concentrations. The other variables have the proportion of missing values that varies from 0 to less than 15%. At the right zone of the graph, we have 44 on 146 rows where all the data are available except the NO₃ concentration and 42 on 146 rows for all data except the oxygen concentration.

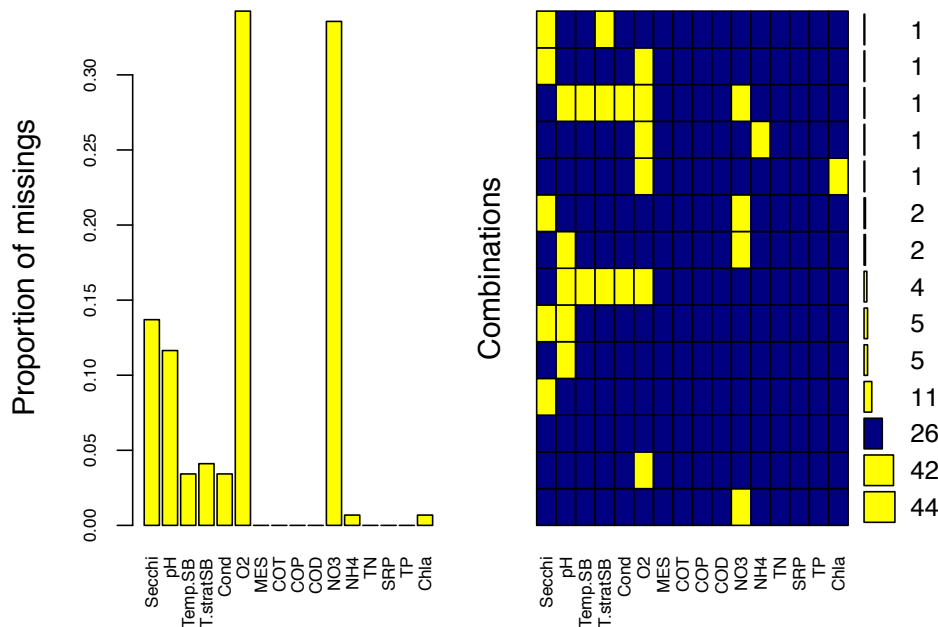


Figure 106 Proportion of missing values (left) and combination of limnological variables (right)

Table 57 Summary of the limnological data in the 49 lakes

Parameters	mean	sd	median	max	min	missing (%)
Secchi	1.22	1.06	0.80	6.17	0.17	14
pH	8.44	0.53	8.37	9.94	7.33	12
Temp.SB	22.40	2.86	21.79	29.81	15.89	3
T.stratSB	0.55	0.65	0.36	2.78	-0.01	4
Cond	584.38	385.42	477.00	2508.00	172.00	3
O2	9.95	2.44	9.99	16.40	1.92	34
MES	13.80	12.85	10.50	83.47	0.91	0
COT	9.09	4.43	8.01	23.76	1.79	0
COP	3.63	3.23	2.52	13.66	0.28	0
COD	5.45	2.17	5.08	12.72	1.38	0
NO3	44.47	91.38	1.70	353.31	0.00	34
NH4	3.38	10.73	1.42	111.80	0.00	1
TN	119.35	100.25	79.80	467.50	17.84	0
SRP	1.78	5.26	0.17	31.63	0.00	0
TP	4.62	6.58	2.41	40.35	0.14	0
Chla	46.00	56.19	23.67	271.43	0.83	1

The hydrological and landuse dataset is more complete (Figure 107 and Table 58). The maximal percent of missing values is 5% for the lake altitude. There are 129 on 146 rows that all the variables are available.

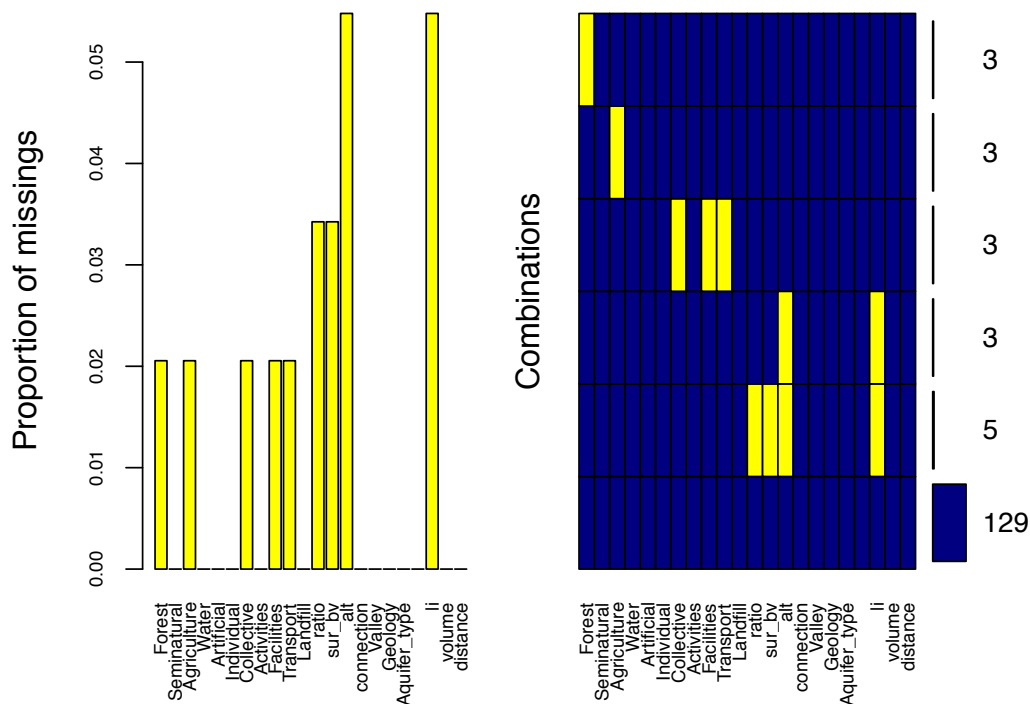


Figure 107 Proportion of missing values (left) and combination of hydrological and landuse data (right)

Table 58 Summary of the hydrological and landuse data in the 49 lakes

Metal	mean	sd	median	max	min	missing (%)
Forest	2697884.12	1986728.82	2427233.75	8463071.42	8535.99	2
Seminatural	659518.37	688687.55	393957.86	3258640.25	11484.12	0
Agriculture	2523509.50	2041310.20	2695958.08	7477568.06	5866.72	2
Water	1005435.87	793750.94	945377.19	3967571.89	33527.60	0
Artificial	1628755.50	953064.07	1441220.52	3662903.53	134424.70	0
Individual	1752996.46	1220374.96	1659655.23	5514062.87	11721.00	0
Collective	531059.19	665961.34	263414.19	3189797.36	1221.37	2
Activities	609389.67	634638.75	315698.36	2485308.40	4596.41	0
Facilities	376434.01	411723.03	268045.11	2394267.85	5086.40	2
Transport	763391.96	798214.46	520723.15	3431544.47	3061.35	2
Landfill	100533.59	123068.01	44727.97	632458.36	144.51	0
ratio	1853.75	5062.80	7.06	20554.51	0.42	3
sur_bv	306662.10	882153.32	20445.90	4525926.00	3.15	3
alt	58.31	40.81	47.00	166.80	14.20	5
connection	0.55	0.98	0.00	3.00	0.00	0
Valley	1.23	0.42	1.00	2.00	1.00	0
Geology	1.78	0.98	1.00	4.00	1.00	0

The missing values of the dissolved metal concentrations are shown in Figure 108 and summarized in Table 59. The missingness of the metal data remains relatively low. The maximal

missingness is 32% for Zn and the minimal is 5% for Ni. There are 72 on 146 rows of the data where every variable is available.

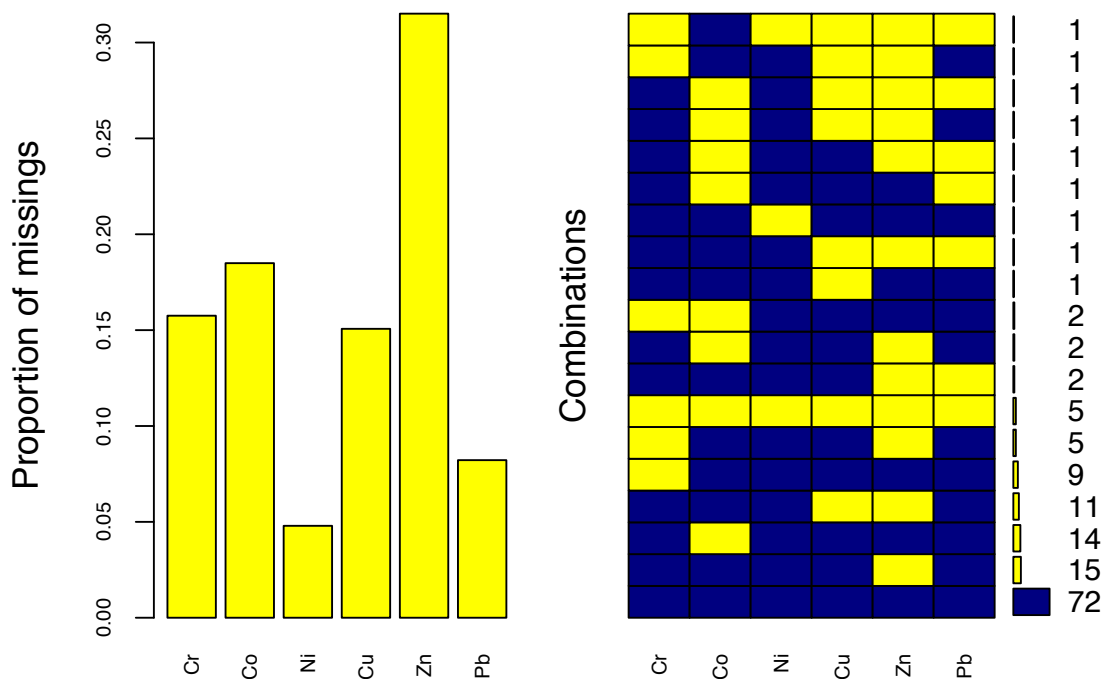


Figure 108 Proportion of missing values (left) and combination of the dissolved metal concentration (right)

Table 59 Summary of the dissolved metal concentrations in the 49 lakes

Metal	mean	sd	median	max	min	missing (%)
Cr	0.35	0.44	0.20	2.19	0.04	16
Co	0.24	0.14	0.20	0.82	0.05	18
Ni	2.86	2.86	1.98	20.74	0.60	5
Cu	1.25	1.02	1.00	9.17	0.35	15
Zn	4.49	4.50	3.05	29.40	0.80	32
Pb	0.17	0.24	0.10	1.59	0.00	8

In general, the dataset of the project PULSE is very complete. The missing value treatment will not generate much bias.

5.8.2. Missing value treatment

The missing values must be substituted or excluded in the final dataset before training the RF model. As mentioned before, the missing value treatment is delicate. Exclusion or imputation could make the dataset either better or worst. We decided to use the imputation algorithm included in the RF model for all variables where the missingness is below 35% and to exclude the variables where the missingness overpasses 35%.

5.8.3. The final dataset

After the missing value treatment, the retained variables can be distinguished into 3 categories: the limnological variables (Table 60), the hydrological and landuse variables (Table 61) and the dissolved metals concentrations (Table 62)

The first sub dataset contains the limnological variables (Table 60) that are used later for the lake-scale RF model. It includes the *in-situ* data and the laboratory analysis of the water samples collected during the PULSE campaigns. Some of these variables are calculated from the data such as the thermal stratification value and the integrated temperature of water column.

Table 60 Limnological variables used in the RF model

Variables	Description	Unit	Reference
Secchi	Secchi depth	m	PULSE
pH	pH	-	
Temp.SB	Integrated temperature of water column measured by Seabird's temperature sensor	°C	
Thermal.strat	Thermal stratification (Δ temp surface/bottom par m)	°C/m	
Cond	Electrical conductivity	μ S/cm	
O2	Dissolved oxygen concentration	mg/L	
MES	Suspension matter	mg/L	
COT	Total organic carbon	mgC/L	
COP	Particulate Organic Carbon	mgC/L	
COD	Dissolved Organic Carbon	mgC/L	
NO3	Nitrate concentration	μ mol/L	
NH4	Ammonium concentration	μ mol/L	
TN	Total nitrogen concentration	μ mol/L	
SRP	Soluble Reactive Phosphorous	μ mol/L	
TP	Total phosphore concentration	μ mol/L	
Chla	Chlorophyll-a concentration	μ g/L	
MCYST	Microcystine-LR equivalent concentration	μ g eq. MC-LR/L	
GreenBBE	Chlorophyceae biomass	μ g Chla/L	
Blue.BBE	Cyanobactery biomass	μ g Chla/L	
BrownBBE	Dinophyta and Diatom biomass	μ g Chla/L	
RedBBE	Cryptophyta and red cyanobacteria biomass	μ g Chla/L	
CDOMBBE	Yellow substances concentration	μ g Chla/L	

The second sub-dataset (Table 61) includes the hydrological and landuse variables which are used for the catchment-scale RF model. The landuse variables are the 11 categories of the dataset provided by IAURIF. The hydrological variables include the descriptive variables of each lake characteristics and its watershed (lake area, altitude, watershed area, connection to a river or a stream, percentage of impervious area, lake volume) and geomorphological variables that describe the lake classification based on these variables.

In this paragraph, we describe more carefully the geomorphological variables. The “Geology” variable includes the information about the type of geology of each lake. This variable is split into 4 sub-categories:

- Class V1: lake in a major valley with modern alluvium; in this class, 4 types exist according to aquifer lithology: for instance, if lake fed by Chalk aquifer, type V1-NCC.
- Class V2: lake in a major valley with a complex of modern and ancient alluvium; again, 4 types from aquifer lithology, e.g. V2-NCD fed by other limestone aquifer (Brie, Champigny).
- Type P3-NS: lake in a minor valley on a plateau (> 70 m), both with and without presence of modern alluvium, fed by a sandy aquifer (sometimes mixed with a calcareous aquifer).
- Type P4: lake fed only by water runoff of its watershed.

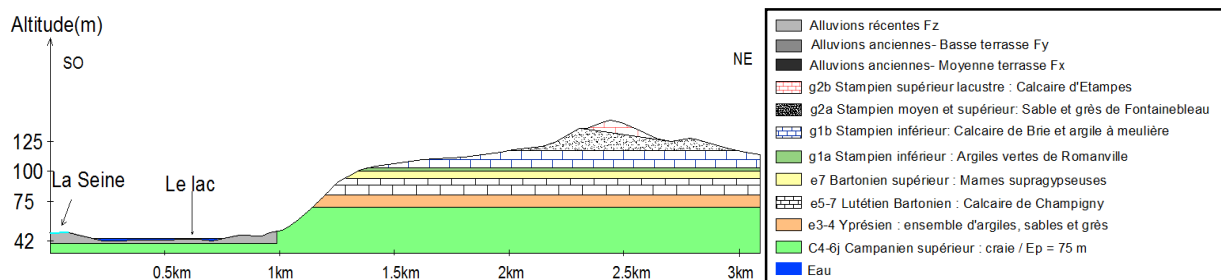


Figure 109 Example of a geological cross section for a lake of type V1-NCC (Ahmad Ali 2016)

The “Aquifer_type” variable indicates the type of aquifer of each lake. There are 4 types of aquifers:

- Sandy aquifer: water is more acidic
- Calcareous aquifer: CaCO₃ dominant, water can be basic or neutral
- Calcareous aquifer with a probable presence of gypsum: sulfate and magnesium concentration is abnormal
- Calcareous aquifer with dominance of chalk

The “Cross_Val_aqui” variable is a crossed variable between the “Valley” and “Aquifer_type” variable.

Table 61 Hydrological and landuse variables used in the RF model

Variables	Description	Unit	Reference
Surface	Lake area	ha	(2)
Forest	Landuse	ha	IAURIF
Seminatural	Landuse	ha	IAURIF
Agriculture	Landuse	ha	IAURIF
Water	Landuse	ha	IAURIF
Artificial	Landuse	ha	IAURIF
Individual	Landuse	ha	IAURIF
Collective	Landuse	ha	IAURIF
Activities	Landuse	ha	IAURIF
Facilities	Landuse	ha	IAURIF
Transport	Landuse	ha	IAURIF
Landfill	Landuse	ha	IAURIF
sur_bv	Watershed area	ha	(1),(2)
alt	Altitude lake	m	(2)
connection	Linked to a river or a stream	factor	(2)
Valley	Lake in the valley or not	factor	(2)
Geology	Geology lake	factor	(2)
Aquifer_type	Aquifer type	factor	(2)
Cross_Val_aqui	Crossed variable between Valley and Aquifer type	factor	(2)
li	Percentage of Impervious Area	%	(1)
volume	Estimated lake volume	m3	PULSE

(1) Catherirne et al., 2010

(2) Ahamad Ali, 2016

The third sub-dataset includes the dissolved metal concentrations of Cr, Co, Ni, Cu, Zn and Pb.

Table 62 Dissolved metal concentrations used in the RF model

Variables	Description	Unit	Reference
Cr_D	Dissolved chromium concentration	µg/L	This study
Co_D	Dissolved cobalt concentration	µg/L	This study
Ni_D	Dissolved nickel concentration	µg/L	This study
Cu_D	Dissolved copper concentration	µg/L	This study
Zn_D	Dissolved zinc concentration	µg/L	This study
Pb_D	Dissolved lead concentration	µg/L	This study

5.8.4. Steps of the RF modelling

Figure 110 describes the successive steps of the RF modelling. The final RF model is a result of its previous modelling steps to determine the optimal parametrization set.

The final dataset, which contains the limnological variables in case of the lake-scale RF model or the hydrological and landuse variables for the catchment-scale RF model, is used as the initial dataset. With this dataset, we train for the first time the RF model to adjust it. The variable importance is ranked by the model to determine which variables to be retained according to (Janitza et al., 2013) (see section 3.6.2.3 in the chapter “Material and methods”). After this step, the RF model is trained

with the selected variables with 50 to 100 iterations and the best model is selected. The best model gives us the information on the parameters (n permutation, ntree, mtry, validation size). We use this parametrization for the final model. The final RF model contains the selected variables with the best combination of parameters and is split into two sub-datasets: training and testing data. The final results are evaluated by the Monte Carlo cross-validation (Mercier et al., 2011),

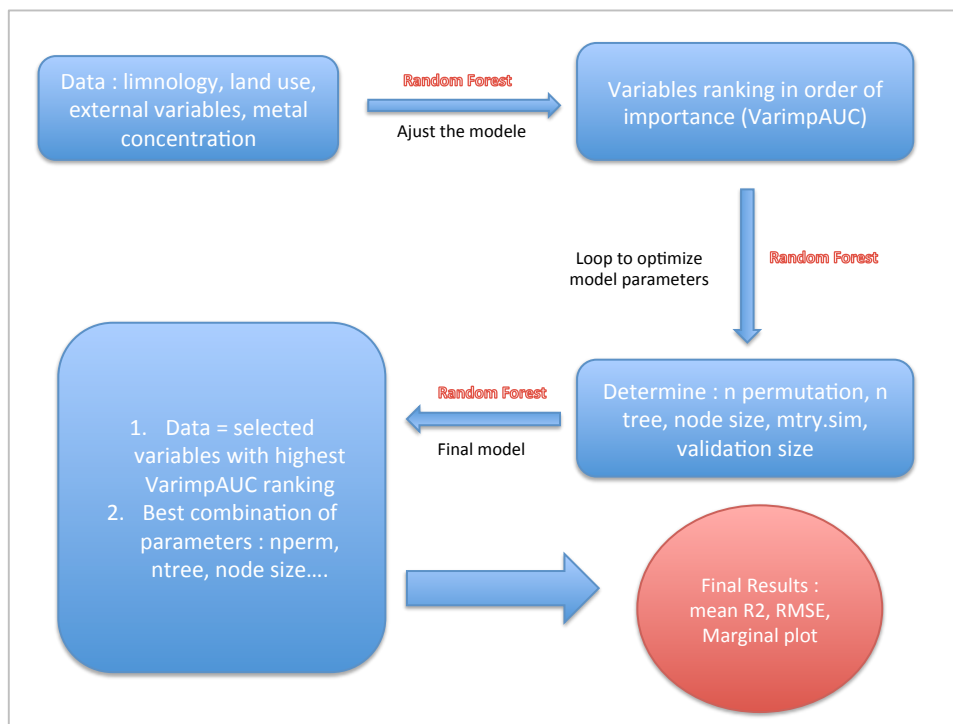


Figure 110 Steps of the RF modelling

5.8.5. Lake-scale and catchment-scale model

After determining the steps of the RF modelling, we applied the RF model on two datasets: lake-scale variables and catchment-scale variables. We called the first one the lake-scale RF model and the second one the catchment-scale RF model. Both models are trained in the same conditions.

The R squared values and their standard deviations of the two models are presented in Table 63. In general, the R squared values of the lake-scale RF model are lower than the ones of the catchment-scale model, except for Cr. However, the standard deviation of the R squared value of the lake-scale model is very high in comparison to the catchment-scale model.

Table 63 Performance of the lake-scale RF model and the catchment-scale RF model

Concentration ($\mu\text{g/L}$)	Lake-scale model		Catchment-scale model	
	R2 (mean)	R2 (sd)	R2 (mean)	R2 (sd)
Cr	0.40	0.24	0.03	0.04
Co	0.49	0.29	0.66	0.15
Ni	0.52	0.23	0.85	0.13

Cu	0.20	0.18	0.34	0.15
Zn	0.25	0.20	0.37	0.25
Pb	0.23	0.17	0.28	0.18

5.8.6. Size of the buffer zone

The next question is which size of the landuse buffer zone will give the best result in the RF model. In order to address this issue, we applied the RF model on the different buffer zones from 1km to 5km around the lakes. We present the R squared values and their standard deviations of the RF model with the different buffer zones from 1km to 5km (Table 64). The R squared value changes slightly from one buffer size to another. The 2km buffer zone gave the best results for all metals. The standard deviations are lower for the 2km buffer zone in comparison to the other buffer zones. According to this result, we decided to choose the 2km buffer zone for the final model.

Table 64 Influence of the buffer zone size on the performance of the model

Dissolved ($\mu\text{g/L}$)	1km		2km		3km		4km		5km	
	R2 (mean)	R2 (sd)	R2 (mean)	R2 (sd)	R2 (mean)	R2 (sd)	R2 (mean)	R2 (sd)	R2 (mean)	R2 (sd)
Cr	0.04	0.07	0.03	0.04	0.04	0.08	0.04	0.07	0.05	0.08
Co	0.64	0.19	0.66	0.15	0.68	0.20	0.69	0.20	0.67	0.18
Ni	0.82	0.16	0.85	0.13	0.82	0.18	0.82	0.19	0.82	0.17
Cu	0.41	0.19	0.34	0.15	0.40	0.18	0.39	0.19	0.38	0.17
Zn	0.32	0.31	0.37	0.25	0.32	0.31	0.3	0.31	0.30	0.30
Pb	0.31	0.23	0.28	0.18	0.34	0.22	0.34	0.23	0.35	0.24

5.8.7. Results of the catchment-scale Random Forest model

According to the multiple tests mentioned in the previous section, the final RF model is trained for the catchment-scale variables where the landuse variables are inside the 2km buffer zone. From now on, the RF model corresponds to the catchment-scale RF model.

The Table 65 shows the parameters used for the selected variables in the Random Forest model and the average R2 of the model. The random forest model is applied for all metals using 80% of dataset for training and 20% for validation. The model is applied for 1000 trees with different parameters (nvar, mtry, node size) depending on each metal. For the detailed explanation on the RF model parameters, see section 3.6.2.3 in the Material and Methods chapter. The cross validation is based on the Monte Carlo cross-validation method (Mercier et al., 2011): for each permutation, the subset of training and validation data is randomly generated.

The Random Forest model uses the selected variables (Table 66) to predict the dissolved metal concentrations. The accuracy of the model is best for dissolved nickel with ($R^2 = 0.85$). For other metals, the range of the R squared value is 0.03 – 0.66. The model can explain 85% of the variance of dissolved nickel using the selected variables: Activities, Semi natural, Land fill, Forest and Transport.

Table 65 Parametrization and results of random forest model on the dissolved metal concentrations

Concentration (µg/L)	Training (%)	nvar	mtry	node size	ntree	n permutation	R2 (fit)	R2 (mean)	R2 (sd)
Cr	0.8	5	3	5	1000	1000	0.41	0.03	0.04
Co	0.8	7	3	5	1000	1000	0.87	0.66	0.15
Ni	0.8	6	3	5	1000	1000	0.96	0.85	0.13
Cu	0.8	6	3	5	1000	1000	0.57	0.34	0.15
Zn	0.8	6	3	5	1000	1000	0.76	0.37	0.25
Pb	0.8	6	3	5	1000	1000	0.60	0.28	0.18

Table 66 shows the first 5 most important variables selected by the RF model for each dissolved metal concentrations.

Table 66 Top 5 explanatory variables selected by the RF model – 49 lakes

Dissolved metal (µg/L)	Ranked selected variables				
Co	Valley	Forest	Volume	Activities	Landfill
Ni	Activities	Semi natural	Land fill	Forest	Transport
Cu	li	Transport	Activities	Valley	Connection
Zn	Valley	Cross_val_aqui	Geology	Volume	Aquifer_type
Pb	Collective	Transport	li	Artificial	Activities

The relationship between the selected variables and the predicted variable, the dissolved nickel concentration is illustrated using the partial dependence plot (Figure 111). Among the selected variables, the marginal effect of the Activities and Forest land use showed a threshold effect.

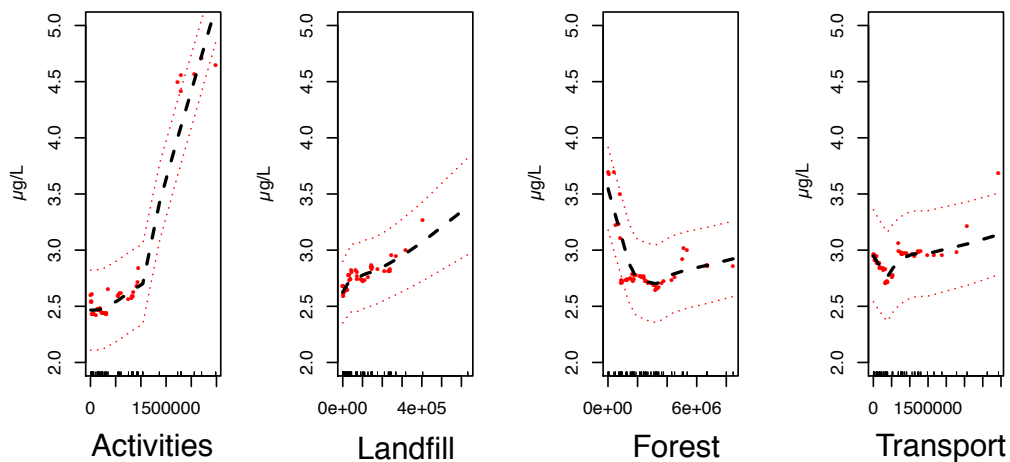


Figure 111 The marginal effect of catchment variables on the dissolved Ni concentration (95% confidence interval)

5.9. Conclusion

We investigated the concentrations of trace metals Cr, Co, Ni, Cu, Zn, Cd and Pb in the water column of 49 lakes in the Ile de France region. In this section, we presented the concentrations of total, dissolved and labile fraction of these metals. The concentrations remain similar during the 3 years, except Zn higher in 2013 and Pb higher in 2011. According to the European Union water directive, the Environmental Quality Standards (EQS) are related to dissolved metal concentration. The dissolved concentrations of Zn, Cu and Pb exceeded the maximum allowance concentration (MAC-EQS). We presented also maps of spatial distribution of the dissolved metals indicating the lakes where the EQS threshold is overpassed. The landuse categories were defined for the 49 lake watersheds and for the buffer zone around the lakes.

In order to explain the variation of the dissolved metal concentrations in the 49 lakes, we conducted a statistical analysis considering the landuse around the lakes, the hydrological and the limnological variables. Three different statistical approaches: Linear Regression (LM), single regression tree (CART) and Random Forest (RF) models were compared considering the landuse categories in the 2km buffer zone around the lakes. The RF model provided the best results.

The RF model showed that the landuse and hydrological variables explained better the variation of the dissolved metal concentrations than the limnological variables. The 2km buffer zone gave the best results with less deviations. Therefore, the final model was based on the landuse and hydrological variables with the 2km buffer zone.

As a final result of the modelling, the model indicated the most important explanatory variables for each metal. The best results were obtained for Ni ($R^2 = 0.85$) and Co ($R^2 = 0.66$).

6. General conclusion and perspectives

This thesis focused specifically on the trace metal concentrations and their speciation in the water column of urban lakes. This work was based on field survey and laboratory analysis during 3 years from 2011 to 2013. One of the most important results is to constitute a large environmental database of the water quality of Lake Créteil (France), Lake Pampulha (Brazil) and the 49 urban lakes in Ile de France region. More specifically, this thesis presents, for the first time to our knowledge, an overview of the trace metal concentrations and speciation and their time and space variation in these water bodies.

In the monthly monitoring of Lake Créteil and Lake Pampulha, we studied the trace metal evolution and their bioavailability at the monthly time step. In the 49 urban lakes in Ile-de-France region, we focused on the trace metal concentrations at a regional scale.

In the water column of Lake Pampulha and Lake Créteil, some similar features are registered: Cd concentration is very low in the water column, often below the quantification limit ($0.01\mu\text{g/L}$) of the analytical method; the time evolution of the total Ni concentration is low in the water column; Co is highly dissolved in the water column.

However, we observed some differences between the two lakes:

- In Lake Créteil, the dissolved and labile fractions of all metals do not present any spatial variation, neither in the horizontal nor in the vertical scales.
- In Lake Pampulha, the dissolved fractions of Cu and Zn are higher at the surface. The labile fraction of Co is higher at the bottom of the water column.
- The dissolved fraction of Ni, Cu and Zn is higher in Lake Créteil than in Lake Pampulha.

In the 49 urban lakes in Ile de France region, we observed a wide distribution of the Zn, Ni and Cu concentrations and a compact distribution of Cr, Co, Pb and Cd. The concentrations remain similar during the 3 years, except Zn higher in 2013 and Pb higher in 2011. We observed also that the inter-lake variability of the metal concentrations is much higher than the inter annual variability of these concentrations in a single lake.

We compared the metal concentrations in the studied lakes with the European Environmental Quality Standard (EQS). In Lake Créteil, all the Ni concentrations overpass the EQS and nearly 50% of Cu concentrations overpass the EQS.

In Lake Pampulha, no dissolved metal concentration overpasses the EQS, except one Cu value. The metal concentrations are also below the Brazilian standards.

In the 49 urban lakes in Ile de France region, the dissolved Cr, Co, Cd, Pb never overpass the EQS threshold. The dissolved concentrations of Ni, Zn, Cu overpass the EQS for some lakes, including Lake Creteil for Ni.

In order to estimate the impact of the raining events on the metal concentrations and bioavailability in Lake Creteil, we monitored specifically the stormwater outlet and the water column during 6 raining events in 2013. In the stormwater, the metal concentrations are several orders of magnitude higher than in the lake, excepted for Ni. Ni concentrations, which are high during the dry weather, remain at nearly the same level after the raining events. For 5 of the 6 monitored events, no spatial impact of the stormwater outlet is observed. For the first event, corresponding to the highest rainfall, a significant impact is observed only at the point close to the outlet.

After validating the database for all the studied lakes, our central scientific question was: “what is the role of the environmental variables on the trace metal speciation in these lakes?”. A first descriptive statistics analysis allowed us to better understand their evolution in the water column. However, it was not sufficient to explain the influence of the environmental variables on the variation

of the trace metal concentrations. We therefore applied a machine learning methodology on our dataset. This approach consists of (1) exploring every single variable to understand its distribution and their correlation, (2) selecting a statistical model based on these observations, (3) performing a careful preprocessing of the data and variable selection, and (4) modelling the trace metal concentrations and their speciation. Indeed, we used the statistical model as an explanatory model.

We tested three methods: linear regression, decision tree and an ensemble learning method – the Random Forest model. The Random Forest model turned out to be the most performant model.

We applied the Random Forest model on the Lake Pampulha dataset and the 49-urban lake dataset with two specific objectives: (1) in Lake Pampulha, understanding the role of environmental variables on the trace metal labile concentration, which is considered as potentially bioavailable and (2) in the 49 lakes, understanding the relationship of the environmental variables, more particularly the watershed variables, on the dissolved metal concentrations. The metal dissolved concentrations must comply with standards of the European Framework Water Directive. The analysis of the relationships between the trace metal speciation and the environmental variables provided key results of this thesis.

Regarding the watershed characteristics of the 49 lakes, we further analyzed the following aspects: (1) we refined the geomorphological variables of the lakes and (2) we identified the best scale of the landuse buffer zone. The geomorphological variables were divided into 4 categories (e.g. lake in a main valley with a specific aquifer type, lake only fed by water runoff). After a sensitivity analysis of the different sizes of the buffer zone (500m to 5km), the 2km buffer zone was chosen for the final model.

In Lake Pampulha, based on the monthly monitoring dataset, the Random Forest model highlighted the impact of the limnological variables on the trace metal speciation. Around 80% of the variance of the labile cobalt is explained by the Random Forest model. The limnological variables, Chlorophyll a, oxygen concentration, pH, and total phosphorus explained most of the variation of the labile Co fraction. We observed a similar behaviour during the monthly campaigns: cobalt is less labile in presence of an important phytoplankton biomass and under anoxic conditions. For the other metals, the Random Forest model did not succeed in explaining more than 50% of the relationships between the metals and the limnological variables.

In the 49 urban lakes in Ile de France region, according to the Random Forest model, the hydrological and landuse variables have an impact on the dissolved metal concentrations. The model gave a good result for Co (66% of explained variance) and very satisfying result for Ni (86% of explained variance). For Ni, the best explanatory variables are landuse variables such as activities, semi-natural, landfill, forest and transport. Activities include facilities for water, sanitation and energy, logistical warehouses, shops, office and zones or spaces allocated for these activities. An increase of the area with this landuse category in the buffer zone increases the dissolved Ni concentration. This result fits with Lake Creteil where dissolved Ni concentration is particularly high and where the “activities” and “landfill” landuse categories are the highest in the buffer zone.

To summarize, we present the range of the total metal concentrations in our studied lakes and in the Marne river (Figure 112). This figure highlights the very high Zn concentration in Lake Pampulha and the very high Ni concentration in Lake Créteil in comparison to the 49 lakes and the Marne river.

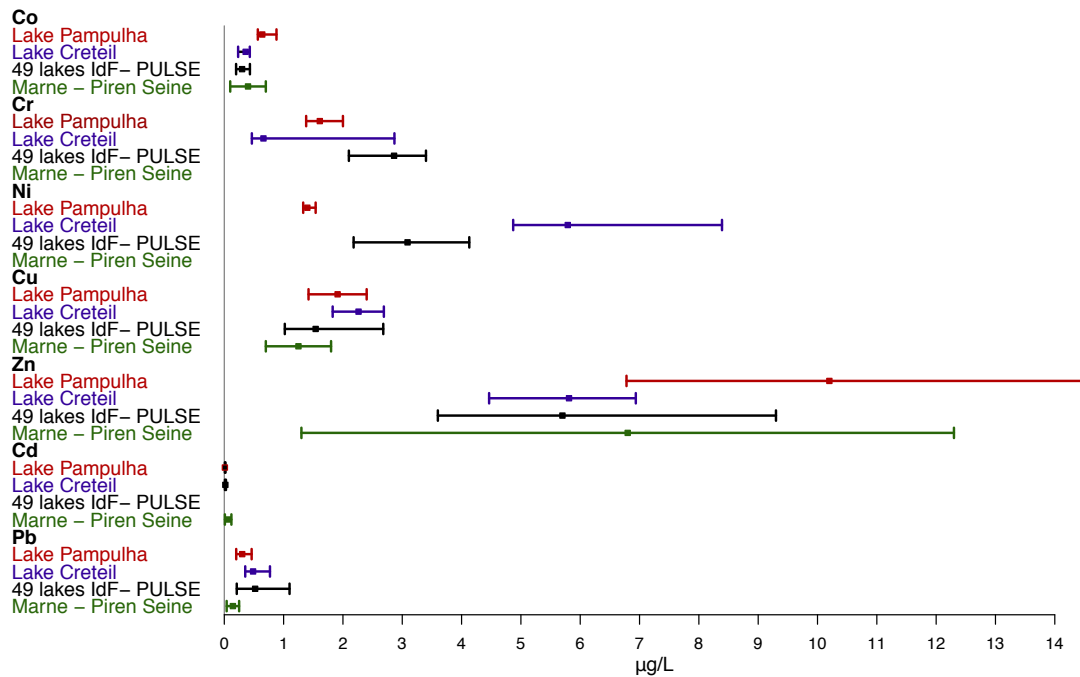


Figure 112 Range of the total metal concentrations in the studied lakes and in the Marne river (1st quartile, median and 3rd quartile)

We identified some important issues that could be addressed in the next studies. Firstly, it will be interesting to analyze our TEP data. The TEP measurements in Lake Pampulha and Lake Créteil were not performed for all the monthly campaigns due to the analysis difficulties. However, we could better analyze our existing data and collect more data in the future.

The second issue regards the application of the Random Forest model on the Lake Créteil database. A third perspective would be to take into account the watershed landuse of Lake Pampulha for comparing its impact on the metal concentrations with the Ile de France 49 lakes.

Finally, we would like to improve our statistical analysis of the 49 lake dataset with other variables, such as the distance between a lake and a reference point (e.g. outlet of the 49 lake whole watershed, transport intensity in the buffer zone...).

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8. Appendix

8.1. Speciation of trace metal in an urban tropical lake, Lake Pampulha, Brazil

The results obtained on Lake Pampulha were presented in June 2016 at the Novatech Congress. The extended abstract is included below.

Speciation of trace metals in an urban tropical lake, Lake Pampulha, Brazil

Spéciation des métaux traces dans un lac tropical
urbain, le lac de Pampulha, Brésil

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RÉSUMÉ

Il est essentiel d'évaluer l'impact du ruissellement des bassins versants urbains sur les milieux récepteurs. Les métaux traces représentent un risque important pour l'environnement et la santé publique. La concentration totale ne reflète pas leur impact environnemental, car leur toxicité dépend de leur spéciation dans le milieu aquatique. Les métaux traces sont principalement étudiés dans les affluents ou dans le sédiment des plans d'eau. Notre objectif est d'étudier la variation saisonnière de leur concentration dans la colonne d'eau et ainsi de contribuer à l'évaluation de l'impact du ruissellement urbain. Cette étude porte sur le suivi saisonnier, durant 10 mois incluant la saison sèche et la saison des pluies, des concentrations en métaux traces dans la colonne d'eau du lac de Pampulha et leur spéciation. Les métaux ont été échantillonnés à deux profondeurs au centre du lac. Trois fractions ont été analysées : total, dissous et inerte. Six métaux ont été étudiés : cadmium, cobalt, cuivre, plomb, nickel et zinc. Les concentrations en cadmium sont sous la limite de détection. Les résultats de spéciation révèlent une biodisponibilité variable de ces métaux, la plus forte étant celle du zinc (~60%). La biodisponibilité du cobalt, fortement dissous, varie selon la profondeur. La biodisponibilité du nickel reste assez stable en surface durant la période étudiée alors que celles du cuivre, du zinc et du plomb sont beaucoup plus variables.

ABSTRACT

Assessing the impact of urban catchment runoff on receiving waters must be addressed. Trace metal contamination represents a significant risk to the environment and public health. But total concentration does not reflect trace metal environmental impact because their toxicity depends especially on the nature of present species. Most studies address the fate of trace metals in lake tributaries or in lake sediments. Our aim was to focus on the seasonal variation of trace metal concentrations in the lake water column in order to improve the assessment of urban runoff impact. This study focuses on the seasonal monitoring, for 10 months including dry and raining seasons, of trace metal concentrations and their speciation in the water column of Lake Pampulha. Trace metals were collected at two depths in the middle of Lake Pampulha. For each collected sample, metal fractions were divided into total, dissolved, and inert metal. Six anthropogenic trace metals were considered: cadmium, cobalt, copper, lead, nickel and zinc. The results showed different behaviour of trace metals in the water column. Cadmium concentration is under the quantification limit. Speciation results indicate a variable metal bioavailability. Zinc is the most bioavailable (~60%). Bioavailability of cobalt which is highly dissolved varies with depth. Nickel bioavailability remains rather constant in the surface layer during the study period and those of copper, zinc and lead are more variable.

KEYWORDS

Tropical urban lake, Trace metal, Speciation, Water column, bioavailability.

8.2. Spatial heterogeneity in Lake Pampulha

In this section, we will present the spatial heterogeneity of Lake Pampulha. Two campaigns on September 2012 and January 2013 were carried out at 6 horizontal points going from inlet to outlet of Lake Pampulha (Figure 1). Based on the precipitation data, the first campaign on September 2012 is considered as dry campaign, and the second campaign on January 2013 as raining campaign.



Figure 1 Localization of the sampling points of the horizontal transect (Google Earth ©)

8.2.1. Temperature, conductivity and suspended matter

Lake Pampulha can be divided in two parts: the western part from the inlet to the middle (points A, B, C) and the eastern part from the middle to the outlet (points D, E, F). The western part is shallow, with high phytoplankton biomass and receives the main tributaries. The eastern part is deeper and the phytoplankton biomass is lower.

In this paragraph, we present the horizontal distribution of temperature, conductivity and suspended matter concentration. These variables are indicators of physical functioning and water quality. In the following paragraph, we will consider the differences between the surface and the bottom of the water column, the gradient inlet/outlet of the lake and the difference between dry and raining campaigns.

The temperature difference at the surface and the bottom is only observed at the western part of Lake Pampulha. The temperature gradient between the surface and the bottom is clearer from inlet to outlet due to the decreasing gradient of depth from outlet to inlet. There is no variation of temperature at the surface from point A to F because the surface layer receives the same solar radiation. We observe a mixing effect of the rain on temperature. Thus, the temperature gap becomes closer during this raining campaign.

Concerning the conductivity, during the dry campaign, the western part of the lake can have a higher conductivity due to the direct wastewater discharge into the lake. The eastern part presents a lower conductivity. The rains have an impact on conductivity gradient. The conductivity decreased clearly in comparison to the 1st campaign. Nevertheless, this dilution effect decreases at the eastern part of the lake due to the depth. It seems that a direct and quick impact of the rain occurs on the surface layer of the lake.

For the suspended matter, the distribution is more heterogeneous regarding the temperature and conductivity. We found more suspended matter at the surface due to phytoplankton biomass presence. At points A and B, the SM concentration is higher than at other points during the dry campaigns. We observe the same effect of the rain.

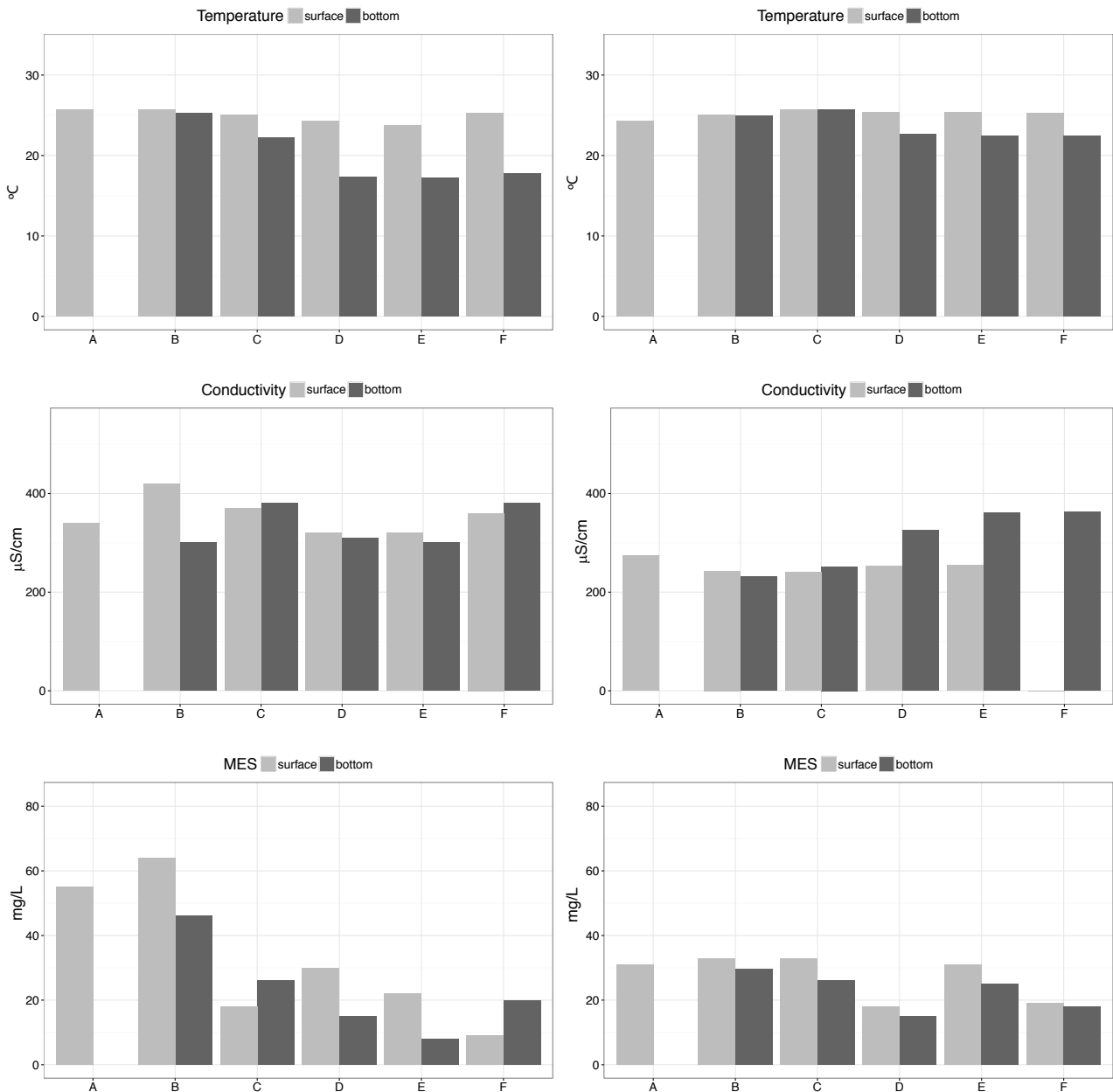


Figure 2 Horizontal transect of temperature, conductivity and suspended matter at the surface and bottom for the dry campaign (left) and raining campaign (right)

8.2.2. Trace metal concentrations in the horizontal transect

In this paragraph, the total and dissolved metal concentrations at the sampling points of the horizontal transect during 2 campaigns will be presented.

- Chromium

Total Cr concentrations are higher in the western part of the lake. There is no difference between the dry and raining campaigns. The dissolved concentration is high up to 100% at the surface in the western part of the lake, at the surface and during the dry campaign. For the point F at both surface and bottom, the blank confirmed this high value.

After the rains, this distribution has changed. The dissolved concentration becomes less than 50% for most of points.

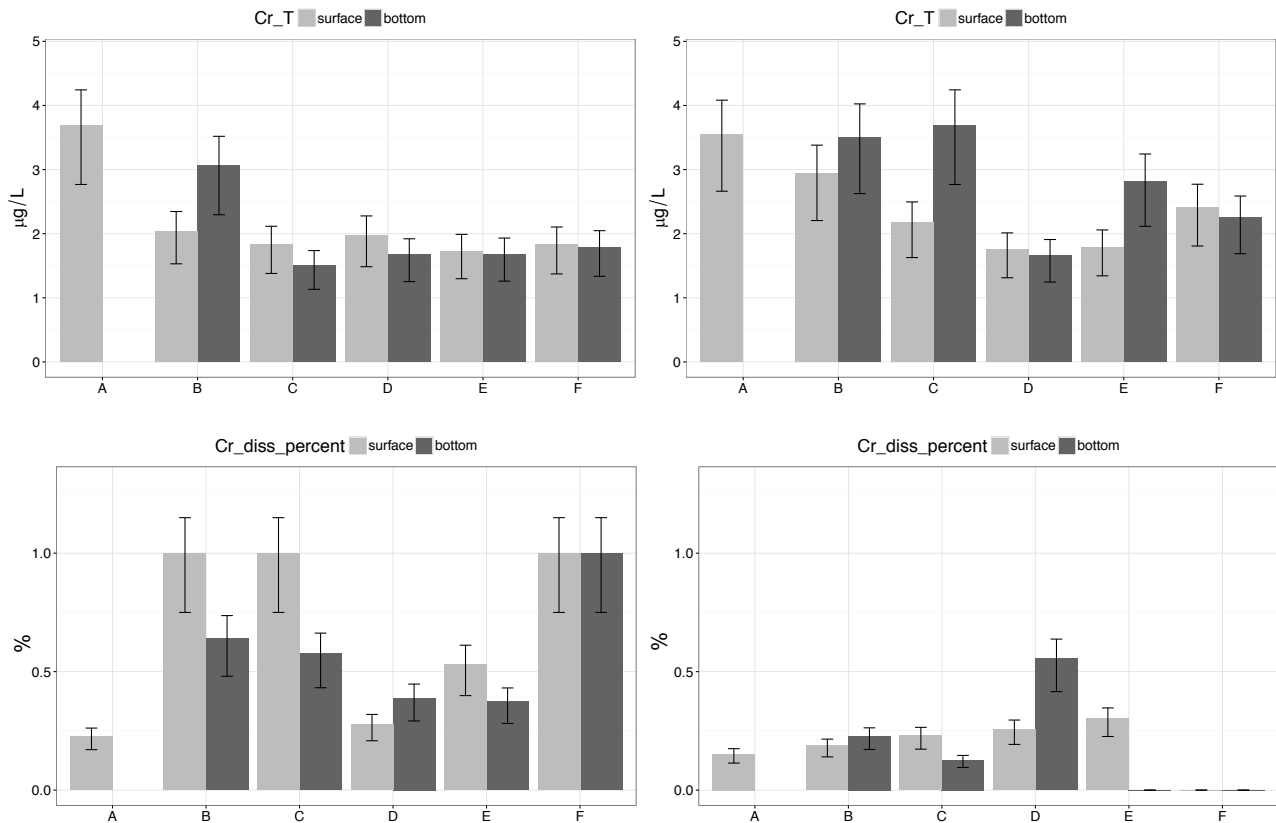
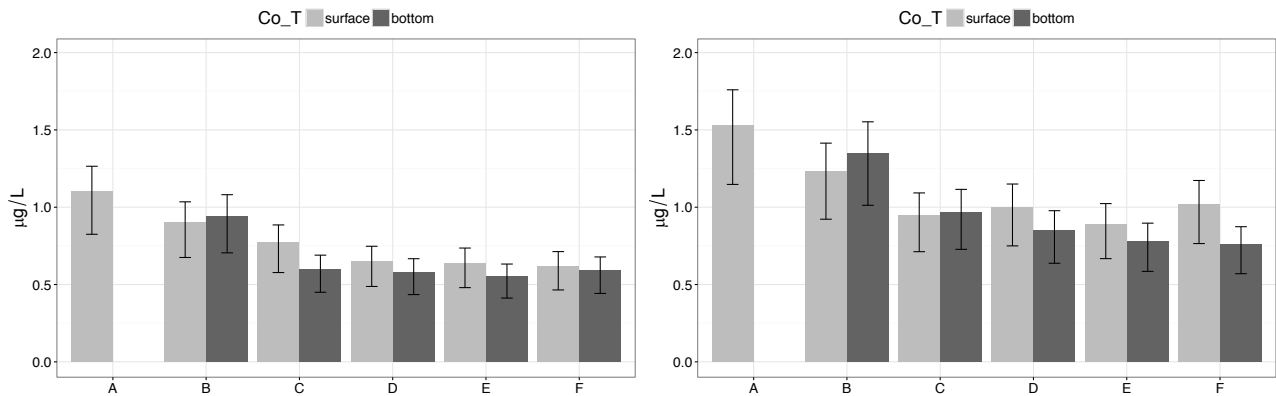


Figure 3 Horizontal transect of total and dissolved percent Cr at the surface and bottom for the dry campaign (left) and raining campaign (right)

- Cobalt

The total concentration of Co is higher in the western part of the lake and decreases to the outlet. Cobalt is highly dissolved around 90% during the dry campaign and there is no difference between the surface and the bottom. For the raining campaign, Cobalt is less dissolved around 50-60%.



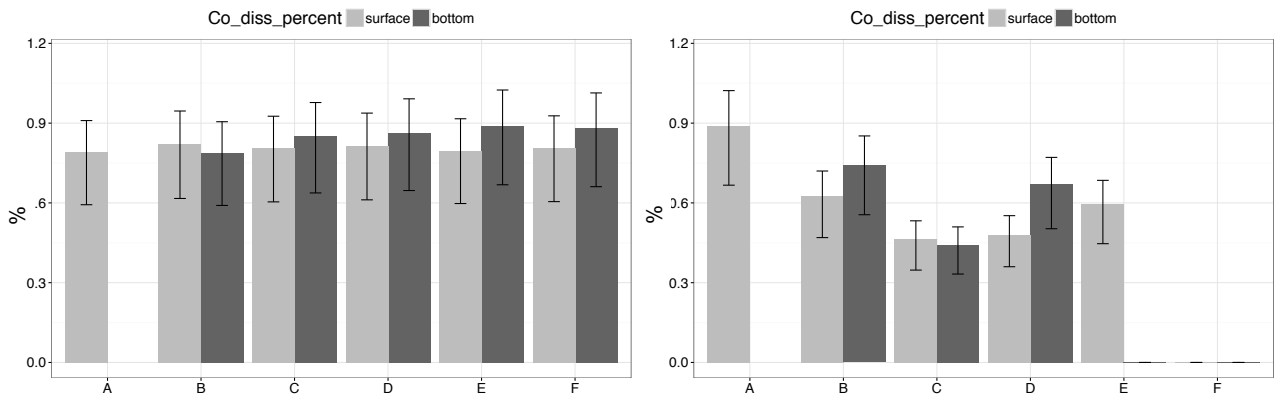


Figure 4 Horizontal transect of total and dissolved percent Co at the surface and bottom for the dry campaign (left) and raining campaign (right)

- Nickel

The difference of Ni concentrations between the dry and raining campaigns are significant. The gradient of total concentration is from the inlet to the outlet during the dry campaigning. This gradient disappeared during the raining period.

For the dissolved concentration, during the dry campaign, we find a high dissolved percent for points B and C at the surface and F at both depths. Nickel becomes more particulate during the raining period.

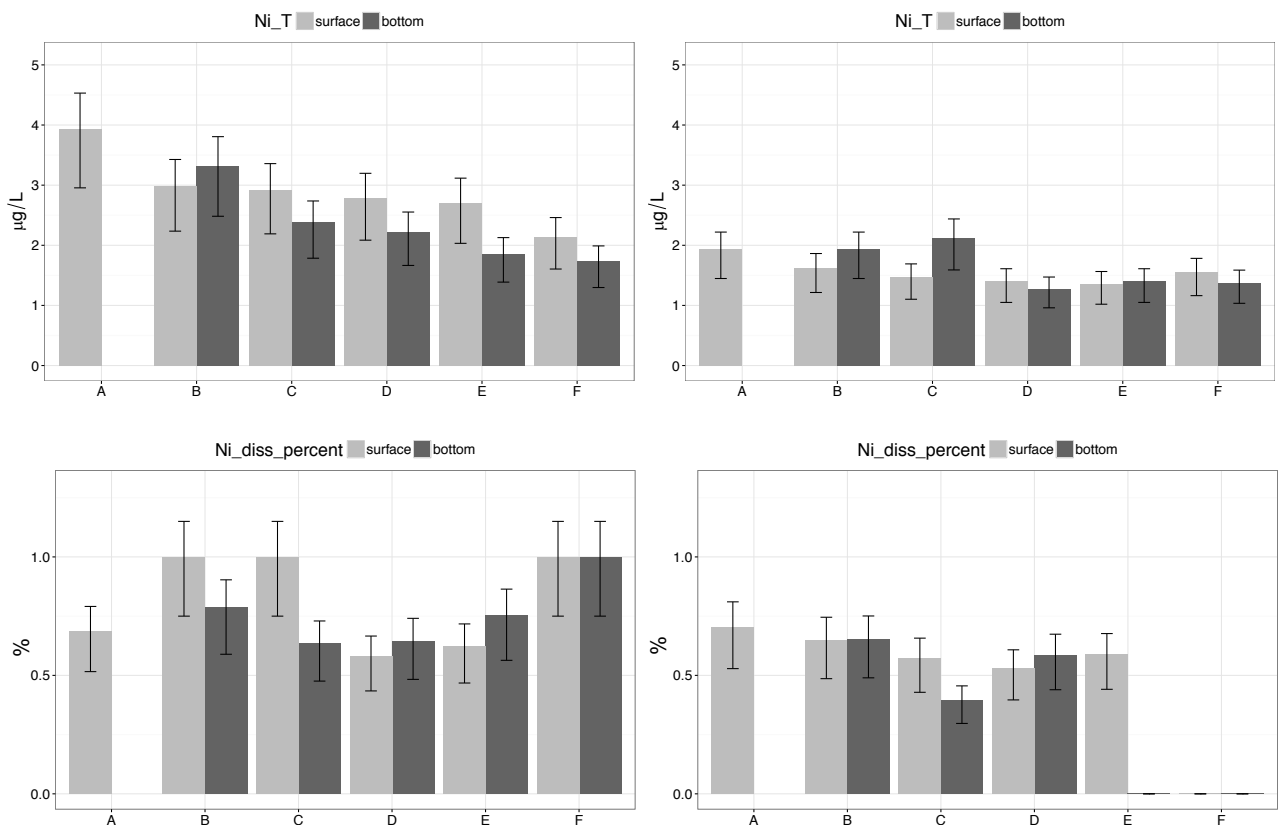


Figure 5 Horizontal transect of total and dissolved percent Ni at the surface and bottom for the dry campaign (left) and raining campaign (right)

- Copper

The total concentration of copper is higher during the raining campaign, except for the point F at the surface (Figure 83). Copper is highly dissolved for most points, except for the point F during the dry campaign. During the raining campaign, this percent can be modified to around 30% or more for most points.

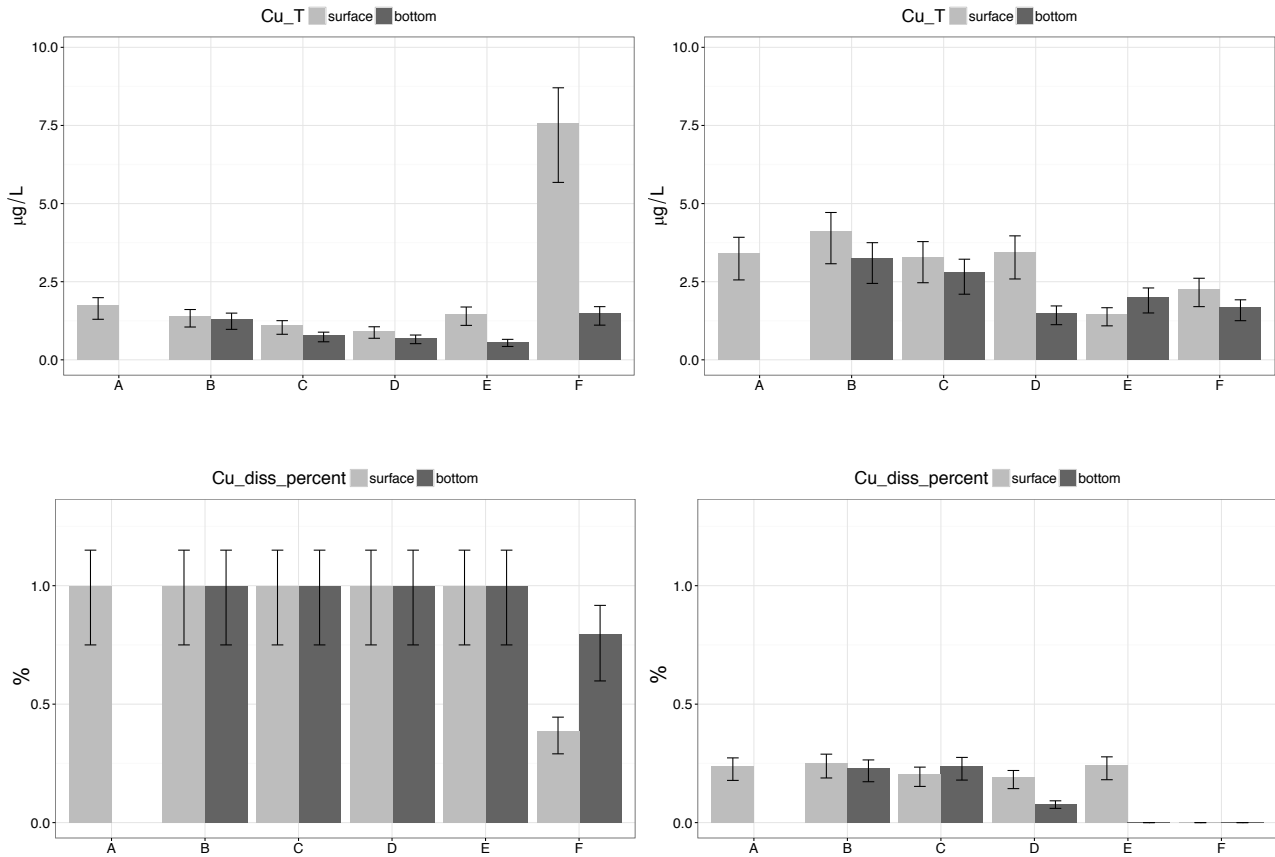


Figure 6 Horizontal transect of total and dissolved percent Cu at the surface and bottom for the dry campaign (left) and raining campaign (right)

- Zinc

Total Zn concentration increases during the raining campaign (Figure 84). The total concentration decreases from inlet to outlet during the raining campaign. On the contrary, Zn is more dissolved during the dry campaign and the dissolved fraction increases toward the outlet. After the rain, the dissolved fraction decreases, similarly for most of points. With an increasing total concentration and decreasing dissolved fraction, we find more particulate Zn during the raining campaign.

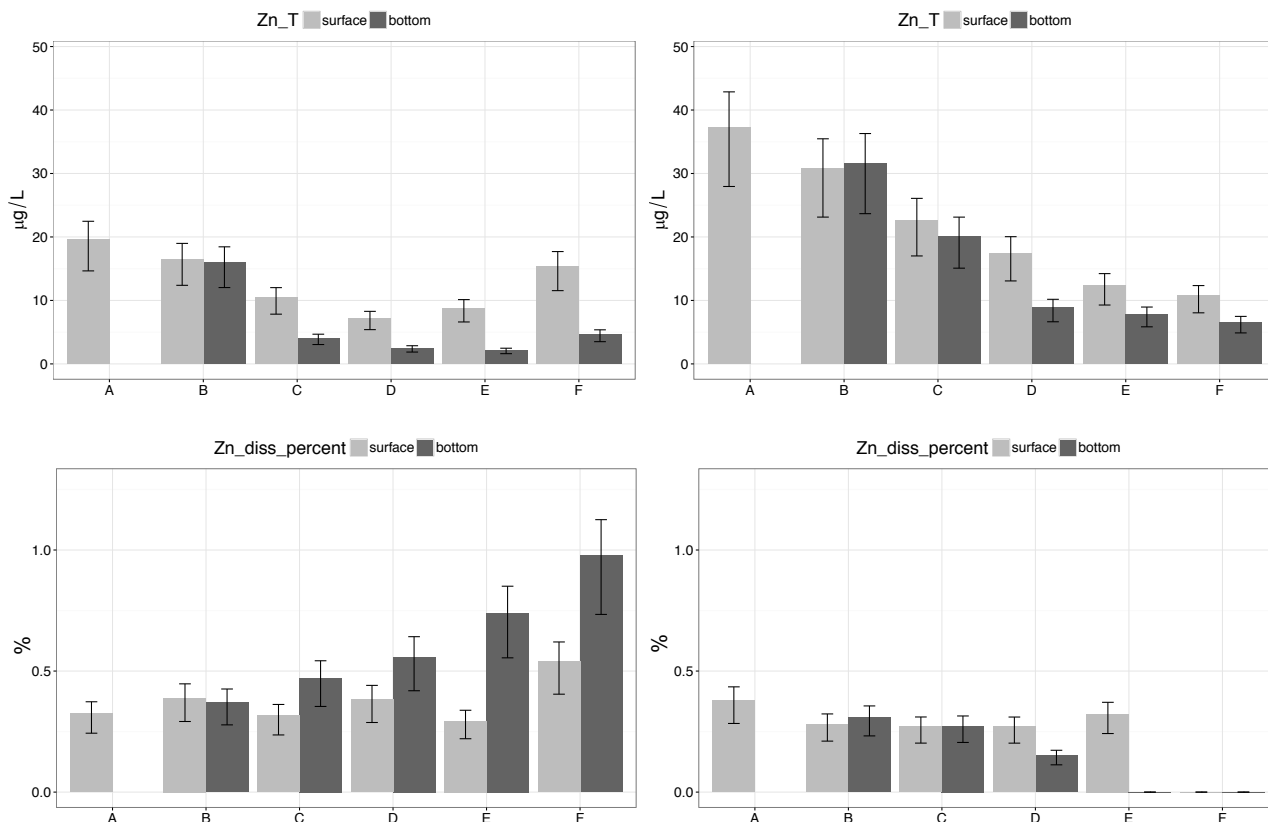
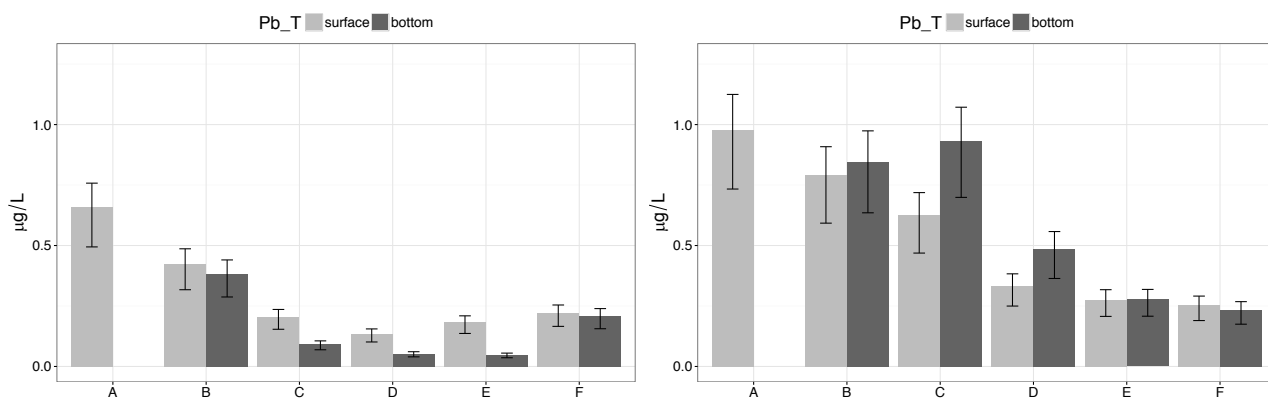


Figure 7 Horizontal transect of total and dissolved percent Zn at the surface and bottom for the dry campaign (left) and raining campaign (right)

- Lead

Lead concentration is higher in the western part of the lake during the dry campaign (Figure 85). We find the same spatial variation during the raining period with an increasing concentration for all the points. Pb is more particulate for most of points but can be highly dissolved at the bottom (point E). After the rain, Pb becomes more particulate except for the point C at the surface with 100% lead dissolved.



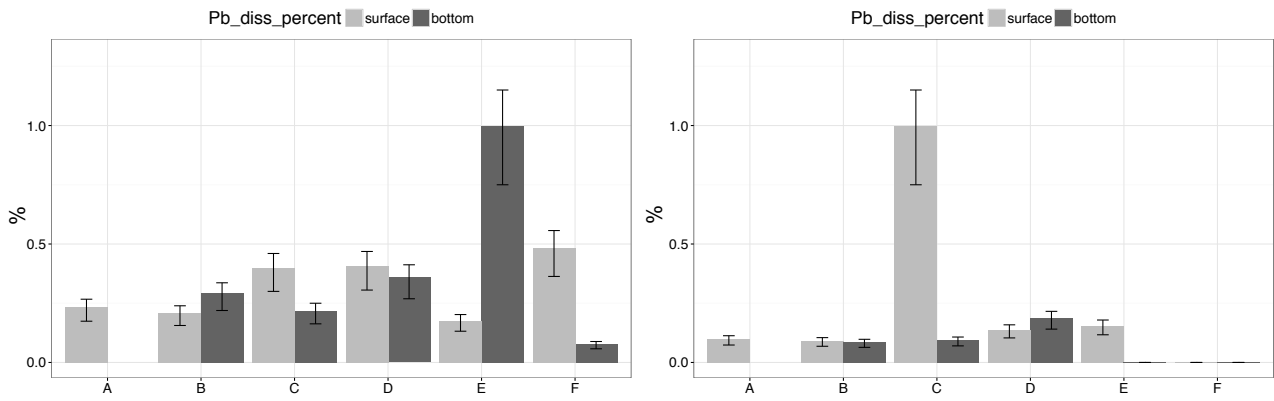


Figure 8 Horizontal transect of total and dissolved percent Pb at the surface and bottom for the dry campaign (left) and raining campaign (right)

Conclusion :

- Chromium:
 - no difference of total concentration during the dry and raining period
 - dissolved fraction decreased during the raining period
- Cobalt:
 - increase of total concentration during the raining period
 - highly dissolved during the dry campaign, modification after the rain.
- Nickel:
 - gradient of total concentration from inlet to outlet.
 - gradient disappeared for the rain campaign
 - more particulate during raining period
- Copper:
 - higher total concentration r during the raining campaign,
 - highly dissolved for most of point during the dry campaign.
 - modification during the raining campaign
- Zinc:
 - increase of total Zn during the raining campaign.
 - decreasing gradient of the total concentration from inlet to outlet during the raining campaign.
 - more dissolved during the dry campaign and this percent increase toward the outlet.
 - decrease and similar for most of points.
- Lead:
 - Higher concentration in the western part of the lake during the dry campaigns
 - more particulate after the rain

8.3. Effet de la matière organique produite dans les bassins de rétention des eaux pluviales sur la spéciation les éléments traces métalliques

A paper published in the “Houille Blanche” journal is presented below. This paper presents the results regarding the impact of the organic matter produced in a stormwater pond on the trace metal speciation.

Effet de la matière organique produite dans les bassins de rétention des eaux pluviales sur la spéciation les éléments traces métalliques

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RÉSUMÉ. – Éléments du réseau d'assainissement pluvial, les bassins de rétention en eau ont un fonctionnement hydrodynamique spécifique, proche de celui d'un étang. Le temps de séjour de l'eau y est plus élevé que dans les conduites, favorisant la sédimentation des particules. Pendant le printemps et l'été, des phases de mélange et de stratification thermique alternent. Une biomasse élevée de phytoplancton peut alors se développer et la matière organique qu'elle produit peut interagir avec les micropolluants. Ainsi, pour mieux comprendre le cycle biogéochimique des éléments traces métalliques (ETM), il paraît important de connaître l'effet de la matière organique produite dans les bassins de rétention sur les ETM.

Pour cela, nous avons étudié la spéciation du nickel, du cuivre, du zinc et du plomb dans l'eau dans un bassin de rétention en eau de Seine-Saint-Denis situé en dérivation d'une rivière canalisée qui l'alimente lors des fortes pluies. Les concentrations de temps sec en ETM totaux, dissous et labiles ont été déterminées. Les paramètres globaux ont également été mesurés. Par temps sec, peu de métaux labiles, potentiellement biodisponibles, sont présents dans le bassin (moins de 50 % de la concentration totale), moins que dans la rivière (autour de 70 %). Par ailleurs, la concentration en chlorophylle est plus élevée dans le bassin (90 à 140 µg/L) que dans la rivière (30 µg/L) : la matière organique dissoute autochtone semble favoriser la complexation des métaux dissous dans le bassin. La réduction de la biodisponibilité du nickel et du cuivre dans le bassin de rétention par rapport à la rivière qui l'alimente, qui devra être confirmée sur la base d'un plus grand nombre de mesures, montre l'intérêt de faire passer les eaux pluviales urbaines dans des bassins de rétention en eau pour réduire leur toxicité avant rejet dans le milieu récepteur.

Mots-clés : eutrophisation, biomasse de phytoplancton, temps sec

Impact of the organic matter produced in stormwater retention ponds on trace metal speciation

ABSTRACT. – Retention ponds, which are part of the stormwater drainage system, have specific hydrodynamics. The residence time of the water, higher than in the conduits, favours the sedimentation of particles. During spring and summer, mixing and thermal stratification alternate. A high phytoplankton biomass can develop and produce organic matter which can interact with micropollutants. That is why it is essential to understand the impact of organic matter locally produced on trace metals. For this purpose, we studied the speciation of nickel, copper, zinc and lead in the waters of a retention pond located in derivation of a channelled river in a Paris suburb (France). Three fractions of trace metals (total, dissolved and labile fractions) were sampled during dry weather and analyzed. During dry weather, few labile metals, potentially bioavailable, were present in the pond (less than 50% of the total concentration), less than in the river (40-70%). The chlorophyll a concentration was higher in the pond (90 to 140 µg/L) than in the river (30 µg/L): autochthonous dissolved organic matter seems to favour the complexation of dissolved metals. The reduction of nickel and copper trace metal bioavailability in the retention pond compared to the river which feeds the pond, which needs to be confirmed with more measurements, shows the interest to have urban storm waters transit through retention ponds to reduce their toxicity before their release in the natural waters.

Key-words: eutrophication, phytoplankton biomass, dry weather

I. INTRODUCTION

Avec l'expansion urbaine, les systèmes classiques basés sur les réseaux se sont révélés insuffisants pour assurer l'assainissement pluvial des agglomérations. Les aménageurs ont dû créer des bassins qui retiennent les eaux pendant la pluie et les évacuent ensuite à faible débit vers l'exutoire, si

possible après une dépollution partielle par décantation des particules. Il existe plusieurs types de bassins de rétention des eaux pluviales : les bassins en eau, enterrés, secs, les bassins de décantation... [STU – Agences de l'eau 1994].

Depuis longtemps, parmi ces différents types de bassins, les bassins de décantation sont connus pour permettre la dépollution des eaux grâce à un long temps de séjour qui

permet une bonne sédimentation des particules. Ils sont largement utilisés pour traiter les eaux de ruissellement pluvial fortement polluées avant leur rejet dans le milieu naturel (autoroutes, pistes d'aéroports, grands parkings, etc.). Ainsi, de nombreuses études *in situ* et en laboratoire ont porté sur le processus de sédimentation et ont montré son importance dans la dépollution des eaux pluviales dans les bassins [Yousef *et al.*, 1996, Lee *et al.*, 1997, Weiss *et al.*, 2006, Karlsson *et al.* 2008 et 2010]. Les particules fines, entraînées par le ruissellement pluvial, servent de site d'adsorption aux micropolluants comme les éléments traces métalliques (ETM). La vitesse de sédimentation élevée de ces particules est favorable à une bonne décantation [Bressy 2010].

Les bassins de rétention en eau font quant à eux l'objet d'une demande sociale croissante. En plus de leur fonction hydraulique principale, ils ont souvent été aménagés pour permettre des activités de loisir, comme la promenade ou la pêche, et présentent ainsi un grand intérêt pour les citoyens [Tassin *et al.*, 2004]. Aujourd'hui, les collectivités cherchent à accroître la biodiversité de ces milieux aquatiques artificiels. C'est le cas du site d'étude présenté dans cet article, le bassin de rétention de Savigny, intégré dans le parc départemental du Sausset dans une zone Natura 2000 [Inventaire national du patrimoine naturel, 2006].

Le devenir des ETM dans un bassin de rétention en eau dépend de leur spéciation. La concentration totale d'un ETM dans le milieu, agrégeant la fraction particulaire et la fraction dissoute, est un mauvais indicateur de sa toxicité [Varrault *et al.*, 2012]. Il faut considérer la fraction biodisponible, c'est-à-dire susceptible d'entrer en contact et/ou de contaminer les organismes [Gourlay-Francé *et al.*, 2010]. Comme celle-ci dépend des organismes, on prend comme indicateur la fraction labile, qui rassemble les métaux libres, c'est-à-dire non complexés, et les complexes métalliques labiles. Ces complexes s'établissent entre les ETM et les différents ligands minéraux (chlorures, nitrates, carbonates,...) ou organiques (matière organique d'origine naturelle ou anthropique) présents dans le milieu. Tout comme les métaux libres, les complexes labiles, qui se dissocient facilement, sont potentiellement biodisponibles, tandis que les complexes inertes, qui se dissocient moins facilement, sont réputés peu ou pas biodisponibles. Généralement, les ligands minéraux forment des complexes labiles avec les ETM tandis que la matière organique forme plutôt des complexes inertes. Beaucoup d'auteurs s'intéressent uniquement à la contamination en ETM des sédiments des bassins de rétention et à la spéciation des métaux dans ces sédiments [Hossain *et al.*, 2007, Stead-Dexter *et al.*, 2004, El Muffleh *et al.*, 2010, Clozel, 2006]. Peu d'études ont porté sur la spéciation des métaux dans l'eau des bassins de rétention pour évaluer leur biodisponibilité pour les organismes vivants.

Par le phénomène de biosorption, des organismes vivants accumulent des micropolluants présents dans l'eau de manière passive sur leur structure cellulaire externe [Chojnacka, 2010]. Une étude faite sur le phytoplancton du lac Novosibirskoye en Russie a montré que la biosorption joue sur la biodisponibilité et la toxicité des métaux. Le phytoplancton a continué d'y croître en présence de fortes concentrations de métaux dans l'eau (concentrations en cuivre de 500 µg/L, en zinc de 250 µg/L en cadmium de 50 µg/L), après une période initiale d'inhibition puis de sélection d'espèces tolérantes. La biosorption sur le phytoplancton a modifié la spéciation des métaux et réduit la fraction dissoute, la plus biodisponible et la plus toxique [Smolyakov *et al.*, 2010]. Ainsi, la biosorption pourrait contribuer à la dépollution des eaux pluviales, mais elle reste peu étudiée dans cette optique.

Les bassins de rétention en eau ont un fonctionnement spécifique qui s'apparente à celui d'un petit lac urbain. Ils sont souvent de petite taille, peu profonds et répondent rapidement aux fluctuations météorologiques. Ils sont particulièrement sensibles aux changements de température de l'air. Ainsi, durant le printemps et l'été des phases de mélange et de stratification de la colonne d'eau alternent. Ces alternances et l'apport de nutriments par ruissellement urbain lors d'événements pluvieux, peuvent favoriser le développement de phytoplancton [Tran Khac *et al.*, 2012]. Celui-ci produit de la matière organique qui peut interagir avec les micropolluants métalliques ou organiques, directement ou après dégradation par les bactéries. De plus, le temps de séjour de l'eau, plus élevé que dans les autres ouvrages d'assainissement, favorise la sédimentation des particules et permet le changement de la répartition des ETM entre fractions particulaire et dissoute ainsi que leur changement de spéciation au sein de la phase dissoute ce qui peut modifier leur biodisponibilité.

Dans ce travail, nous nous sommes intéressés à l'effet de la matière organique produite dans un bassin de rétention en eau sur la spéciation des ETM. Nous avons tout d'abord étudié la spéciation de quelques métaux traces caractéristiques des eaux de ruissellement urbain (Cu, Zn, Pb, Cd et Ni), présents dans un bassin par temps sec. L'article présente la méthode d'échantillonnage par temps sec, la technique de spéciation des métaux ainsi que le suivi des paramètres globaux dans le bassin de rétention, et les concentrations et la spéciation des métaux mesurées par temps sec dans le bassin et dans la rivière qui l'alimente lors des fortes pluies.

II. MATÉRIELS ET MÉTHODES

II.1. Site d'étude

Le bassin de rétention en eau de Savigny se situe dans le parc départemental du Sausset à Aulnay-sous-Bois (Seine-Saint-Denis). La surface du plan d'eau permanent est de 4,3 ha, sa profondeur moyenne est de 1,5 m, soit un volume permanent de 64 000 m³. Lors d'un remplissage, la hauteur d'eau peut s'accroître de 1,4 m pour stocker jusqu'à 80 000 m³ supplémentaires, grâce à la faible pente des berges. La situation géographique du bassin de Savigny l'amène à recevoir des eaux potentiellement chargées en ETM : eaux issues du ruissellement urbain (autoroute A104, ZAC Paris Nord II...), eaux pluviales issues des lagunes d'épuration de l'aéroport Roissy-Charles-de-Gaulle. Ainsi, ce site nous permet d'étudier le devenir des ETM dans un bassin de rétention en eau.

Le bassin de Savigny est alimenté par la nappe phréatique de Saint-Ouen et le ruisseau canalisé du Sausset. Le débit du ruisseau du Sausset est limité en aval du bassin par une vanne. Lors d'épisodes pluvieux intenses, le ruisseau alimente le bassin de Savigny par deux déversoirs situés en amont et en aval sur le Sausset. Les eaux s'écoulent par deux prébassins prévus pour limiter l'envasement du bassin de rétention. Hors épisodes de pluie exceptionnels, les écoulements entrant et sortant passent par le seul prébassin aval (PAV), dont le seuil est le plus bas (Figure 1).

II.2. Campagnes de mesure

II.2.1. Stratégie d'échantillonnage

Pour connaître les concentrations en ETM dans le bassin en absence de déversement du Sausset, deux campagnes de

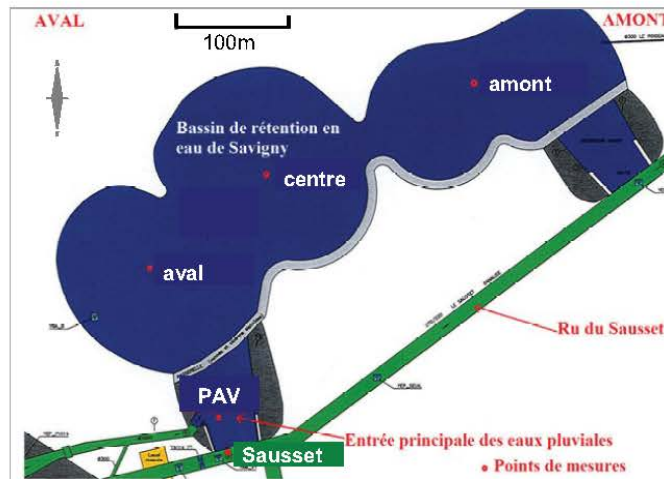


Figure 1 : Situation du bassin de rétention en eau de Savigny et localisation des points d'échantillonnage (PAV : prébassin aval ; source : DEA 93).

temps sec ont été organisées. Trois points d'échantillonnage ont été choisis dans le bassin : « amont » vers le prébassin amont, « centre » au centre du bassin de rétention, « aval » vers le prébassin aval. Un point est situé dans le prébassin aval (« PAV »). Un dernier point d'échantillonnage est situé dans le ru du Sausset au droit du prébassin aval (Figure 1). Les échantillons ont été prélevés sous la surface.

II.2.2. Paramètres mesurés in situ

Aux trois points de mesure situés dans le bassin de Savigny, des profils de sonde sur toute la hauteur d'eau ont été réalisés. La température, la concentration en oxygène dissous, la conductivité et le pH sont déterminés avec une sonde multi-paramètres (Sea-Bird SBE 19-03). Les profils de concentrations en chlorophycées, cyanobactéries, diatomées, cryptophycées et la concentration totale en chlorophylle sont obtenus avec une sonde fluorimétrique (BBE-Moldaenke Fluoroprobe 3). La transparence de l'eau est mesurée au disque de Secchi.

II.2.3. Analyses au laboratoire

Trois fractions métalliques, totale, dissoute et inerte, sont mesurées sur les échantillons d'eau du Sausset et du bassin. La concentration totale en métaux est obtenue après la digestion des échantillons bruts, conservés à pH 2 (HNO_3 Optima), par une attaque acide par HNO_3 (Optima, 65 %) et HCl (Optima, 30 %) à chaud (2h30 à 95°C, système DigiPREP) qui permet l'extraction des métaux liés aux particules. Les échantillons sont filtrés avant analyse sur un filtre en téflon (0.45 μm). La fraction dissoute est obtenue par filtration d'eau brute non acidifiée sur un filtre en acétate de cellulose (0.45 μm). La fraction inerte des ETM est obtenue par le passage de ce filtrat à travers un disque chélatant (EMPORE™ Chelex 100™). Constitué de polymères (polystyrène divinylbenzène) portant des groupes chélatants iminodiacétiques, il permet de séparer les métaux dissous labiles, incluant les métaux libres, retenus par le disque, d'une part, de la fraction inerte, d'autre part

[Varrault *et al.*, 2012, Bracmort, 2010]. Les fractions dissoute et inerte sont conservées à pH inférieur à 2 (HNO_3 Optima) jusqu'à l'analyse.

Les fractions totale, dissoute et inerte sont ensuite analysées par spectrométrie de masse couplée à un plasma inductif (ICP-MS). Les ETM dont les concentrations ont été étudiées sont le nickel, le cuivre, le cadmium, le plomb et le zinc. Ils sont tous toxiques pour les organismes vivants, mais le cuivre et le zinc sont essentiels, contrairement au cadmium, au plomb et au nickel. Les limites de quantification de l'ICP-MS sont très basses, de 0.01 $\mu\text{g/L}$ pour Cd, Pb, Ni, Cu et 0.05 $\mu\text{g/L}$ pour le Zn. L'incertitude de mesure est de l'ordre de 10 %. La fraction labile est obtenue par différence entre la fraction dissoute et la fraction inerte.

De plus, nous avons mesuré les concentrations de différents paramètres permettant de caractériser les interactions de la matière organique avec les métaux : carbone organique dissous (COD), carbone organique particulaire (COP), matières en suspension (MES), chlorophylle a, et les nutriments permettant la production phytoplanktonique dans le bassin : nitrates, phosphates et phosphore total.

III. RÉSULTATS

Nous avons caractérisé la qualité de l'eau du bassin Savigny par temps sec grâce à deux campagnes réalisées le 21/02/2013 et le 25/04/2013. Les derniers remplissages partiels du bassin de rétention par débordement du Sausset qui ont précédé ces campagnes représentaient un volume de 1500 m^3 environ chacun, et avaient eu lieu respectivement environ un mois et quinze jours auparavant.

III.1. Paramètres globaux

Les concentrations des paramètres globaux des deux campagnes de temps sec (21/02/2013 et 25/04/2013) sont présentées dans le Tableau 1.

Tableau 1 : Paramètres globaux lors des deux campagnes de temps sec (matières en suspension (MES), carbone organique particulaire (COP), carbone organique dissous (COD), nitrates, phosphore total (P_t), phosphates, chlorophylle a).

Date	Point	MES (mg/L)	COP (mgC/L)	COD (mg/L)	NO ₃ ⁻ (mgN/L)	P _t (µgP/L)	phosphates (µgP/L)	Chlorophylle a (µg/L)
21/02/2013	Sausset	-	-	-	-	-	-	-
	Amont	23.6	8.2	2.1	0.36	153	17	87
	Centre	28.9	9.3	2.2	0.30	173	17	111
	Aval	26.0	10.0	2.2	0.28	202	43	110
	PAV	-	-	-	-	-	-	-
25/04/2013	Sausset	17.5	3.4	3.1	3.80	129	2	29
	Amont	39.5	11.3	4.3	0.03	321	12	107
	Centre	38.5	11.1	4.1	0.04	242	9	108
	Aval	51.7	13.6	4.3	0.03	319	17	136
	PAV	46.0	13.2	4.5	0.02	300	29	148

La concentration en chlorophylle augmente entre les deux campagnes dans le bassin de rétention, elle est comprise entre 87 et 110 µg/L le 21/02/13 et entre 107 et 136 µg/L le 25/04/13 (points amont, centre et aval). On observe une légère baisse de la concentration en chlorophylle de l'aval vers l'amont du bassin de rétention lors des deux campagnes. La concentration en chlorophylle dans le Sausset n'a été mesurée que le 25/04/2013 ; à cette date elle est nettement plus faible que dans le bassin (29 µg/L).

Lors de la campagne du 21/02/2013, une sursaturation en oxygène de 115 à 118 % selon les points est mesurée, indiquant une forte activité photosynthétique du phytoplancton présent dans le bassin. Le pH élevé, de l'ordre de 8.6, traduit également une forte activité photosynthétique. Lors de la seconde campagne du 25/04/13, la sursaturation est encore plus forte. Elle décroît de 180 % à la surface à 120 % vers le fond.

III.2. Métaux

Les concentrations en nickel, cuivre, plomb et zinc totaux des deux campagnes de temps sec sont présentées sur la Figure 2. Pour ces deux campagnes, les concentrations totales de ces métaux sont très variables entre les points de mesure dans le bassin et dans le ru du Sausset. Elles sont comprises entre 2.5 et 7.7 µg/l pour le nickel, 1.5 et 3.8 µg/l

pour le cuivre, entre 6.1 et 30 µg/l pour le zinc et entre 1.4 et 2.3 µg/l pour le plomb. Les concentrations en cadmium restent toujours en dessous ou proches de la limite de quantification (0.01 µg/L) et ne sont pas présentées.

Les concentrations en ETM dissous observées dans le bassin de rétention (moyenne sur les deux campagnes et les points amont, centre et aval) et dans le ru du Sausset (2^e campagne), sont largement au-dessous des normes de qualité environnementales en moyenne annuelle (NQE-MA) [MEDDE, 2012] hors fond géochimique pour le cadmium (non présenté), le nickel et le plomb (Figure 3). Par contre, les concentrations en cuivre et zinc sont proches de la norme dans le bassin de rétention. Pour ces deux éléments, les concentrations observées dans le ru du Sausset la dépassent largement.

La spéciation des ETM, mesurée lors de la campagne du 25/04/2013, varie elle aussi en fonction des points, comme le montre la Figure 4. Les ETM dissous sont principalement sous forme inerte aux points aval, centre et amont, dans le bassin de rétention. La spéciation diffère entre le bassin de rétention et le Sausset pour le nickel et le cuivre dont la fraction labile est pratiquement absente dans le bassin. Le zinc dissous est majoritairement sous forme inerte dans le Sausset et le bassin de rétention. En ce qui concerne le plomb, la fraction dissoute est pratiquement absente dans le Sausset comme dans le bassin.

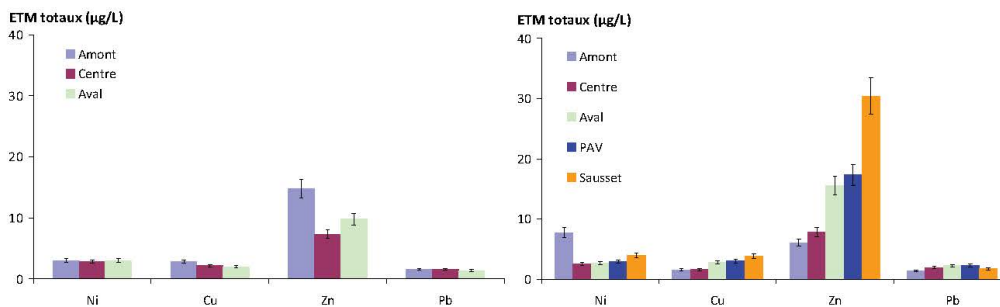


Figure 2 : Concentrations en nickel, cuivre, plomb et zinc totaux des deux campagnes de temps sec (à gauche, 21/2/2013 et à droite, 25/4/2013).

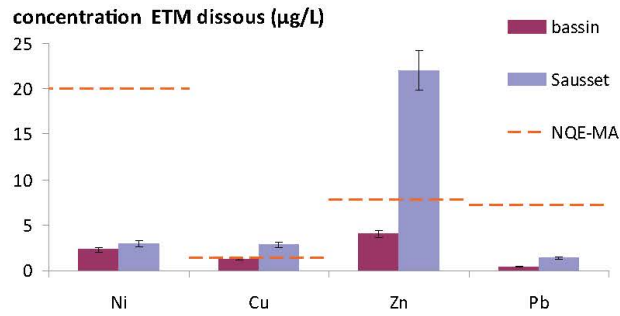


Figure 3 : Concentrations en Ni, Cu, Zn et Pb dissous dans le bassin de rétention (moyenne sur les points amont, centre et aval et sur les deux campagnes de temps sec) et dans le ru du Sausset (campagne du 25/04/2013) et normes de qualité environnementale en moyenne annuelle (NQE-MA), hors fond géochimique.

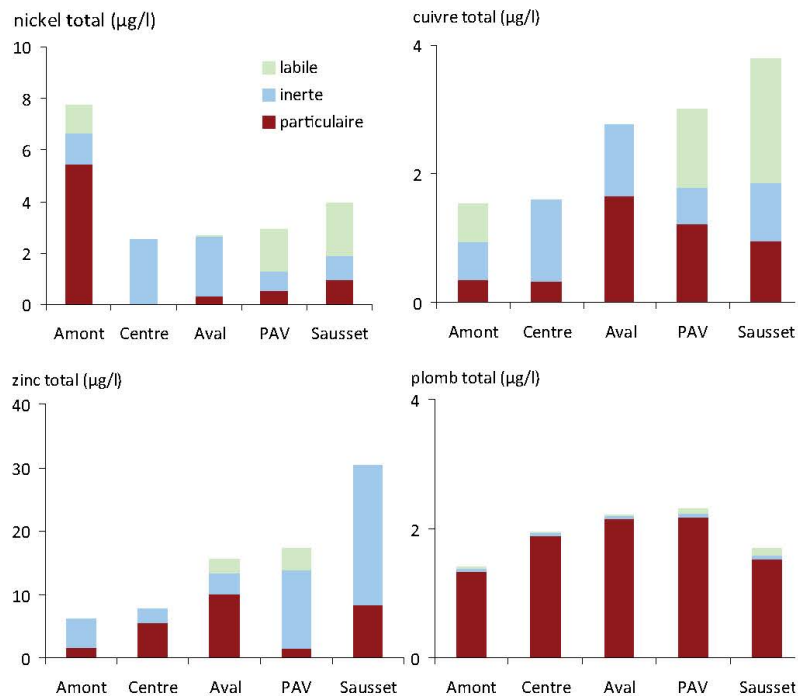


Figure 4 : Campagne du 25/04/2013 – variation de la concentration totale en nickel, cuivre, zinc et plomb et de sa répartition entre fractions labile, inerte et particulaire aux différents points de mesures du bassin de rétention et du ru du Sausset.

La Figure 5 présente le rapport entre les fractions labile et dissoute pour le nickel, le cuivre, le zinc et le plomb. Ce pourcentage (inférieur à 50 %) est beaucoup plus faible pour les points situés dans le bassin de rétention que dans le Sausset (environ 70 %). Pour le zinc qui ne présente pas de fraction labile dans le Sausset, aucune conclusion ne peut être tirée de cette campagne. Le bassin de rétention semble réduire la biodisponibilité de ces micropolluants métalliques, car la fraction labile est un indicateur de la fraction biodisponible.

IV. DISCUSSION ET CONCLUSION

Nous avons comparé nos mesures avec des mesures plus anciennes. En 1989, des mesures de concentration en plomb, zinc et cadmium dans les eaux transitant dans des réseaux séparatifs et unitaires ont été effectuées sur six sites d'études, dont le bassin de Savigny, intégré dans le réseau séparatif de la commune d'Aulnay-sous-Bois [Flores-Rodríguez, 1989]. Nous avons comparé les données

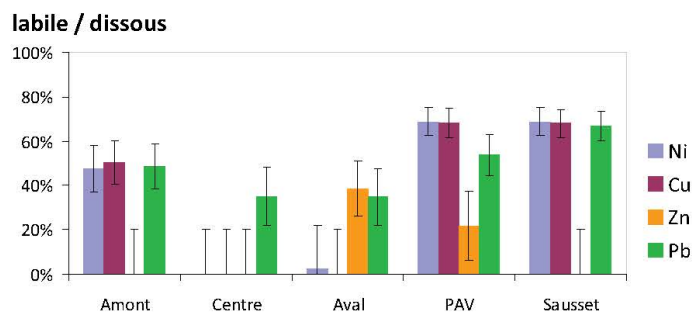


Figure 5 : Pourcentage de la fraction labile par rapport à la totalité du dissous pour le nickel, le cuivre, le zinc et le plomb lors de la campagne du 25/04/2013.

pour le plomb, le zinc et le cadmium. Les concentrations en plomb dissous ont nettement diminué de $3.05 \pm 0.72 \mu\text{g/L}$ en 1989 à $0,07 - 0.127 \pm 0.01 \mu\text{g/L}$ en 2013 dans la partie « amont » du bassin. Dans le prébassin aval, elles ont également diminué de $10.5 \mu\text{g/L}$ en 1989 à environ $0.12 \pm 0.01 \mu\text{g/L}$ en 2013. La diminution de la concentration en plomb peut s'expliquer par l'arrêt de l'utilisation du plomb comme additif dans les essences, appliqué en France métropolitaine depuis le 2 janvier 2000 (Miquel, 2001). La concentration en cadmium dissous a également baissé pendant cette période. Elle est maintenant en dessous des limites de quantification ($0.01 \mu\text{g/L}$) au point amont et à environ $0,015 \mu\text{g/L}$ dans le prébassin aval. Par contre la concentration en zinc dissous a nettement augmenté de $2.4 \mu\text{g/L}$ dans le prébassin aval en 1989 à $15.3 \pm 1.5 \mu\text{g/L}$ en 2013. Dans la partie « amont » du bassin de rétention, en 1989, la concentration était de $3.5 \mu\text{g/L}$ alors qu'elle est de $4.7 \pm 0.5 \mu\text{g/L}$ en 2013. Cette augmentation peut être due à la corrosion des toitures, à l'augmentation du trafic routier ou encore à un rejet particulier sur le bassin versant.

Sur la base de nos deux campagnes de temps sec, l'étang de Savigny peut être classé hypereutrophe selon la classification de Vollenweider [Vollenweider, 1982]: la transparence de l'eau est inférieure à 1 m, la concentration en phosphore total est supérieure à $100 \mu\text{g/L}$, la concentration en chlorophylle est supérieure à $25 \mu\text{g/L}$, le pH est élevé (8.5 à 9.7 lors des deux campagnes) et le lac est sursaturé en oxygène (115 à 180 %).

D'après les résultats de la campagne de temps sec du 25/04/13, il semble que la production phytoplantonique a un effet sur la spéciation des métaux. Les valeurs élevées de chlorophylle, MES et pH sont sous la dépendance du développement algal qui constitue l'essentiel des MES, lesquelles constituent des sites d'adsorption des métaux. Lors de cette campagne, la fraction inerte est plus importante pour le nickel, le cuivre, et le plomb dans le bassin de Savigny que dans le Sausset. Ce n'est pas le cas pour le zinc, majoritairement sous forme inerte dans le Sausset comme dans le bassin de rétention, résultat inattendu car le zinc n'est pas réputé pour former des complexes stables. La réduction de la fraction labile, potentiellement biodisponible, dans le bassin de rétention, qui devra être validée par d'autres campagnes, est à rapprocher des résultats de Pernet-Coudrier (2008) et Matar (2012), qui ont montré que la matière organique dissoute urbaine diminue la biodisponibilité des métaux. Le phytoplancton et les bactéries excrètent de la matière organique autochtone colloïdale,

avec laquelle les métaux dissous peuvent se complexer. Comme la matière organique urbaine, cette matière organique d'origine aquatique produite dans le bassin de rétention présente de nombreux groupements fonctionnels fixateurs de métaux et notamment des groupements azotés. Par ailleurs, le phytoplancton, en consommant du dioxyde de carbone pour la photosynthèse, entraîne une augmentation du pH, qui modifie à son tour les équilibres de solubilité des métaux (Meybeck *et al.* 1998).

La réduction de la biodisponibilité du nickel et du cuivre dissous dans le bassin de rétention, qui devra être confirmée sur la base d'un plus grand nombre de mesures, montre l'intérêt de faire passer les eaux pluviales dans des bassins de rétention en eau pour réduire leur toxicité avant rejet dans le milieu récepteur. Ce séjour entraînera par ailleurs la décantation d'une partie des particules et des ETM qui y sont liées, ce qui suppose de surveiller la contamination des sédiments et leur remise en suspension sous l'effet de la bioturbation, du vent ou lors des remplissages.

La suite du travail portera sur la comparaison des résultats des analyses des différentes fractions métalliques sur les échantillons prélevés par temps de pluie et par temps sec, afin de mettre en évidence d'éventuelles différences de la spéciation des métaux et le rôle joué par le bassin de rétention.

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