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Spatio-temporal variability of solid, total dissolved and labile metal: passive vs. discrete sampling evaluation in river metal monitoring

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Abstract:

In order to obtain representative dissolved and solid samples from the aquatic environment, a spectrum of sampling methods are available, each one with different advantages and drawbacks. This article evaluates the use of discrete sampling and time-integrated sampling in illustrating medium-term spatial and temporal variation. Discrete concentration index (CI) calculated as the ratio between dissolved and solid metal concentrations in grab samples are compared with time-integrated concentration index (CI) calculated from suspended particulate matter (SPM) collected in sediment traps and labile metals measured by the diffusive gel in thin films (DGT) method, collected once a month during one year at the Seine River, upstream and downstream of the Greater Paris Region. Discrete CI at Bougival was found to be significantly higher than at Triel for Co, Cu, Mn, Ni and Zn, while discrete metal partitioning at Marnay was found to be similar to Bougival and Triel. However, when using timeintegrated CI, not only was Bougival CI significantly higher than Triel CI, CI at Marnay was also found to be significantly higher than CI at Triel which was not observed for discrete CI values. Since values are timeaveraged, dramatic fluctuations were smoothed out and significant medium-term trends were enhanced. As a result, time-integrated concentration index (CI) was able to better illustrate urbanization impact between sites when compared to discrete CI. The impact of significant seasonal phenomenon such as winter flood, low flow and redox cycles was also, to a certain extent, visible in time-integrated CI values at the upstream site. The use of timeintegrated concentration index may be useful for medium- to long-term metal studies in the aquatic environment.

1. Introduction

In freshwater systems, metals are found as various forms ranging from cationic, inorganic, organometallic, sorbed on oxides and clay surfaces, metal alloys or incorporated in crystalline structures [1-3]. Defining all the metal forms (i.e. its speciation) in the water column is currently analytically difficult because it involves various forms in multiple pools. Yet, to illustrate and predict the environmental fate and transport of metal contaminants in this dynamic system, there is a need to investigate metal partitioning, and not just isolating specific phases [4-6]. One possible approach is to define metal partitioning as Kd, a ratio between metal adsorbed in the solid fraction, operationally-defined as the filter-retained fraction (>0.45 µm) and the metal concentration in the dissolved fraction (<0.45 µm). Kd is often used in defining metal partitioning in the river system [7-9]. With relatively simple measurements, it may indicate a useful general view of metal distribution in the water column[10], [11] and the ability of the suspended particulate matter (SPM) to bind trace metals [1].

K_d is usually derived from discrete spot measurements. It is a parameter that may vary easily with even a slight fluctuation of dissolved fraction [10] for which concentrations may oscillate 2-3 folds in urbanized water at the same location and is prone to analytical contamination [1]. Hence, K_d is often considered to have limited predictive capability [4]. Alternatively, K_d values can be empirically calculated as a function of water chemistry variables, using metal speciation models such as WHAM, SCAMP or MINTEQ [11,12], although significant uncertainties were identified [4].

Consequently, there is a need to explore other possibilities in-field metal partitioning that depend less on rapidly fluctuating physico-chemical parameters but are still responsive to medium and long-term water chemistry evolution and seasonal and spatial evolution. Discrete sampling-related problems may be solved by calculating partitioning using dissolved and particulate metal concentrations from time-weighted averaged samples. When deployment time is selected correctly, time-averaging samplers are able to measure changes of heavy-metal concentrations related to various physico-chemical parameters [13,14] . Inthe water column, time-integrated solid fractions may be sampled by sediment traps[15,16]. However, sampling of time-integrated dissolved fractions for metal analysis is currently difficult in practice. A possible approach is using in situ passive samplers. The diffusion gradient in thin films (DGT) technique was initially developed[17] to quantitatively measure time-weighted average concentrations of labile metals in water. Tusseau-Vuillemin et al.[18] and Buzier et al.[19] then further developed the use of restrictive pore gels in DGTs, measuring labile metals composed of inorganic metals plus a fraction of easily exchangeable organic complexes that correlated with metal toxicity in Daphnia magna. With the combination of sediment traps and DGTs, it would then be possible to examine medium-term metal partitioning.

To what extent is metal partitioning obtained from time-averaged samples comparable and representative for spatial and temporal variations as opposed to those calculated from discrete samples? This paper aims to take a closer look at metal partitioning calculated from time-averaged and discrete samples and to evaluate their comparability in the need of robust and representative environmental monitoring parameters. It will also discuss how far these metal partitioning methods allow the study of urbanization impacts on metal behaviour in the water column. For the purpose of this study, suspended sediments are completely digested and thus metal concentration in the solid fraction includes not only adsorbed metals but also incorporated metals related to background geology. In order to avoid term confusion, this study will use concentration index (CI), defined as a ratio between metal concentration in the solid and metal concentration in the dissolved phase.

2. Methodology

2.1. Study site

For this work, samples were collected along the Seine River, France. The Seine River is located in a sedimentary basin in the north of France (Fig. 1), flowing through the Greater Paris Region. Before its estuary, the Seine River drains an area of 64700 km^2 with an average density of 215 people km^{-2}. It is an ideal example of an highly anthropized basin as it hosts 25% of French agriculture, 30% of French industry and 23% of the French population[20]. Previous studies have indicated a significant metal load within the watershed[20–22], representative of multi-metal contamination in an urban catchment.

The sampling scheme aimed to distinguish the impacts of two sources of anthropogenic influence to the Seine River. The first source is the wastewater treatment plant (WWTP) Seine- Aval treating around 1.7 million m^3 water per day[23]. The second is the area of greater Paris, including the most densely urbanized area in the region with more than 3700 inhabitants km^{-2} [24].Treated municipal wastewater from smaller units and urban runoff are the major identified metal sources to the river in this area. The first sampling site is located at Marnay-sur-Seine, situated far upstream on the Seine River (Fig. 1). It was chosen to represent a site non-affected by the Greater Paris Region, where the Seine is a Strahler order 6 river, the population density upstream of Marnay is only 15– 30 inhabitants km^{-2} [24]. The second site is the Seine at Bougival, situated 40 km downstream of Paris city (Strahler order 7). It was chosen to demonstrate the impact of greater Paris without the influence of the major WWTP Seine-Aval. Another 40 km further downstream, Triel-sur-Seine was selected to demonstrate the influence of Greater Paris Region including all its inputs to the river. The Triel station is situated downstream of the confluent of the Seine River with one of its major tributaries, the Oise River, making it a Strahler order 8. Sampling was performed from October 2008 to October 2009. Unless mentioned otherwise, samples are collected around the 20th of each month.

2.2. Physico-chemical parameters

pH was measured with either a pH meter WTW 330i (VWR) or a Waterproof pHtester 20 (Eutech Instruments) with a sensitivity of 0.05. Temperature was continuously monitored with a temperature sensor (Hobo) with a sensitivity of 0.001°C. Conductivity was measured in the laboratory within 6 h of field sampling with an Orion conductivity cell (Thermo). Daily discharge values were obtained from www.hydro.eaufrance.fr. Water was collected in plastic bottles for chlorophyll, pheopigment and ion analysis. Water was collected in 1 L precombusted glass bottles for dissolved organic carbon (DOC), TSS and particulate organic carbon (POC) analysis[25]. The absorbance at 254 nm (A254) of the GF-F filtrate was measured and the specific ultra-violet absorbance (SUVA) was calculated as SUVA = A254/DOC in $cm^{-1} g^{-1} L$. SUVA can be considered as an indicator of the aromaticity of dissolved organic matter (DOM)[26].

2.3. Metal sampling and analysis

Material and sample handling were performed following clean methodologies. All bottles and containers were soaked in 2 M HNO_3 for at least 3 days. Afterwards they were rinsed thoroughly 3 times with de-ionised water. In the field, all bottles, buckets and containers were rinsed 3 times with river water. Sampling was done from the riverbank where a PVC bucket collected water around 3 m from the riverbank.

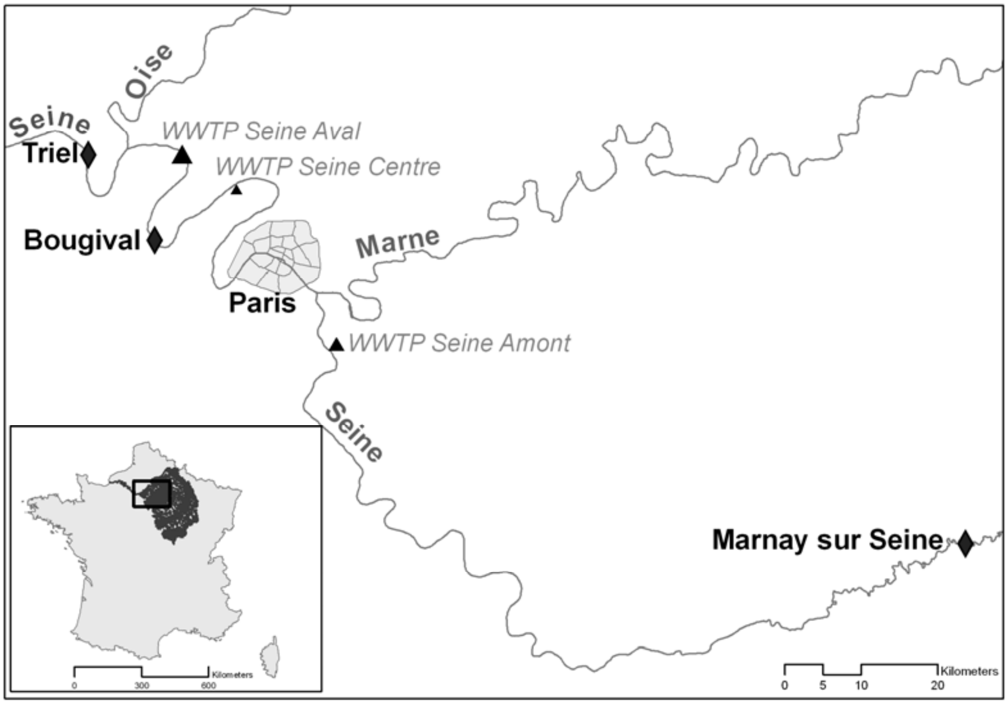


Figure 1 Sampling sites marked with diamonds; from upstream to downstream: Marnay sur Seine, Bougival and Triel. Black triangle indicates waste water treatment plants (WWTP) with triangle size indicating approximate treatment volume.

2.3.1. Dissolved fraction sampling.

The dissolved 0.45 µm fraction was obtained on-site by filtering with disposable Millex- LH Millipore syringe filters and 20 mL disposable syringe, acidified with pure 200 mL HNO_3 65% (Merck Suprapur) to avoid any precipitation. Sterile disposable 50 mL polyethylene tubes, previously tested for clean handling, were used. All samples are transported and kept at 4°C in the dark before analysis.

2.3.2. Labile fraction sampling.

Six diffusive gradient in thin films (DGT) were deployed in each site once a month in order to assess time-weighted average labile metal contamination. The method for assembling DGT is explained thoroughly elsewhere[22]. In brief, after passing through a 0.45 µm polyethersulfone (PES) filter and a 0.4 µm polycarbonate filter, labile metals diffuse through a restrictive diffusive gel layer (0.8 mm thickness) and are strongly bound by chelex resins. After DGT retrieval, they were brought back to the laboratory and the chelex resins were eluted in 1 M nitric acid in which the analysis was performed. Labile metal concentrations were calculated according to the method detailed in Bourgeault et al[27]. The deployment duration was previously validated by Bourgeault et al. to avoid bio-fouling[28].

2.3.3. Suspended particulate matter (SPM) sampling.

For discrete SPM sampling, water was collected in 2 L polyethylene bottles, kept in the dark at 4°C and filtered in the laboratory 1–5 days after sampling to minimize biological activity and SPM accumulation on the bottle walls. Only the September sample was filtered 1 month after sampling due to technical reasons. Filtration was performed on a 0.45 µm Millipore MF-Millipore cellulose ester filter mounted on the Millipore filtration system (diameter 47 mm). The sample bottle was vigorously shaken to ensure all SPM was evacuated during filtration. When possible, filtration was done on one filter, but in extreme cases where turbidity was high, filtration was done on two filters. Filters were weighted before and after filtration after drying at 40°C and stabilizing weight for up to 2 days in a desiccated jar.

A sediment trap was also installed at each site. It consisted of a 2L polyethylene terephtalate (PET) water bottle hung top-down at least 1 m from the river bank at mid-depth. Two holes (4 cm diameter) were cut on two opposite sides on the upper part of the bottle, and placed in the flow direction. This method was previously successfully used by Tessier[14] to collect SPM in slow flowing rivers. After sampling, the total sediment trap content (water and SPM) was stored in the dark at 4°C before analysis. Storage duration ranged from 2–5 days for most samples to one month for the September sample. Samples were then centrifuged in the laboratory at 2800 g for 20 m and SPM was recovered. The SPM was then freeze-dried for at least 48 h and homogenized in an agate mortar.

All discrete SPM recovered on the filters and 0.1 g of time-integrated SPM from the sediment trap were totally digested using a method adapted for the Seine River carbonated SPM[29,30], and allowing total SPM digestion. Details are presented in the ESI.† All solutions used were ultrapure reagents to assure minimum contamination (HNO_3 and HCl Normatom grade (VWR France), HF and $HClO_4$ "for trace metal analyses", (Baker, Sodipro France)).

2.3.4. Trace metal analysis. Major and trace metal concentrations (Ag, Al, As, Ca, Cd, Cr, Co, Cu, Fe, K, Mg, Mn, Ni, Se, Ti, Pb, V, and Zn) were determined in the dissolved fraction and digested SPM fraction using inductively coupled plasma quadrupolar mass spectrometry (ICP-QMS) (XIICCT-Series, ThermoElectron, France). The ICP-QMS spectrometer was calibrated using standard solutions and routinely checked with certified river water (SRM 1640, National Institute for Science and Technology, Gaithersburg, USA). Instrumental drifts and plasma fluctuations were corrected using internal standards (Re, Rh, and In (SPEX, SCP Science, France)) for all studied metals, and Ge for major elements including Ca, Al, and Mg. To minimize isobaric interferences, analysis with collision cell technology (CCT) introducing a supplementary gas mixture of H_2 (7%) and He (93%) was applied for Fe, Mn, Cd, Cr, Co, Cu, Mn, Ni, Pb, and Zn determination.

Overall, sampling representativeness and analytical accuracy was satisfactory. Ten dissolved fractions collected at one time in one site showed a standard deviation of 2% or less for Co, Mn, Ni, Pb and Zn; 5% for Cu and 9% for Cr and Cd. Variation of labile metals recovered by DGT depended on time and metals. Standard deviation (SD) of the 6 DGT is displayed as ESI.† Values obtained for the reference sediment SL1 (12 replicates) were compared to certified values, recovery was 90–99% for all analyzed elements except Cd (116%), with a standard deviation of 10% or less for all elements except Mn with a SD of 18% and Cd with a SD of 24%.

2.4. Two-phase concentration index (CI) calculation

Results and interpretation of two-phase concentration index (CI) was limited to 8 elements, Cd, Cr, Co, Cu, Mn, Ni, Pb and Zn, for which the ability for DGTs to estimate a one-month labile concentration has been validated[27]. "Discrete" CI (10^3 L g^{-1}) were calculated as the concentration ratio between metals in SPM (> 0.45 µm) to discrete dissolved metals (< 0.45 µm) both collected by discrete sampling (Eq (1)). Superscript *m* refers to the month of sampling.

$$"Discrete"CI = \left[Me\right]^{m}_{SolidMeas} / \left[Me\right]^{m}_{DissMeas} \quad \text{(Eq.1)}$$

"Integrated" CI (10^3 L g^{-1}) were calculated as the concentration ratio between metal in SPM collected in the sediment trap to labile metal (DGT) both integrating one month of sampling. (Eq (2)). Integrated CI with superscript *m* is based on integrated samples deployed between dates *m* 1 and *m*.

$$"Integrated"CI = \left[Me\right]^{m}_{trap} / \left[Me\right]^{m}_{labile} \quad \text{(Eq.2)}$$

where $\left[Me\right]^{m}_{Trap}$ is the concentration of settleable sediment collected in the sediment trap deployed on month *m 1* and collected on month m and $\left[Me\right]^{m}_{Labile}$ is the concentration of labile metals measured by the DGT method trap deployed on month *m*1 and collected on month *m*.

2.5. Labile–inert–solid partitioning

Average metal proportion in the three different pools of the water column: labile metals measured by DGT, inert metals as the difference between labile and dissolved metals, and solid metals; were estimated. Due to different sampling methods for each pool (discrete *vs.* integrating) and variable quantification limits (much lower for labile metals *via* DGT than for total dissolved metals), a specific procedure was set to derive inert (non labile) dissolved metal concentrations. When

$$\left([Me]^{m-1}_{DissMeas} + [Me]^{m}_{DissMeas}\right)\Big/2 > [Me]^{m}_{labile}$$

Inert metal concentrations (Eq (3)) were calculated as thedifference between the averaged dissolved metal concentration (Eq (4)) and the labile metal concentration.

$$\left([Me]^{m-1}_{DissMeas} + [Me]^{m}_{DissMeas} / 2 < [Me]^{m}_{Labile} \quad \text{(Eq.3)}$$

where for month *m*, discrete dissolved metal concentration wereaveraged between measurements taken on month *m* and the month before (*m*-1).

$$[Me]^{m}_{DissAvg} = [Me]^{m-1}_{DissMeas} + [Me]^{m}_{DissMeas}\Big/2 \quad \text{(Eq.4)}$$

When dissolved concentrations were lower than quantificationlimit (QL) and average dissolved concentration calculated from Eq (3) became lower than labile concentration, inert metals were considered as negligible in the balance and integrated labile metals were considered as a relevant proxy for integrated total dissolved metals (Eq (5)).

$$[Me]^{m}_{DisAvg} = [Me]^{m}_{labile} \quad \text{(Eq.5)}$$

when $\left([Me]^{m-1}_{DissMeas} + [Me]^{m}_{DissMeas}\right)\Big/2 < [Me]^{m}_{labile}$ Total solid metal, defined as total solid metal per liter of water, was obtained by multiplying metal content ((µg g^{-1}) of each month with SPM concentration (g L^{-1}). Average solid metal (µg L^{-1}) for month m ($[Me]^{m}_{SolidAvg}$) was then calculated similarly to the calculation of the average dissolved concentration in Eq (3).

Total metal (µg L^{-1}) was calculated as a sum between the average solid metal and dissolved metal concentration, both in µg L^{-1} (Eq.6).

$$[Me]^{m}_{Total} = [Me]^{m}_{DisAvg} + [Me]^{m}_{SolidAvg} \quad \text{(Eq.6)}$$

Distribution of metal in each phase (labile, inert and solid) was then calculated using the total metal calculated using Eq.(6).

3. Results

In order to optimally present data of monthly variation, median values were used. Comparisons between samples were performed using Mann–Whitney ranked tests (p = 0.01).

3.1. River chemistry

Table 1 Summary of measured physico-chemical parameters during 13 months of sampling between 2008-2009 indicating minimum-maximum values with 1st quartile – median – 3rd quartile in parenthesis; Q: discharge; DOC: dissolved organic carbon; SPM: suspended particulate matter; POC: particulate organic carbon (n=13)

	Marnay	**Bougival**	**Triel**
Q (m3/s)	25 - 89 (37 - 50 - 54)	92 - 324 (116 - 184 - 215)	198 - 550 (225 - 340 - 384)
pH	8.06 - 8.32 (8.14 - 8.18 - 8.28)	7.20 - 8.24 (7.76 - 7.91 - 8.09)	7.10 - 8.01 (7.58 - 7.73 - 7.85)
Alkalinity (mg/L)	152.5 - 286.7 (218.08 - 237.9 - 262.3)	182 - 281 (224 - 244 - 259)	189 - 281 (236 - 253 - 264)
Conductivity (µS/cm)	268 - 526 (387 - 479 - 499)	449 - 611 (490 - 527 - 570)	506 - 668 (588 - 619 - 655)
Temperature (°C)	5.6 - 23 (7 - 13.1 - 17.1)	4.5 - 22.8 (8.5 - 15.2 - 19.9)	4.9 - 22 (8.9 - 14.4 - 19.2)
Chlorophyll (µg/L)	0.5 - 3.5 (0.7 - 1.0 - 1.7)	0.4 - 15.1 (2.7 - 3.7 - 8.1)	0.3 - 16.4 (2.1 - 2.5 - 7.9)
DOC (mg/L)	1.62 - 2.68 (1.83 - 2.05 - 2.38)	2.56 - 4.34 (2.77 - 2.94 - 3.25)	3.42 - 5.45 (3.72 - 3.87 - 3.97)
Ca^{2+} (mg/L)	58.01 - 105.35 (72.36 - 88.27 - 93.19)	73 - 100 (80 - 95 - 98)	77 - 109 (89 - 99 - 102)
Mg^{2+} (mg/L)	0.54 - 8.93 (3.28 - 3.97 - 4.66)	0.64 - 10.3 (3.45 - 6.4 - 7.03)	0.68 - 8.63 (5.79 - 7.34 - 8.12)
K^{+} (mg/L)	1.55 - 6.26 (1.93 - 2.06 - 3.28)	0.42 - 4.61 (2.49 - 3.36 - 4.19)	1.54 - 9.18 (3.79 - 4.32 - 5.55)
Na^{+} (mg/L)	3 - 20 (6 - 8 - 9)	6.7 - 17.7 (12.6 - 14.9 - 16.1)	10.4 - 27.5 (15.3 - 19.5 - 22.2)
Cl^{-} (mg/L)	11 - 27 (13 - 14 - 20)	17.4 - 34.2 (23.9 - 26.6 - 30.1)	19.9 - 41.9 (34 - 37 - 41.2)
NH_4^{+} (mg/L)	0.3 - 1.4 (0.4 - 0.6 - 1)	0.09 - 2.92 (0.17 - 0.41 - 0.74)	0.23 - 4.28 (0.38 - 0.51 - 1.39)
NO_3^{-} (mg/L)	7.8 - 26 (11.3 - 18 - 24.9)	13.2 - 26.7 (15.1 - 21.3 - 25)	20.2 - 35.2 (27.9 - 28.5 - 31.3)
SO_4^{2-} (mg/L)	13.7 - 22.4 (14.3 - 17.3 - 18.8)	24.4 - 44.6 (31.1 - 36.1 - 38.4)	28 - 51.5 (43.6 - 46.4 - 49.5)
SPM (mg/L)	4.1 - 21.9 (7.8 - 9.8 - 11.9)	6.4 - 44.1 (8.5 - 10.9 - 15.7)	4.0 - 33.4 (5.7 - 9.5 - 19.4)
POC (mg/L)	0.05 - 1.9 (0.42 - 0.56 - 0.9)	0.38 - 3.92 (0.69 - 0.88 - 1.03)	0.04 - 2.47 (0.72 - 0.89 - 1.08)
Ca (%)	13.9 - 44.2 (17.0 - 17.8 - 18.7)	7.2 - 15.5 (11.6 - 12.1 - 12.7)	4.0 - 30.8 (9.1 - 9.7 - 10.1)
Fe (%)	0.65 - 2.87 (1.53 - 1.84 - 2.20)	1.42 - 3.26 (2.35 - 2.62 - 2.91)	0.29 - 5.17 (2.40 - 2.78 - 3.09)
Al (%)	0.4 - 4.77 (2.22 - 3.10 - 3.41)	1.19 - 5.30 (2.69 - 4.06 - 4.55)	0.25 - 8.47 (3.02 - 3.80 - 3.94)
Mg (mg/kg)	158 - 12227 (2661 - 3382 - 3970)	3515 - 19076 (4429 - 5766 - 8270)	1397 - 8815 (4965 - 5462 - 7656)
K (mg/kg)	183 - 9478 (5288 - 7306 - 8088)	2726 - 11946 (7317 - 8883 - 10320)	1446 - 17945 (7944 - 9052 - 9885)

Most water quality parameters measured throughout the campaign displayed a Marnay–Bougival–Triel gradient indicating evident evolution in water chemistry (Table 1). The pH at the upstream site is relatively more basic, pH 8.20 ± 0.04, where the river drains calcareous rocks. As the catchment becomes more urbanized, pH drops to 7.91 ± 0.04 and 7.73 ± 0.04 downstream at Bougival and Triel, respectively. Downstream sites had significantly higher values of DOC and POC and higher photosynthetic activities indicated by higher chlorophyll concentration. Major ions showed two different trends; Ca and NH_4^{+} concentrations remained constant at the 3 sites, while the others increased downstream. From upstream to downstream, the median of magnesium and potassium ion concentrations doubled, while chloride and sulfate increased by a factor of 2.5.

Median metal concentrations in different pools in the water column showed an evident upstream–downstream increasing trend from Marnay to Bougival and Triel, although in general, Bougival displayed higher metal content than Triel for all except Co and Mn (Table 2). The dilution effect of the confluence between the Seine and the Oise River (25 km downstream from Bougival and 15 km upstream from Triel-sur-Seine) may be the cause of the decrease in metal concentration in Triel.

Table 2 Summary of metal concentration at the three studied sites in four measured phases indicating minimum-maximum values with 1st quartile – median – 3rd quartile in parenthesis (n=13)

			Marnay	**Bougival**	**Triel**
Cd	Grab	<0.45µm (µg.L-1)	<LQ	0 - 0.015 (0 - 0 - 0.013)	0 - 0.019 (0.012 - 0.013 - 0.014)
		>0.45µm (µg.g-1)	0 - 4.42 (0.43 - 0.54 - 1.05)	0.77 - 20.53 (1.69 - 2.47 - 4.05)	0.44 - 2.29 (0.88 - 1.41 - 2.06)
	time integrated	Labile DGT (µg.L$^{-1)}$	0 - 0.002 (0.001 - 0.001 - 0.001)	0 - 0.007 (0.002 - 0.003 - 0.005)	0 - 0.005 (0.003 - 0.004 - 0.005)
		sed.trap (µg.g-1)	0.269 - 0.444 (0.294 - 0.309 - 0.332)	1.53 - 8.07 (1.73 - 2.65 - 3.57)	0.35 - 3.03 (0.85 - 1.23 - 1.86)
Cr	Grab	<0.45µm (µg.L-1)	0 - 1.086 (<LQ)	0 - 1.041 (0 - 0 - 0.508)	0 - 1.235 (0 - 0.212 - 0.324)
		>0.45µm (µg.g-1)	7.7 - 101.7 (41.9 - 53.6 - 64.8)	46.3 - 102.4 (73 - 84.2 - 88.9)	35.9 - 121.9 (58.1 - 69.1 - 88.1)
	time integrated	Labile DGT (µg.L-1)	0 - 0.035 (0.018 - 0.02 - 0.025)	0 - 0.093 (0.024 - 0.028 - 0.035)	0 - 0.086 (0.025 - 0.031 - 0.037)
		sed.trap (µg.g-1)	42.1 - 54.2 (50 - 50.5 - 51.4)	69.2 - 109.3 (71.3 - 85.4 - 96.4)	56.4 - 86.7 (65 - 73.5 - 80.9)
Co	Grab	<0.45µm (µg.L-1)	0.04 - 0.18 (0.09 - 0.12 - 0.16)	0.13 - 0.25 (0.17 - 0.21 - 0.23)	0.2 - 0.39 (0.26 - 0.3 - 0.32)
		>0.45µm (µg.g-1)	2.48 - 9.17 (6.49 - 7.59 - 8.52)	6.42 - 38.4 (10.75 - 11.51 - 12.7)	5.9 - 25.2 (10.9 - 14 - 17.5)
	time integrated	Labile DGT (µg.L-1)	0 - 0.022 (0.006 - 0.012 - 0.019)	0 - 0.051 (0.016 - 0.023 - 0.042)	0 - 0.078 (0.029 - 0.038 - 0.057)
		sed.trap (µg.g-1)	5.76 - 7.13 (6.44 - 6.68 - 6.87)	8.25 - 11.81 (9.1 - 9.79 - 11.2)	7.69 - 13.04 (9 - 10.33 - 11.76)
Cu	Grab	<0.45µm (µg.L-1)	0.27 - 0.67 (0.35 - 0.37 - 0.46)	0.77 - 1.76 (1.02 - 1.12 - 1.27)	0.8 - 1.56 (1.07 - 1.22 - 1.45)
		>0.45µm (µg.g-1)	5.7 - 95.5 (18.7 - 19.4 - 28)	44.7 - 169.3 (67.9 - 103.9 - 147)	21.1 - 130.3 (56.2 - 72.2 - 93.6)
	time integrated	Labile DGT (µg.L-1)	0 - 0.104 (0.062 - 0.074 - 0.085)	0 - 0.481 (0.172 - 0.253 - 0.298)	0 - 0.388 (0.21 - 0.251 - 0.307)
		sed.trap (µg.g-1)	13.5 - 18.1 (15.3 - 16.1 - 17.2)	78.8 - 185.3 (90.2 - 121.7 - 150.1	53.4 - 96.8 (56 - 81.8 - 88.9)
Mn	Grab	<0.45µm (µg.L-1)	1.44 - 3.19 (1.81 - 2.43 - 2.6)	3.07 - 17.39 (7.01 - 8.3 - 10.75)	4.37 - 27.63 (11.62 - 15.38 - 17.67)
		>0.45µm (µg.g-1)	130 - 910 (394 - 444 - 761)	514 - 1762 (817 - 1035 - 1186)	484 - 2314 (1097 - 1428 - 1911)
	time integrated	Labile DGT (µg.L-1)	0 - 3.21 (0.41 - 1.13 - 2.24)	0 - 8.38 (2.27 - 3.72 - 7.18)	0 - 10.23 (4.45 - 4.71 - 9.65)
		sed.trap (µg.g-1)	268 - 527 (317 - 431 - 452)	281 - 1825 (492 - 637 - 653)	414 - 966 (502 - 594 - 872)
Ni	Grab	<0.45µm (µg.L-1)	0.48 - 1.93 (0.8 - 1.45 - 1.59)	0.94 - 2.25 (1.48 - 1.76 - 1.98)	1.49 - 2.74 (1.96 - 2.17 - 2.36)
		>0.45µm (µg.g-1)	9.1 - 83.5 (20.5 - 25.4 - 32)	20.9 - 40.5 (26.3 - 32.1 - 36)	0 - 59.5 (21.5 - 30.1 - 39.5)
	time integrated	Labile DGT (µg.L-1)	0 - 0.212 (0.135 - 0.173 - 0.202)	0 - 0.47 (0.228 - 0.322 - 0.419)	0 - 0.796 (0.443 - 0.543 - 0.578)
		sed.trap (µg.g-1)	20.5 - 26.2 (20.6 - 21.3 - 21.6)	26.2 - 40.2 (28.4 - 31.3 - 37.4)	21.2 - 30.7 (25.2 - 27.7 - 29.3)
Pb	Grab	<0.45µm (µg.L-1)	0 - 0.071 (<LQ)	079 - 0.255 (0.152 - 0.195 - 0.23	0 - 0.327 (0.145 - 0.162 - 0.204)
		>0.45µm (µg.g-1)	1 - 69 (29 - 36 - 47)	71 - 307 (118 - 139 - 161)	34 - 145 (82 - 109 - 115)
	time integrated	Labile DGT (µg.L-1)	0 - 0.031 (0.004 - 0.007 - 0.011)	0 - 0.161 (0.024 - 0.032 - 0.058)	0 - 0.039 (0.018 - 0.019 - 0.023)
		sed.trap (µg.g-1)	18.7 - 23.5 (19.7 - 20.2 - 21.7)	80 - 245.2 (93.3 - 123 - 155.2)	50.7 - 98.5 (58.7 - 81.8 - 84.1)
Zn	Grab	<0.45µm (µg.L-1)	0 - 9.768 (0 - 2.257 - 2.611)	3.28 - 24.11 (4.39 - 6.22 - 7.35)	3.47 - 14.6 (4.53 - 6.72 - 9)
		>0.45µm (µg.g-1)	45 - 713 (134 - 185 - 395)	336 - 671 (383 - 480 - 567)	43 - 1402 (256 - 351 - 434)
	time integrated	Labile DGT (µg.L-1)	0 - 1.488 (0.159 - 0.444 - 0.756)	0 - 3.13 (1.51 - 1.83 - 2.47)	0 - 3.74 (1.55 - 2.68 - 3.06)
		sed.trap (µg.g-1)	106 - 149 (110 - 120 - 126)	307 - 694 (406 - 506 - 544)	225 - 415 (249 - 342 - 395)

Dissolved metal concentrations compared with other rivers with strong urban influence[1] showed that the Seine River dissolved concentrations (Table 2) are higher but are still in the same order of magnitude. Data found during this campaign were also comparable to other dissolved metal concentrations earlier reported in the Seine River[31]. Labile metal concentrations of Co, Cu, Mn and Ni were within the range of those measured in the Seine River basin[26]. Concentrations of metals in SPM collected by discrete sampling were much more variable than those measured in SPM collected with the sediment trap on a monthly basis. Median values between the two sets were comparable. When metal concentrations in SPM were normalized by background geological values obtained from numerous sites in the Seine River basin,[32] SPM collected downstream at Bougival and Triel showed an average enrichment of 2–3 times for Ni, Cr and Co, 7–8 times for Pb, Cu and Zn, and 15–18 times for Cd.

3.2. Labile–inert–solid partitioning

Partitioning of each metal in the defined phases varied according to metals and sites (Fig. 2). The approach described in Eq (2)–(6) consisted of averaging discrete total metal for the dissolved and solid phases causing the total median values of the three phases displayed in Fig. 2 to be occasionally less or more than 100% of the total metal calculated through Eq (6). This is mainly true for Cd, Mn and Zn that displayed high variation of discrete concentrations to which this averaging method may constitute uncertainties of total partitioning of around 5–10%. Nevertheless, averaged median values were considered representative because Co, Cr, Cu, Ni and Pb showed total averages close to 100%.

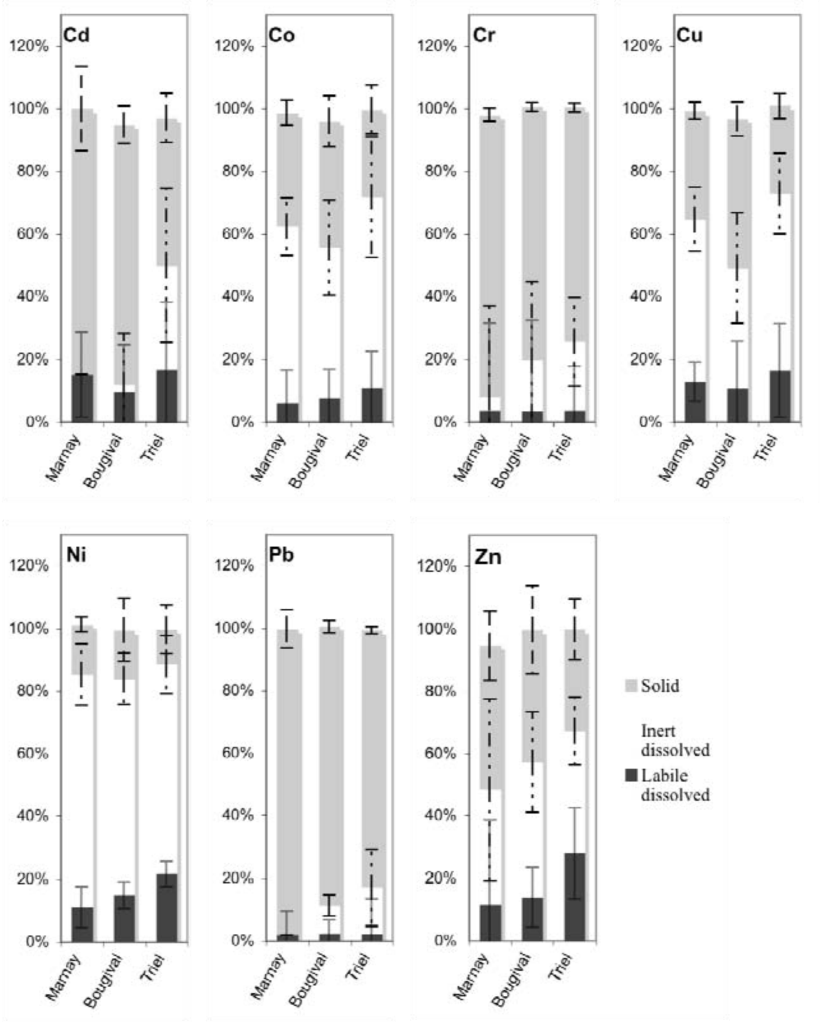


Figure 2. Bar charts represent average proportion of metal in each pool relative to the total of metal in the three defined pools. Individual labile dissolved metals were measured by DGT. Discrete inert dissolved metals were calculated from the average of dissolved metals for two months between the deployment and the collection of DGT subtracted by the labile metal pool. When labile metals were larger than the average dissolved metals, the dissolved metal pool was represented by concentration in the labile pool. Individual solid metals were calculated from the average of dissolved metals for two months between the deployment and the collection of DGT (n=12).

Despite complete digestion of particulate metals, the proportion of dissolved metals in these samples was relatively high compared to literature data. Our data showed that for most metals, the median proportion of dissolved metal in the water column exceeded more than 50%. Nguyen et al. found Zn, Co, Cd and Pb in a contaminated lake highly associated to the solid phase (for about 70% of the total metal load) [9]. Previous metal partitioning values on the Seine River accounted for higher solid fraction (70 to 90%) mostly due to relatively high approximation of SPM concentration used to theoretically calculate total solid metal[24]. Nevertheless, our dissolved and particulate metal data were in agreement with other Seine reference data[31,33], indicating that calculated CI was fairly accurate despite differences with other water bodies.

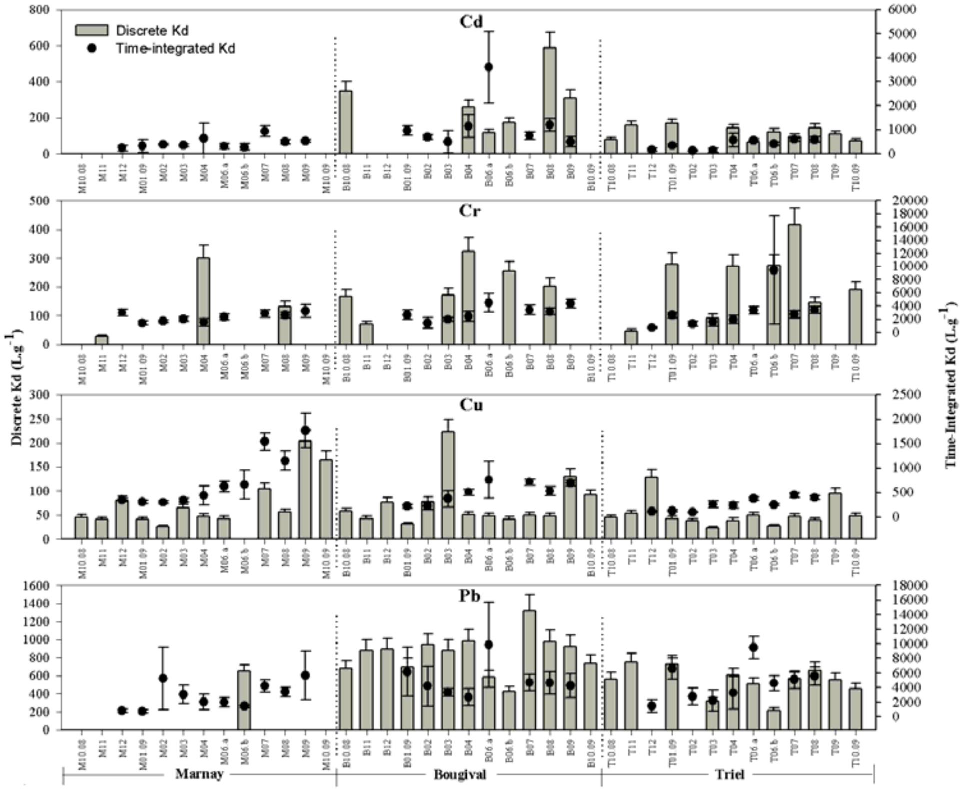
3.3. Two-phase concentration index (CI)

Metals were ranked by their preference to the solid phase using the average discrete CI indicating Pb > Cr > Mn ~ Cd > Zn > Cu ~ Co > Ni (Table 3). When time-integrated CI is compared, a similar order is observed for most of the metals, except for Co and Cu that moved up the ranking: Pb > Cr> Cd > Co> Cu > Zn > Mn > Ni. Most studies display logarithmic CI values but for this study, basic CI was chosen to better observe the fluctuations in metal partitioning.

Table 3 Summary of metal partitioning at the three studied sites (in $L.g^{-1}$), “discrete CI” is the ratio between concentration of a given metal in the solid fraction to the dissolved fraction (water collected by discrete sampling and filtered at 0.45 µm) and “time-integrated CI” is the ratio between concentration of a given metal in the settleable suspended particles collected by a sediment trap to the labile fraction measured with the Diffusive Gradient Thin (DGT) films. Indicated values correspond to minimum-maximum values with 1st quartile – median – 3rd quartile in parenthesis (n=13 for “discrete CI” and n=10 for “Time-integrated CI). QL: quantification limit.

		Marnay	**Bougival**	**Triel**
Cd	"Discrete" CI	<QL	118 - 590 (196 - 284 - 339)	64 - 169 (83 - 116 - 145)
	"Time-integrated" CI	236 - 936 (316 - 364 - 522)	497 - 3591 (647 - 859 - 1160)	131 - 595 (168 - 414 - 567)
Cr	"Discrete" CI	28 - 301 (80 - 132 - 216)	70 - 325 (167 - 186 - 240)	47 - 415 (131 - 230 - 276)
	"Time-integrated" CI	1422 - 3256 (1687 - 2334 - 2868)	1425 - 4461 (2292 - 2914 - 3628)	712 - 9420 (1565 - 2586 - 3326)
Co	"Discrete" CI	26 - 204 (43 - 52 - 87)	31 - 224 (48 - 51 - 78)	23 - 129 (39 - 45 - 50)
	"Time-integrated" CI	302 - 1766 (345 - 532 - 1028)	222 - 760 (336 - 519 - 703)	99 - 452 (132 - 252 - 376)
Cu	"Discrete" CI	16 - 269 (41 - 52 - 103)	52 - 166 (58 - 102 - 115)	21 - 103 (42 - 52 - 85)
	"Time-integrated" CI	153 - 277 (174 - 202 - 241)	349 - 831 (473 - 513 - 567)	223 - 469 (242 - 258 - 300)
Mn	"Discrete" CI	79 - 553 (163 - 189 - 345)	49 - 337 (62 - 133 - 189)	37 - 505 (61 - 93 - 114)
	"Time-integrated" CI	132 - 1665 (158 - 331 - 973)	74 - 887 (97 - 164 - 249)	49 - 208 (60 - 96 - 128)
Ni	"Discrete" CI	6 - 73 (13 - 18 - 42)	11 - 43 (13 - 19 - 22)	0 - 30 (11 - 14 - 20)
	"Time-integrated" CI	97 - 221 (110 - 121 - 147)	75 - 218 (87 - 113 - 128)	41 - 66 (48 - 51 - 55)
Pb	"Discrete" CI	654 - 654 (654 - 654 - 654)	424 - 1325 (701 - 881 - 945)	217 - 749 (483 - 563 - 634)
	"Time-integrated" CI	718 - 5644 (1577 - 2543 - 4023)	2698 - 9863 (3992 - 4459 - 5044)	1494 - 9509 (2803 - 4593 - 5593)
Zn	"Discrete" CI	19 - 577 (53 - 100 - 171)	17 - 165 (46 - 94 - 109)	5 - 360 (29 - 50 - 71)
	"Time-integrated" CI	100 - 1064 (143 - 158 - 413)	205 - 872 (250 - 291 - 536)	60 - 172 (119 - 144 - 156)

The CI for each month in the three sites was also individually compared in order to evaluate spatial evolution (Fig. 3). Discrete CI at Bougival was found to be significantly higher than at Triel ($p = 0.011$) for all metals except for Cd, Cr and Pb which were excluded from the comparison because many dissolved concentration values at Marnay were lower than the quantification limit (QL). Nevertheless, no difference was found between discrete metal partitioning at Marnay when compared to Bougival and Triel ($p > 0.05$) because CI variation at Marnay was very high. When the same test was applied to time-integrated CI, values at Bougival were also found to be significantly higher than at Triel ($p < 0.0001$). Moreover, CI at Marnay was also found to be significantly higher than CI at Triel ($p < 0.0002$), which was not observed for discrete CI values. As time-integrated CI had lower detection limits, CI for Cd, Cr and Pb were better defined for Marnay. When this statistical comparison was performed on all elements without excluding Cd, Cr and Pb, similar conclusions were obtained.


Cd
Cr
Cu
Pb
Discrete Kd
Time-integrated Kd
Discrete Kd (L.g^{-1})
Time-Integrated Kd (L.g^{-1})
0
200
400
600
800
1000
2000
3000
4000
5000
6000
100
300
500
4000
6000
8000
10000
12000
14000
16000
18000
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B10 09
T10 08
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Marnay
Bougival
Triel

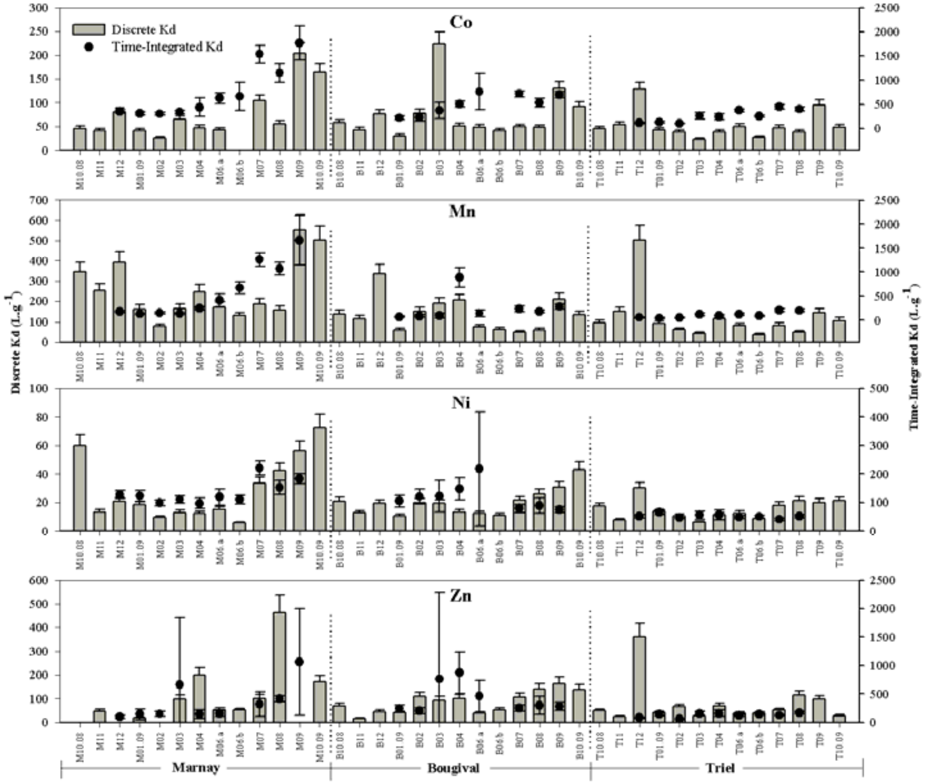

Figure 3. "Discrete" CI (concentration ratio of metals in SPM (>0.45 µm) to dissolved metals (<0.45 µm) both collected by discrete sampling) (L/g) are presented as bars, indicating "discrete" CI from Marnay, Bougival and Triel from left to right from October 2008 to October 2009. "Time - Integrated" CI (concentration ratio of metals in SPM collected in sediment trap to labile metals measured by DGT) (L/g) are presented as dotted line indicating "time-integrated" CI from Marnay, Bougival and Triel for each month during sampling from December 2008 – September 2009 (Indicated month corresponding to collection time with deployment time the month before)

Individual CI values were also compared in order to identify temporal variation during the one-year campaign (Fig. 3). In general, temporal variations were higher at Marnay than at Bougival and Triel, except for a few extreme events where CI values increased dramatically at the two downstream sites. Indeed, there was a high variation of discrete CI values for five elements, Co, Cu, Mn, Ni and Zn at Marnay that was significantly less visible at Triel: at Marnay, relative standard deviations for discrete CI were 69%, 84% and 73% for Co, Cu and Ni, respectively, whereas at Triel, RSD for discrete CI were 54%, 44% and 51% for Co, Cu and Ni, respectively. These higher variations of discrete CI values at Marnay compared to Triel were also observed for time-integrated CI for Cu and Ni. RSD for time-integrated CI at Marnay were 102% and 29% for Co and Ni, respectively, and at Triel, RSD for time-integrated CI at Triel were 51% and 12% for Co and Ni, respectively. In addition to Co, Cu and Ni, Mn and Zn average values of time-integrated CI decreased at Triel compared to those at Marnay. This evolution was not observed on average values of discrete CI for Mn and Zn. Cr, Cd and Pb were not compared because most of their discrete CI at Marnay was lower than QL.

Observing the different trends on temporal variation of CI, it was possible to divide the metals into two groups. The first group consisted of Co, Mn, Ni, and Zn with a significantly higher discrete and time-integrated CI at Marnay than at Triel notably for the summer months from July to October. The second group included Cd, Cr, Cu and Pb. Due to discrete CI at Marnay being below quantification limits for these metals, observations are made on time-integrated CI. These metals have relatively comparable CI values between Marnay and Triel both in low and high flows, with higher CI at Bougival during certain periods. The only period where Cd displayed a discrete CI at Marnay higher than at Triel was in the month of October 2008. The discrete CI of Cr multiplied up to six to ten fold in one site between two different periods. Values increased from 27 ± 3.9, 70 ± 9.9, and 47 ± 6.7 at Marnay, Bougival and Triel, respectively, and 272 ± 38.8 on April 2009, an increase of 11, 5 and 6 times at Marnay, Bougival and Triel, respectively.

4. Discussion

4.1. Discrete vs. time-integrated concentration indexes

The comparison between discrete and time-integrated metal concentration index (CI) originated from the need for an environmental indicator representative of the medium- and long-term trend in the milieu. As the frequency of discrete sampling for metal monitoring is often limited by labor factors, this study was aimed at considering time-integrated metal concentration index as an option. Difficulties faced in measuring CI for Cd, Pb and Cr due to low dissolved concentrations were overcome by using DGT that concentrates labile metals over a period of time. Passive and time-integrated samplers also hold great potential in the cross-validation of biological accumulation under field conditions[6,34]. The source of the high variability in time integrative CI was DGT measurements, their uncertainty levels are higher than metal concentrations in sediment traps.

The authors are aware that the two CI values do not represent the same partitioning, mostly because dissolved metals do not coincide with labile metals. Some inert dissolved metal complexes are not sampled by DGT. Consequently, time-integrated CI calculated using labile metals measured by DGT would result in higher CI values than discrete CI, and the difference is amplified for metals with a low lability in water. This would be the reason why Cu, Zn and Co were ranked differently between discrete and time-integrated CI.

In order to further investigate whether time-integrated CI could be representative as an environmental indicator, partitioning evolution between sites over a year was investigated. Statistical tests performed previously in section 3.3 showed that time-integrated metal partitioning is more effective in differentiating spatial evolution. As physico-chemical parameters between the three sites are significantly different, metal partitioning at the three sites are also expected to vary. Differences in CI values between Marnay and Triel were not significant when evaluated with discrete values whereas it was considered different when comparing time-integrated values. Regarding temporal variation, Co, Mn and Ni had significantly higher discrete and time-integrated CI at Marnay than at Triel notably for the summer months from July to October. On the other hand, Cr and Cu showed relatively stable discrete and time-integrated CI values between Marnay and Triel both in low and high flows, with possible higher CI at Bougival during certain periods. This similarity of temporal variation between discrete and time-integrated CI means that to a certain extent, one month time-integrated CI is capable of illustrating temporal variation of metal partitioning in the water column.

The biggest challenge in performing environmental monitoring is the representativeness of samples in respect with spatial and temporal evolution. Collected samples are expected to represent the water column without being over or under-magnified by extreme events or sudden variations. Although discrete CI captures instant variations that may be significantly different, variations are irregular depending on sampling period and thus a general trend is hardly observable. The differences observed when comparing discrete and time-integrated CI in this study suggest that although time-averaged CI gives averaged and consequently ‘‘buffered’’ values, it averages short-term variation and enhances sustainable and medium- to long-term variation in a given site.

4.2. Urbanization impacts observed by time-integrated CI

Recent studies showed that metal speciation in the solid phase[35] and metal accumulation in aquatic species[34] were modified downstream of the urbanized Greater Paris Region. With this study, change in land use not only affects metal speciation but also partitioning between the solid and the dissolved phase of urban-enriched metals. Previously discussed results demonstrated the difference in temporal variation between upstream and downstream (smaller standard variation for the upstream Marnay data set compared to the Triel data set for Co, Cu and Ni) and higher discrete and time-integrated CI at Marnay from July to October for Co, Mn, Ni, and Zn. Urbanization was likely to affect metal partitioning in the Seine River. This impact is evidenced by time-integrated CI differences between upstream and downstream of the Greater Paris Region observed for enriched metals above. On the other hand, such differences were not observed for Cr, a non-enriched metal in the Seine River despite the physico-chemical evolution on a given period from Marnay to Triel.

The behavior of metals enriched by anthropogenic activities downstream seems to be controlled by different parameters compare to metal behavior at the upstream site. This is seen both through statistical differences between CI at Marnay and Triel and the higher fluctuating CI at Marnay compared to Triel. Spearman correlation tests (significance level $p < 0.05$) were performed separately between Marnay representing the non-urban site, and Bougival and Triel, representing the anthropogenic sites, to further investigate key factors affecting metal behavior in the water column. No significant direct correlation between CI and the measured physico-chemical parameters was found. This is due to differences in governing processes and response level between metal concentrations in the solid and the dissolved fraction. While no significant correlation was found either between solid metals and physico-chemical parameters, dissolved metals appeared to be correlated to some water parameters. Higher temporal variation in Marnay compared to Triel is likely due to the dissolved metal concentration at Marnay being more correlated with flow-related parameters which can fluctuate significantly. Upstream, correlations of some dissolved metals with conductivity were relatively high (Cu r^2=0.657; Mn r^2=0.699; Ni r^2=0.804) while being negatively correlated with discharge (Cu r^2=-0.736; Mn r^2 =-0.813; Zn r^2=-0.688). Downstream, dissolved metal concentrations were less correlated with fluctuating flow-related parameters and were more correlated with redox-related parameters such as DOC (Co r^2=0.655; Cu r^2=0.469; Mn r^2= 0.507; Ni r^2= 0.574) and temperature (Cd r^2=0.531; Cu r^2=0.523; Mn r^2=0.602; Pb r^2=0.724) while displaying negative correlation with pH (Cd r^2=-0.608; Co r^2=-0.552; Cu r^2= -0.805; Mn r^2= -0.697; Pb r^2= -0.501). Higher temporal fluctuations of CI at Marnay compared to Triel may be explained by the correlation of metal concentrations with these different water parameters. As discharge varies considerably compared to DOC, temperature and pH, metal concentrations at Marnay would also vary to a higher extent than at Bougival and Triel. Downstream, dissolved metal concentrations seemed more affected by sorption processes. Their concentrations are more correlated with DOC, temperature and pH than at Marnay. These three parameters are known to control adsorption and desorption reactions on surfaces. Temperature and pH are known to control point zero charge (PZC) of adsorption on many mineral surfaces[36,37] and DOC is known to form complexes with available dissolved metals[38]. Adsorption to the solid phase maybe an important process controlling fluctuation of metal partitioning and mobility in the water column downstream.

5. Conclusion

Comparison of discrete and time-integrated metal partitioning in the water column of the Seine River demonstrated the capability of time-integrated concentration index (CI) to represent spatial and temporal variation of metal variation trend. Although it is recognized that time-integrated CI does not measure the exact same pool as discrete CI, time-integrated CI could be useful to study medium- and longterm trends of metal partitioning in river systems related to urbanization, reducing the labor costs needed to obtain representative discrete metal sampling. It could also be related to bioaccumulation, which is also a time-integrated phenomenon. µFurther investigation of time-integrated CI should be performed on other watersheds to study the effectiveness of this method on other water systems.

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Environmental impact

Using metal concentration data from the water column, discrete concentration index, calculated from the ratio between discrete solid metal concentration and discrete dissolved metal concentration, was compared with time-integrated concentration index, calculated as a ratio between solid metal concentration from sediment traps and labile metals measured by DGT. The comparison of the two data sets demonstrated the capability of time-integrated concentration index to represent spatio-temporal trends in metal variation trends. Time-integrated concentration index is useful to study medium and long-term trends of metal partitioning in river systems related to urbanization, reducing the labor costs needed to obtain representative discrete metal sampling. It could also be related to bioaccumulation, which is also a time-integrated phenomenon. This study will contribute to enriching the existing methods of environmental monitoring in aquatic systems so that water agencies and stakeholders may have a monitoring option which suits their budget and human resource constraints.

Supporting Information 1 : Sediment digestion protocol

SPM was digested completely during 3-4 weeks using various acids at different temperatures. The complete discrete SPM samples+filter (MF-Millipore cellulose ester filters) and 0.1 g of time-integrated SPM from sediment trap were digested in Teflon vessels under laminar flow hood using a heating block (Digiprep, SCP Science) using 3 solutions:

1. The first attack uses 15 mL *aqua regia* (HNO_3 65%: HCl 30%, 3:1) for 3 days at room temperature (vessel capped). Excess nitrogen dioxide was then evaporated at 90°C for 2 hours. This step assured the dissolution of Ca and Mg, abundant in the Seine River. Remaining liquid in vessels were pipetted (VWR, low density polyethylene) into a disposable tube (Falcon, polypropylene) and carefully avoiding pipetting the sediment. The remaining sediment was rinsed with 10 mL 0.5 N HNO_3 This was performed 3 times to ensure the evacuation of Ca and Mg, previously dissolved by *aqua regia,* and avoid re-precipitation of Ca and Mg fluorides in HF solution.
2. Digestion continued with 10 mL of a HF(48.9%) : HNO_3 (65%) mixture (1:1) to attack siliceous minerals during 24h at room temperature (vessels capped). Sample was then evaporated to near dryness at 100°C to eliminate hexafluorosilicic acid (3-5 days).
3. The solid residue was then attacked with 12 mL of a HNO_3 65% : $HClO_4$ 69- 72% (1:1) mixture heated at 120°C during 5 days (vessels capped). This step is aimed to oxidize organic matter. Final solutions were again evaporated to near dryness to eliminate perchloric acid. Pipetted solution recovered in separate tubes during the first step using *aqua regia* were re-introduced to the Teflon vessels and were again evaporated near to dryness. Afterwards, 1 mL 618 of 65% HNO_3 was added to the remaining solution and evaporated to near dryness. This step was repeated three

times to ensure minimal residue of chloride ions. The solutions were then brought into a 50 mL 0.5 N HNO_3 solution for ICP-MS analysis. This method was adopted for total SPM digestion of the highly carbonated SPM of Seine River. All solutions were made from ultrapure reagents to minimize contamination (HNO_3 and HCl Normatom grade, VWR France, and HF and $HClO_4$ “for trace metal analyses”, Baker, from Sodipro France). For each digestion, 0.1 g of a certified lake sediment reference material was also digested (SL1, International Atomic Energy Agency IAEA).

S2 : concentration of various parameters during sampling campaign

Date	[SPM] (mg/L)	Flowrate (m^3/s)	Conductivity (µS/cm)	dissolved oxygen (mg/L)	POC (mg/L)	DOC (mg/L)
Marnay						
22.10.08	4,0	59	395	nm	0,42	2,68
25.11.08	9,5	49	474	nm	0,61	1,83
16.12.08	33,4	73	495	nm	1,90	1,94
19.01.09	20,2	37	485	nm	1,20	1,62
24.02.09	19,4	89	nm	nm	0,88	1,95
24.03.09	10,8	50	509	nm	0,56	1,75
22.04.09	20,4	34	516	nm	0,90	2,57
09.06.09	7,0	27	490	nm	0,45	2,16
22.06.09	5,9	25	526	nm	0,05	2,05
22.07.09	11,4	54	402	nm	0,42	2,23
19.08.09	4,4	47	364	nm	0,29	1,73
24.09.09	5,7	52	268	nm	1,23	2,44
22.10.09	4,7	50	350	nm	0,34	2,38
Bougival						
22.10.08	10,9	187	446	9,5	0,88	2,94
25.11.08	11,1	221	490	10,5	0,94	2,79
16.12.08	44,1	295	501	12,2	1,06	3,51
19.01.09	21,2	215	557	12,8	3,92	2,77
24.02.09	15,7	324	nm	11,8	1,03	2,77
24.03.09	9,3	212	570	11,3	0,89	2,69
22.04.09	7,7	184	611	8,9	0,66	3,00
09.06.09	16,8	167	606	6,3	1,61	4,34
22.06.09	6,4	116	609	5,1	0,73	3,21
22.07.09	10,9	148	550	6,8	0,55	3,25
19.08.09	7,9	97	527	6,8	0,69	3,73
24.09.09	9,7	92	474	7,4	0,38	2,56
22.10.09	8,5	112	498	8,0	0,69	2,64
Triel						
22.10.08	7,8	334	538	7,5	0,04	4,16
25.11.08	4,1	391	506	9,1	0,72	3,87
16.12.08	14,1	495	513	12,5	0,93	4,14
19.01.09	14,3	383	612	12,1	2,47	3,97
24.02.09	21,9	550	nm	12,7	1,46	3,42
24.03.09	10,2	384	619	10,0	0,97	3,72
22.04.09	9,8	340	655	8,0	0,88	3,77
09.06.09	11,9	375	668	6,0	1,16	5,45
22.06.09	6,9	228	668	6,0	0,67	3,63
22.07.09	11,6	209	655	5,8	1,08	3,96
19.08.09	9,7	211	604	6,1	0,73	3,54
24.09.09	8,8	198	619	5,9	0,50	3,84
22.10.09	4,8	225	625	6,1	0,89	3,93

nm = non measured
<QL = lower than quantification limit

Date	Temperature (°C)	Chlorophyll (µg/L)	pH	Alcalinity (mg/L)	Sodium (mg/L)	Ammonium (mg/L)
Marnay						
22.10.08	11,2	0,50	8,14	226	20,3	0,6
25.11.08	6,5	0,70	8,28	287	7,9	<QL
16.12.08	5,6	nm	8,30	287	5,8	<QL
19.01.09	6,0	1,40	8,32	262	9,0	<QL
24.02.09	7,2	2,00	8,19	262	2,5	0,3
24.03.09	8,0	3,50	8,15	250	7,5	<QL
22.04.09	14,9	2,10	8,14	244	12,1	1,4
09.06.09	16,4	0,70	8,18	226	7,7	<QL
22.06.09	19,0	0,60	8,23	232	10,8	<QL
22.07.09	21,7	nm	8,06	195	6,2	<QL
19.08.09	23,0	1,24	8,30	171	5,7	<QL
24.09.09	16,4	1,02	8,07	153	9,0	<QL
22.10.09	nm	nm	8,13	nm	6,4	<QL
Bougival						
22.10.08	14,4	1,10	7,88	226	6,7	<QL
25.11.08	9,0	0,40	8,07	268	13,6	0,4
16.12.08	5,1	nm	8,24	281	9,9	0,1
19.01.09	4,5	9,50	7,76	256	16,9	<QL
24.02.09	7,0	3,30	8,11	268	8,6	0,1
24.03.09	10,4	6,60	8,09	250	12,6	<QL
22.04.09	16,0	3,70	7,91	250	14,5	0,8
09.06.09	19,8	2,10	7,20	238	16,1	2,9
22.06.09	20,7	3,20	7,71	232	16,3	0,5
22.07.09	22,8	11,36	7,77	220	14,9	<QL
19.08.09	20,3	15,05	7,93	182	16,1	<QL
24.09.09	19,5	5,64	7,71	207	17,7	<QL
22.10.09	nm	nm	8,10	nm	14,9	<QL
Triel						
22.10.08	13,9	0,90	7,59	250	13,6	0,3
25.11.08	8,9	0,30	7,83	281	16,1	1,3
16.12.08	5,2	nm	8,01	281	10,9	0,5
19.01.09	4,9	10,00	7,10	262	22,7	<QL
24.02.09	6,9	2,10	7,93	268	10,4	0,5
24.03.09	10,2	5,10	7,93	256	15,3	<QL
22.04.09	15,4	2,10	7,73	256	17,6	1,8
09.06.09	19,0	2,00	7,55	250	20,6	4,3
22.06.09	20,1	2,50	7,61	238	19,5	0,4
22.07.09	22,0	12,64	7,58	232	22,2	0,2
19.08.09	19,6	16,38	7,85	220	20,0	<QL
24.09.09	19,2	5,82	7,58	189	27,5	<QL
22.10.09	14,4	nm	7,81	nm	23,3	<QL

nm = non measured
<QL = lower than quantification limit

Date	Potassium (mg/L)	Magnesium (mg/L)	Calcium (mg/L)	Chloride (mg/L)	Nitrite (mg/L)	Nitrate (mg/L)
Marnay						
22.10.08	6,3	6,8	88,3	13,9	<QL	14,8
25.11.08	<QL	4,7	98,4	14,3	<QL	20,4
16.12.08	<QL	3,3	105	12,7	<QL	24,8
19.01.09	1,9	3,9	93,2	18,6	<QL	26,0
24.02.09	<QL	0,5	88,1	15,1	<QL	24,9
24.03.09	1,6	4,0	88,9	19,6	<QL	25,7
22.04.09	6,0	4,3	93,2	27,2	<QL	25,9
09.06.09	2,1	3,6	89,2	21,1	<QL	16,1
22.06.09	2,4	4,0	87,8	23,3	<QL	18,0
22.07.09	2,0	7,6	72,4	12,9	<QL	11,3
19.08.09	1,9	8,9	64,8	12,0	<QL	8,8
24.09.09	<QL	1,3	58,0	11,4	<QL	7,8
22.10.09	<QL	1,4	59,6	12,7	<QL	7,8
Bougival						
22.10.08	2,2	3,4	77,3	23,9	<QL	19,2
25.11.08	<QL	6,7	94,7	19,1	<QL	19,2
16.12.08	<QL	0,6	99,6	17,4	<QL	25,0
19.01.09	3,4	6,4	100	30,1	<QL	26,1
24.02.09	2,8	6,2	97,7	22,7	<QL	25,5
24.03.09	2,9	6,4	96,8	26,2	<QL	26,7
22.04.09	3,4	7,8	97,6	30,7	<QL	24,1
09.06.09	4,6	6,7	95,5	34,2	<QL	24,4
22.06.09	4,4	7,1	91,4	32,3	<QL	21,3
22.07.09	4,3	10,3	85,0	29,2	<QL	15,1
19.08.09	4,0	7,0	79,8	29,0	<QL	14,5
24.09.09	0,4	3,2	72,9	25,5	<QL	13,2
22.10.09	0,7	3,3	74,1	26,6	<QL	13,9
Triel						
22.10.08	3,9	5,4	77,5	34,7	1,2	27,9
25.11.08	<QL	7,9	98,7	<QL	26,4	20,2
16.12.08	<QL	0,7	98,6	19,9	<QL	28,5
19.01.09	4,3	7,3	102	41,3	0,8	28,2
24.02.09	3,2	7,0	109	25,7	0,8	28,3
24.03.09	3,7	7,3	102	31,9	<QL	35,2
22.04.09	4,0	8,1	102	35,5	0,9	31,9
09.06.09	5,7	7,9	101	41,9	<QL	33,7
22.06.09	5,3	8,6	95,5	38,3	<QL	29,5
22.07.09	6,0	8,6	94,1	41,1	<QL	31,3
19.08.09	5,4	8,6	89,1	35,6	<QL	22,1
24.09.09	1,5	5,8	84,6	40,3	2,2	28,7
22.10.09	9,2	5,5	86,3	41,6	3,2	25,3

nm = non measured
<QL = lower than quantification limit

Date	Sulfate (mg/L)	Cd dissolved <0.45 µm (µg/L^{-1})	solid >0.45 µm (µg.g^{-1})	labile (DGT) (µg.L^{-1})	sediment trap (µg.g^{-1})
Marnay					
22.10.08	15,9	<QL	0,54	nm	nm
25.11.08	17,3	<QL	0,43	0,0007 ± 0,0002	nm
16.12.08	17,6	<QL	0,49	0,0014 ± 0,0006	0,34
19.01.09	18,8	<QL	0,68	0,0010 ± 0,0007	0,31
24.02.09	18,5	<QL	0,43	0,0012 ± 0,0001	0,44
24.03.09	20,0	<QL	1,05	0,0009 ± 0,0001	0,29
22.04.09	22,4	<QL	2,30	0,0004 ± 0,0004	0,27
09.06.09	16,8	<QL	nm	0,0009 ± 0,0003	0,27
22.06.09	19,0	<QL	4,42	0,0011 ± 0,0005	0,30
22.07.09	14,3	<QL	0,05	0,0004 ± 0,0001	0,34
19.08.09	14,2	<QL	1,64	0,0006 ± 0,0001	0,31
24.09.09	13,7	<QL	0,38	0,0006 ± 0,0000	0,32
22.10.09	14,3	<QL	0,85	0,0017 ± 0,0003	nm
Bougival					
22.10.08	31,1	0,012	4,05	nm	nm
25.11.08	29,4	<QL	1,87	0,0041 ± 0,0006	nm
16.12.08	24,4	<QL	0,77	0,0051 ± 0,0009	nm
19.01.09	36,1	<QL	1,69	0,0021 ± 0,0003	2,02
24.02.09	30,3	<QL	1,68	0,0022 ± 0,0002	1,53
24.03.09	36,4	<QL	2,88	0,0031 ± 0,0028	1,56
22.04.09	42,6	0,015	3,93	0,0016 ± 0,0006	1,79
09.06.09	44,6	0,013	1,55	0,0022 ± 0,0008	8,07
22.06.09	43,1	0,010	2,63	0,0041 ± 0,0028	nm
22.07.09	38,4	<QL	20,5	0,0054 ± 0,0009	4,09
19.08.09	38,1	0,014	8,04	0,0028 ± 0,0005	3,40
24.09.09	33,4	0,014	4,22	0,0066 ± 0,0024	3,29
22.10.09	35,0	<QL	2,47	0,0066 ± 0,0014	nm
Triel					
22.10.08	43,9	0,015	1,19	nm	nm
25.11.08	<QL	0,012	1,83	0,0022 ± 0,0010	nm
16.12.08	28,0	<QL	2,15	0,0051 ± 0,0017	0,85
19.01.09	44,7	0,013	2,22	0,0036 ± 0,0005	1,23
24.02.09	35,4	<QL	0,66	0,0027 ± 0,0004	0,35
24.03.09	42,8	<QL	0,44	0,0050 ± 0,0026	0,72
22.04.09	46,8	0,014	1,95	0,0021 ± 0,0009	1,17
09.06.09	51,5	0,013	0,84	0,0032 ± 0,0003	1,78
22.06.09	49,8	0,019	2,29	0,0045 ± 0,0005	1,86
22.07.09	50,2	0,015	1,41	0,0051 ± 0,0004	3,03
19.08.09	46,1	0,014	2,06	0,0043 ± 0,0006	2,55
24.09.09	47,8	0,013	1,38	0,0050 ± 0,0007	nm
22.10.09	49,4	0,012	0,88	0,0050 ± 0,0009	nm

nm = non measured
<QL = lower than quantification limit

			Cr	
Date	dissolved <0.45 µm (µg/L^{-1})	solid >0.45 µm (µg.g^{-1})	labile (DGT) (µg.L^{-1})	sediment trap (µg.g^{-1})
Marnay				
22.10.08	<QL	7,7	nm	nm
25.11.08	1,09	30,0	0,0184 ± 0,0025	nm
16.12.08	<QL	68,7	0,0180 ± 0,0021	53,7
19.01.09	<QL	41,9	0,0352 ± 0,0062	50,1
24.02.09	<QL	14,9	0,0250 ± 0,0020	42,1
24.03.09	<QL	57,2	0,0249 ± 0,0038	50,0
22.04.09	0,22	64,8	0,0333 ± 0,0110	50,8
09.06.09	<QL	50,2	0,0214 ± 0,0033	49,9
22.06.09	<QL	64,8	<QL ± 0,0000	50,2
22.07.09	<QL	46,0	0,0178 ± 0,0027	51,2
19.08.09	0,41	53,6	0,0196 ± 0,0026	51,4
24.09.09	<QL	65,3	0,0167 ± 0,0041	54,2
22.10.09	nm	102	0,0196 ± 0,0078	nm
Bougival				
22.10.08	0,54	88,9	nm	nm
25.11.08	1,04	73,0	0,0574 ± 0,0248	nm
16.12.08	<QL	65,2	0,0926 ± 0,0131	nm
19.01.09	<QL	46,3	0,0270 ± 0,0060	71,8
24.02.09	<QL	84,2	0,0583 ± 0,0304	83,0
24.03.09	0,60	102	0,0353 ± 0,0033	69,2
22.04.09	0,28	90,6	0,0291 ± 0,0081	70,0
09.06.09	<QL	75,5	0,0244 ± 0,0065	109
22.06.09	0,25	77,5	0,0024 ± 0,0035	nm
22.07.09	<QL	82,0	0,0323 ± 0,0054	109
19.08.09	0,51	102	0,0277 ± 0,0033	87,8
24.09.09	<QL	84,7	0,0211 ± 0,0024	92,2
22.10.09	<QL	85,4	0,0246 ± 0,0108	nm
Triel				
22.10.08	<QL	94,9	nm	nm
25.11.08	1,24	58,1	0,0314 ± 0,0112	nm
16.12.08	<QL	122	0,0857 ± 0,0081	61,0
19.01.09	0,23	65,6	0,0284 ± 0,0035	73,5
24.02.09	<QL	46,6	0,0452 ± 0,0111	56,4
24.03.09	0,39	35,9	0,0415 ± 0,0144	65,0
22.04.09	0,32	88,3	0,0372 ± 0,0101	71,7
09.06.09	<QL	69,1	0,0243 ± 0,0031	80,9
22.06.09	0,21	58,1	0,0083 ± 0,0069	78,3
22.07.09	0,21	88,1	0,0314 ± 0,0047	86,0
19.08.09	0,51	74,2	0,0256 ± 0,0026	86,7
24.09.09	<QL	77,3	0,0319 ± 0,0165	nm
22.10.09	0,32	60,5	0,0252 ± 0,0039	nm

nm = non measured
<QL = lower than quantification limit

Date	Co					
	dissolved <0.45 µm (µg/L^{-1})	solid >0.45 µm (µg.g^{-1})	labile (DGT) (µg.L^{-1})			sediment trap (µg.g^{-1})
Marnay						
22.10.08	0,16	7,39		nm		nm
25.11.08	0,18	7,61	0,0132	±	0,0013	nm
16.12.08	0,11	8,62	0,0203	±	0,0016	7,13
19.01.09	0,16	6,49	0,0218	±	0,0021	6,78
24.02.09	0,10	2,48	0,0191	±	0,0013	5,76
24.03.09	0,12	7,59	0,0193	±	0,0019	6,63
22.04.09	0,18	8,52	0,0145	±	0,0062	6,39
09.06.09	0,13	5,69	0,0099	±	0,0016	6,21
22.06.09	0,14	9,17	0,0107	±	0,0046	7,11
22.07.09	0,06	6,55	0,0044	±	0,0004	6,73
19.08.09	0,09	5,12	0,0057	±	0,0009	6,60
24.09.09	0,04	8,85	0,0039	±	0,0007	6,90
22.10.09	0,05	8,48	0,0120	±	0,0036	nm
Bougival						
22.10.08	0,22	12,7		nm		nm
25.11.08	0,25	10,7	0,0416	±	0,0088	nm
16.12.08	0,15	11,2	0,0509	±	0,0079	nm
19.01.09	0,21	6,42	0,0416	±	0,0079	9,25
24.02.09	0,17	13,3	0,0503	±	0,0154	11,4
24.03.09	0,17	38,4	0,0232	±	0,0100	8,64
22.04.09	0,25	12,6	0,0162	±	0,0019	8,25
09.06.09	0,24	11,5	0,0147	±	0,0071	11,1
22.06.09	0,22	12,6	0,0319	±	0,0057	nm
22.07.09	0,17	8,29	0,0164	±	0,0012	11,8
19.08.09	0,23	11,1	0,0181	±	0,0029	9,61
24.09.09	0,13	16,3	0,0143	±	0,0010	9,97
22.10.09	0,13	11,7	0,0309	±	0,0042	nm
Triel						
22.10.08	0,39	17,5		nm		nm
25.11.08	0,32	17,2	0,0347	±	0,0137	nm
16.12.08	0,20	25,2	0,0729	±	0,0080	8,10
19.01.09	0,32	13,9	0,0727	±	0,0118	9,63
24.02.09	0,21	8,07	0,0780	±	0,0062	7,69
24.03.09	0,26	5,95	0,0464	±	0,0113	12,1
22.04.09	0,33	12,8	0,0376	±	0,0091	9,00
09.06.09	0,31	15,4	0,0275	±	0,0020	10,3
22.06.09	0,30	7,98	0,0435	±	0,0031	11,0
22.07.09	0,38	18,0	0,0288	±	0,0026	13,0
19.08.09	0,28	10,9	0,0294	±	0,0027	11,8
24.09.09	0,21	20,3	0,0287	±	0,0053	nm
22.10.09	0,29	14,0	0,0567	±	0,0073	nm

nm = non measured
<QL = lower than quantification limit

			Cu	
Date	dissolved <0.45 µm (µg/L^{-1})	solid >0.45 µm (µg.g^{-1})	labile (DGT) (µg.L^{-1})	sediment trap (µg.g^{-1})
Marnay				
22.10.08	0,36	95,5	nm	nm
25.11.08	0,36	18,7	0,0615 ± 0,0117	nm
16.12.08	0,34	18,8	0,0751 ± 0,0075	18,1
19.01.09	0,37	25,0	0,0655 ± 0,0063	17,5
24.02.09	0,35	5,72	0,0748 ± 0,0077	13,5
24.03.09	0,38	19,4	0,0736 ± 0,0059	16,4
22.04.09	0,57	21,8	0,0970 ± 0,0096	14,9
09.06.09	0,60	14,0	0,0907 ± 0,0197	15,7
22.06.09	0,67	69,2	0,0852 ± 0,0086	15,2
22.07.09	0,46	18,8	0,0581 ± 0,0098	16,1
19.08.09	0,42	18,2	0,1038 ± 0,0123	16,0
24.09.09	0,27	28,0	0,0730 ± 0,0055	17,5
22.10.09	0,29	34,5	0,0569 ± 0,0443	nm
Bougival				
22.10.08	1,04	120	nm	nm
25.11.08	1,02	104	0,2663 ± 0,0435	nm
16.12.08	0,89	45,9	0,2590 ± 0,0469	nm
19.01.09	1,27	150	0,1716 ± 0,0125	93,6
24.02.09	0,77	44,7	0,2181 ± 0,0760	100
24.03.09	0,96	63,5	0,1408 ± 0,0568	80,0
22.04.09	1,22	69,6	0,1649 ± 0,0290	78,8
09.06.09	1,76	102	0,1867 ± 0,0696	155
22.06.09	1,27	103	0,2981 ± 0,0485	nm
22.07.09	1,12	116	0,3864 ± 0,0328	185
19.08.09	1,42	154	0,2532 ± 0,0481	143
24.09.09	1,28	147	0,4257 ± 0,0726	148
22.10.09	1,02	169	0,4811 ± 0,0683	nm
Triel				
22.10.08	1,38	72,2	nm	nm
25.11.08	1,22	79,0	0,1511 ± 0,0640	nm
16.12.08	0,93	93,6	0,2511 ± nm	56,0
19.01.09	1,52	130	0,1743 ± 0,0139	81,8
24.02.09	0,80	24,7	0,2095 ± 0,0158	54,1
24.03.09	1,03	21,1	0,2167 ± 0,0545	53,4
22.04.09	1,21	56,2	0,2406 ± 0,0707	58,2
09.06.09	1,39	58,7	0,2798 ± 0,0229	83,9
22.06.09	1,56	54,1	0,3004 ± 0,0216	91,1
22.07.09	1,56	66,5	0,3878 ± 0,0299	88,9
19.08.09	1,45	84,3	0,3336 ± 0,0373	96,8
24.09.09	1,12	95,5	0,3628 ± 0,0444	nm
22.10.09	1,07	111	0,3074 ± 0,0226	nm

nm = non measured
<QL = lower than quantification limit

Date	Mn					
	dissolved <0.45 µm (µg/L^{-1})	solid >0.45 µm (µg.g^{-1})	labile (DGT) (µg.L^{-1})			sediment trap (µg.g^{-1})
Marnay						
22.10.08	2,20	761	nm			nm
25.11.08	2,60	658	1,89	±	0,183	nm
16.12.08	1,51	593	2,40	±	0,178	441
19.01.09	2,73	444	3,21	±	0,285	425
24.02.09	1,64	130	2,24	±	0,181	334
24.03.09	2,55	417	2,27	±	0,209	311
22.04.09	3,19	793	1,13	±	0,107	282
09.06.09	2,45	422	0,650	±	0,1857	268
22.06.09	3,01	394	0,787	±	0,1181	527
22.07.09	1,82	343	0,361	±	0,0277	456
19.08.09	2,43	379	0,406	±	0,0335	436
24.09.09	1,44	798	0,279	±	0,0755	464
22.10.09	1,81	910	1,14	±	0,876	nm
Bougival						
22.10.08	7,01	972	nm			nm
25.11.08	8,01	917	4,99	±	1,171	nm
16.12.08	3,07	1035	8,32	±	1,068	nm
19.01.09	8,68	514	7,18	±	1,312	532
24.02.09	6,97	1057	7,82	±	2,211	679
24.03.09	6,77	1282	3,72	±	1,758	372
22.04.09	7,40	1528	2,06	±	0,391	1825
09.06.09	10,7	817	1,95	±	0,883	281
22.06.09	17,4	1450	8,38	±	1,228	nm
22.07.09	13,5	665	2,66	±	0,572	633
19.08.09	13,1	797	3,49	±	0,351	642
24.09.09	8,30	1762	2,27	±	0,327	644
22.10.09	8,89	1186	6,55	±	0,824	nm
Triel						
22.10.08	17,7	1678	nm			nm
25.11.08	12,7	1911	3,43	±	1,436	nm
16.12.08	4,37	2209	9,82	±	1,083	594
19.01.09	13,2	1224	10,2	±	1,73	502
24.02.09	9,37	570	9,93	±	0,741	513
24.03.09	11,2	484	6,56	±	1,462	780
22.04.09	11,6	1329	4,56	±	1,172	437
09.06.09	17,6	1428	3,24	±	0,284	414
22.06.09	20,2	752	9,38	±	0,687	872
22.07.09	27,6	2314	4,63	±	0,634	966
19.08.09	22,1	1097	4,71	±	0,373	948
24.09.09	15,4	2208	4,45	±	0,554	nm
22.10.09	15,8	1667	9,65	±	1,670	nm

nm = non measured
<QL = lower than quantification limit

Date	Ni					
	dissolved <0.45 µm (µg/L^{-1})	solid >0.45 µm (µg.g^{-1})	labile (DGT) (µg.L^{-1})			sediment trap (µg.g^{-1})
Marnay						
22.10.08	1,39	83,5	nm			nm
25.11.08	1,77	23,7	0,154	±	0,0155	nm
16.12.08	1,53	32,0	0,205	±	0,0171	26,2
19.01.09	1,43	26,4	0,202	±	0,0274	24,8
24.02.09	1,45	13,8	0,209	±	0,0154	20,5
24.03.09	1,54	19,9	0,195	±	0,0178	21,6
22.04.09	1,93	23,8	0,212	±	0,0356	20,5
09.06.09	1,68	25,4	0,173	±	0,0370	20,6
22.06.09	1,59	9,13	0,196	±	0,0227	21,6
22.07.09	0,61	20,5	0,095	±	0,0082	21,1
19.08.09	0,80	33,8	0,135	±	0,0184	20,6
24.09.09	0,51	28,5	0,116	±	0,0076	21,4
22.10.09	0,48	35,2	0,166	±	0,0444	nm
Bougival						
22.10.08	1,76	36,7	nm			nm
25.11.08	2,15	27,3	0,369	±	0,0287	nm
16.12.08	1,66	32,1	0,446	±	0,0353	nm
19.01.09	1,95	20,9	0,297	±	0,0523	31,2
24.02.09	1,79	36,0	0,322	±	0,0582	38,8
24.03.09	1,76	33,9	0,228	±	0,0982	27,8
22.04.09	2,25	30,3	0,177	±	0,0411	26,2
09.06.09	2,12	26,3	0,185	±	0,1641	40,2
22.06.09	1,98	27,3	0,324	±	0,0534	nm
22.07.09	1,21	26,2	0,470	±	0,0656	37,0
19.08.09	1,48	38,5	0,321	±	0,0857	28,7
24.09.09	1,07	32,7	0,419	±	0,0478	31,4
22.10.09	0,94	40,5	0,458	±	0,0420	nm
Triel						
22.10.08	2,74	47,8	nm			nm
25.11.08	2,43	18,4	0,172	±	0,1870	nm
16.12.08	1,96	59,5	0,545	±	0,0412	28,0
19.01.09	2,21	30,2	0,465	±	0,0440	30,5
24.02.09	2,04	21,5	0,451	±	0,0308	21,2
24.03.09	2,11	12,9	0,426	±	0,0927	23,6
22.04.09	2,59	30,1	0,443	±	0,1258	25,2
09.06.09	2,34	29,3	0,578	±	0,0451	27,7
22.06.09	2,36	20,6	0,543	±	0,0446	27,2
22.07.09	2,17	39,5	0,752	±	0,0564	30,7
19.08.09	1,79	38,5	0,564	±	0,0534	29,3
24.09.09	1,49	30,0	0,681	±	0,0707	nm
22.10.09	1,96	41,5	0,796	±	0,0550	nm

nm = non measured

<QL = lower than quantification limit

Date	Zn			
	dissolved <0.45 µm (µg/L^{-1})	solid >0.45 µm (µg.g^{-1})	labile (DGT) (µg.L^{-1})	sediment trap (µg.g^{-1})
Marnay				
22.10.08	<QL	45	nm	nm
25.11.08	2,67	128	0,444 ± 0,0794	nm
16.12.08	<QL	171	1,49 ± 0,3041	149
19.01.09	9,77	188	0,988 ± 0,6036	141
24.02.09	<QL	71	0,836 ± 0,2054	126
24.03.09	3,94	395	0,159 ± 0,2726	106
22.04.09	2,26	451	0,756 ± 0,3556	108
09.06.09	2,61	140	0,693 ± 0,1770	109
22.06.09	2,53	134	0,000 ± 0,0000	125
22.07.09	1,82	185	0,365 ± 0,2242	117
19.08.09	1,24	713	0,274 ± 0,0185	113
24.09.09	<QL	219	0,115 ± 0,0942	122
22.10.09	2,43	417	0,578 ± 0,1292	nm
Bougival				
22.10.08	6,68	465	nm	nm
25.11.08	24,1	410	2,64 ± 0,366	nm
16.12.08	7,35	336	3,13 ± 0,469	nm
19.01.09	15,1	642	1,79 ± 0,382	439
24.02.09	4,39	480	2,47 ± 0,517	506
24.03.09	6,02	567	0,402 ± 0,778	307
22.04.09	6,28	645	0,352 ± 0,128	307
09.06.09	9,76	380	1,51 ± 0,824	694
22.06.09	6,22	409	2,07 ± 0,329	nm
22.07.09	3,55	383	2,49 ± 0,378	629
19.08.09	4,77	671	1,69 ± 0,805	505
24.09.09	3,28	542	1,83 ± 0,329	515
22.10.09	3,65	508	2,34 ± 0,384	nm
Triel				
22.10.08	7,08	351	nm	nm
25.11.08	14,6	363	1,46 ± 0,704	nm
16.12.08	3,90	1402	3,57 ± 0,333	299
19.01.09	14,6	608	2,79 ± 0,456	408
24.02.09	3,47	232	3,74 ± 0,270	226
24.03.09	4,72	135	1,44 ± 0,291	225
22.04.09	6,15	434	1,55 ± 0,472	249
09.06.09	7,88	302	2,89 ± 0,262	342
22.06.09	9,45	43	2,68 ± 0,207	387
22.07.09	6,72	350	3,07 ± 0,229	395
19.08.09	4,53	522	2,42 ± 0,186	415
24.09.09	4,10	399	2,37 ± 0,386	nm
22.10.09	9,00	256	3,06 ± 0,398	nm

nm = non measured
<QL = lower than quantification limit

	Pb			
Date	dissolved <0.45 µm (µg/L^{-1})	solid >0.45 µm (µg.g^{-1})	labile (DGT) (µg.L-1)	sediment trap (µg.g^{-1})
Marnay				
22.10.08	0,00	36	nm	nm
25.11.08	0,00	29	0,0022 ± 0,0014	nm
16.12.08	0,00	29	0,0285 ± 0,0080	23
19.01.09	0,00	42	0,0308 ± 0,0099	22
24.02.09	0,00	11	0,0039 ± 0,0030	20
24.03.09	0,00	33	0,0067 ± 0,0025	20
22.04.09	0,00	46	0,0093 ± 0,0045	19
09.06.09	0,00	<QL	0,0099 ± 0,0028	19
22.06.09	0,07	47	0,0136 ± 0,0011	20
22.07.09	0,00	25	0,0047 ± 0,0008	20
19.08.09	0,00	67	0,0058 ± 0,0009	20
24.09.09	0,00	66	0,0041 ± 0,0022	23
22.10.09	0,00	69	0,0108 ± 0,0016	nm
Bougival				
22.10.08	0,23	157	nm	nm
25.11.08	0,15	135	0,161 ± 0,0711	nm
16.12.08	0,08	71	0,143 ± 0,0648	nm
19.01.09	0,17	118	0,0171 ± 0,0088	105
24.02.09	0,08	77	0,0227 ± 0,0142	95
24.03.09	0,14	125	0,0239 ± 0,0031	80
22.04.09	0,15	149	0,0323 ± 0,0126	87
09.06.09	0,24	139	0,0249 ± 0,0139	245
22.06.09	0,25	159	0,0868 ± 0,0307	nm
22.07.09	0,23	307	0,0378 ± 0,0080	177
19.08.09	0,25	245	0,0302 ± 0,0088	141
24.09.09	0,19	181	0,0348 ± 0,0121	148
22.10.09	0,22	161	0,0578 ± 0,0313	nm
Triel				
22.10.08	0,20	115	nm	nm
25.11.08	0,15	112	0,0272 ± 0,0219	nm
16.12.08	0,00	145	0,0393 ± 0,0225	59
19.01.09	0,16	119	0,0124 ± 0,0023	82
24.02.09	0,00	40	0,0197 ± 0,0075	55
24.03.09	0,11	34	0,0225 ± 0,0136	51
22.04.09	0,14	88	0,0194 ± 0,0127	64
09.06.09	0,16	82	0,0088 ± 0,0012	84
22.06.09	0,33	71	0,0180 ± 0,0034	83
22.07.09	0,20	111	0,0176 ± 0,0036	90
19.08.09	0,16	109	0,0176 ± 0,0034	99
24.09.09	0,21	119	0,0339 ± 0,0216	nm
22.10.09	0,24	109	0,0199 ± 0,0051	nm

nm = non measured
<QL = lower than quantification limit