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The geochemistry of Seine River Basin particulate matter: distribution of an integrated metal pollution index

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Abstract

Spatial analysis (1994–2001) and temporal trends (1980–2000) for particulate-associated metals at key stations in the Seine River Basin have been determined using a new metal pollution index (MPI). The MPI is based on the concentrations of Cd, Cu, Hg, Pb and Zn, normalized to calculated background levels estimated for each particulate matter samples for four fractions (clays and other aluminosilicates, carbonates, organic matter, and quartz). Background levels ascribed to each fraction were determined from a specific set of samples collected from relatively pristine areas in the upper Seine basin and validated on prehistoric samples. The unitless MPI is designed to vary between 0 for pristine samples to 100 for the ones extremely impacted by human activities and to assess the trends of general metal contamination and its mapping. Throughout the Seine basin, MPI currently range from 1 to 40, but values exceeding 100 have been found in periurban streams and the Eure tributary. Based on the MPI spatial distribution, the Seine River Basin displays a wide range of anthropogenic impacts linked to variations in population density, stream order, wastewater discharges and industrial activities. Correlations between the MPI and other trace elements indicate that anthropogenic impacts also strongly affect the concentrations of Ag, Sb, and P, marginally affect the concentrations of Ba, Ni, and Cr, and appear to have little effect on the concentrations of Li, Be, V, Co, and the major elements. Temporal MPI trends can also be reconstituted from past regulatory surveys. In the early 1980s, MPI were 2–5 times higher than nowadays at most locations, particularly downstream of Greater Paris where it reached levels as high as 250 (now 40), a value characteristic of present Paris urban sewage. The exceptional contamination of the Seine basin is gradually improving over the last 20 years but remains very high.

Keywords: Heavy metals; Contamination; Seine basin; Flood plain deposits; Metal pollution index

1. Introduction

The major goals of many water quality surveys are to establish spatial and/or temporal trends. Spatial surveys are useful for determining the occurrence and distribution of a variety of chemical constituents, for identifying potential anthropogenic sources, and for assessing the effects of various socioeconomic factors (e.g. changes in population density, in land use or in seasonal changes…). Temporal surveys are useful for delin-

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eating the impacts of changing socioeconomic factors and to evaluate the efficacy of various remediation efforts (Chapman, 1992).

Particulate trace element concentrations result from both bedrock weathering and anthropogenic contributions. To be effective, spatial and/or temporal surveys generally require data on local background levels (Turekian and Wedepohl, 1961; Wedepohl, 1969; Thomas, 1972; Aston et al., 1973; Forstner and Wittmann, 1981; Salomons and Forstner, 1984; Horowitz, 1991; Horowitz et al., 1991, 1999). In the case of various solid-phase sampling media (e.g. suspended matter, bed sediment, overbank deposits), a knowledge of local background levels may not be enough. For example, compensation for variations in grain-size distributions or varying levels of locally derived weathering products may be required (Horowitz et al., 1991). One common approach is to work with a limited grain-size fraction (e.g. <63 μm). Another approach entails data normalization to so-called 'conservative' elements such as Al, Ti, or Cs… (Forstner and Wittmann, 1981; Horowitz, 1991). As noted previously, both suspended and bed sediments can display for a given river basin marked short- and long-term spatial and temporal chemical and/or mineralogical variability (Horowitz, 1991, 1995; Idlafkih et al., 1997). Hence, even though a normalization procedure employing a single basinwide background value may be useful in determining broad spatial and temporal trends, it may not be sufficiently sensitive to facilitate the detection of interstation and even intrastation differences.

Water quality managers require integrated indicators that can be used to address the temporal and spatial variations of multiple constituents. The combination of several trace elements into a single indicator is fairly common since Müller (1979) developed the Index of geoaccumulation. Some of these new indices give different weights to various trace elements based on their assumed toxicity. The metal pollution index (MPI), presented in this paper, does not consider the toxicity, neither their speciation, of its five components (Cd, Cu, Hg, Pb and Zn), although these are known to be toxic. Instead, it is designed to be viewed as a multiple normalization procedure that has been performed on each sample, for all trace elements.

To evaluate the utility of the MPI, it was applied to the Seine River Basin, well studied within the Piren–Seine program since 1989 (Meybeck et al., 1998). With the exception of mining activities, the Seine River Basin encompasses all the major anthropogenic sources to impact particulate-associated trace element concentrations. These include: (1) high population densities; (2) intensive agriculture; (3) heavy industry; and (4) navigation, river channelization and reservoir construction (Guerrini et al., 1998). The MPI was calculated at 50 sites (sampled between 1994 and 2001 with 165 samples) to evaluate the range of anthropogenic impacts throughout the basin. It was also used to test the level of sensitivity of other trace elements to the multiple anthropogenic sources found in the Seine River Basin. Finally, these MPI were compared to the ones from the 1980–1999 regulatory surveys (suspended matter and bed sediments) of the French Ministry of Environment (RNB, 2001).

2. The Seine River Basin

The Seine River Basin, located in northwest France, is 1047 km long and drains approximately 65 000 km^2 at Poses, the last lock before the estuarine section of the basin (Fig. 1). Three major tributaries, from upstream to downstream, are the Yonne river (11 250 km^2), the Marne river (13 160 km^2), and the Oise River (16 900 km^2). The Eure river (7000 km^2) is a direct tributary of the estuary but was included in this study.

The Seine Basin is nearly uniform in terms of relief, geology and hydrology. It is characterized by very low erosion rates (10 t km^{-2} $year^{-1}$) owing to limited relief (Meybeck et al., 1999). Bedrock is more than 93% sedimentary (Jurassic limestone, and marl, Cretaceous chalk, carbonaceous alluvial deposits, Tertiary quartz sand); the remaining 7% is crystalline in the Morvan hills. The hydrologic regime is pluvial oceanic, with a mean rainfall between 500 and 1000 mm/year. Low flow is from July to September, whereas high

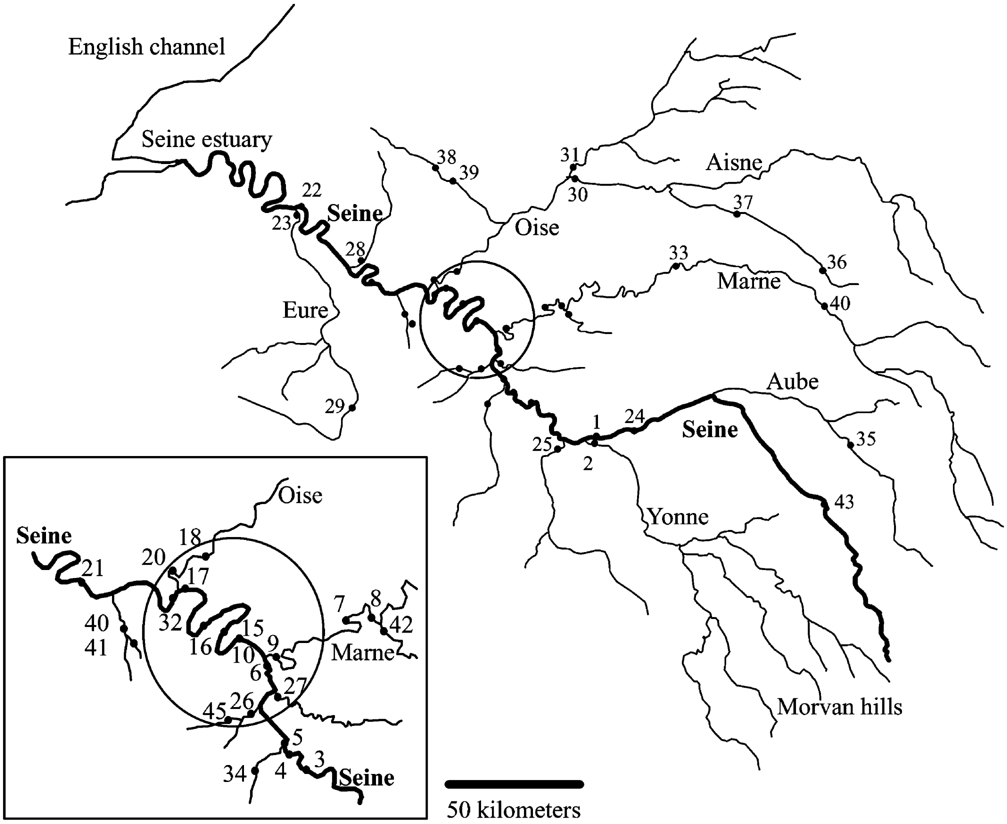

Fig. 1. Map of the Seine River Basin with major sampling stations. #1 : Seine at Montereau, #2: Yonne at Montereau, #3: Seine at Ponthierry, #4: Seine at Morsang, #5: Seine at Corbeil, #6: Seine at Ivry, #7: Marne at Annet, #8: Marne at Noisiel, #9: Marne at Maison Alfort, #10: Seine at Tolbiac ; #15: Seine at Puteaux, #16: Seine at Chatou, #17: Seine at Conflans, #18: Oise at Beaumont, #20: Oise at Conflans, #21: Seine at Mantes, #22: Seine at Poses, #23: Eure at Lery, #24: Seine at Bray, #25: Loing at Moret, #26: Orge at Savigny, #27: Yerres at Villeneuve, #28: Epte, #29: Eure, downstream from Chartres, #30: Aisne at Choisy, #31: Oise at Longueil, #32: Seine at Denouval, #33: Marne at Chartreves, #34: Upper Essonne, #35: Aube at Dienville, #36: Upper Vesles, #37: Lower Vesles, #38: Upper Therain, #39: Lower Therain, #40: Meauldre, #41: Ru de Gally, #42: Grand Morin, #43: Seine at Bar, #44: Marne at Sogny, #45: Yvette at Villebon. Greater Paris is represented by the circle.

flow occurs from December to March, with an average interannual discharge of 435 $m^3\ s^{-1}$ at Poses.

The population density in the Seine Basin averages approximately 250 p km^{-2}, but ranges from as low as 15 p km^{-2} in rural areas, mostly in the center and upstream area of the basin, to 1800 p km^{-2} in the Yvette River (station #45), a periurban tributary (Fig. 1). Upstream from Greater Paris, agriculture represents 80% of the land use whereas most major industries are located in or downstream of Greater Paris (Meybeck, 1998; Thevenot et al., 1998; Chesterikov et al., 1998).

One important particularity of the Seine River Basin concerns the collection, treatment, and discharge of waste waters generated by 10 million people living in Greater Paris. Most waste waters are treated in the Seine-Aval plant, some 60 km downstream from the center of Paris, then are reinjected (27 $m^3\ s^{-1}$ on average) into the Seine River on the left bank, a few kilometer upstream of the Seine–Oise confluence, at the Conflans station (#17, Fig. 1). Complete mixing between the Seine, the Oise, and the Seine-Aval effluent does not occur until Mantes (#21, Fig. 1), some 30 km further downstream.

3. Sampling and analytical methods

The PIREN-Seine sampling stations, designed to delimit and model anthropogenic impacts since 1994, are spread throughout the basin. They range from forested, agricultural and/or rural stations, draining 10–100 km^2, to mainstream river stations. Here, the sampling approach employs fresh floodplain deposits (FD; Horowitz et al., 1999). FD are manually collected from the surface of river banks, stairs, or levees, either as dried deposits a few days after peak discharge, or 10 cm underwater immediately after peak discharge. In some cases, several samples were collected contemporaneously at the same station to test sampling reproductibility.

Further, at the Seine-Aval treatment plant, daily average samples were obtained from the three major collectors during 1 week in July 2000. The seven daily samples were mixed and represent average raw influent to the facility. Additional sample data for this study were derived from trapped and from manually collected suspended particulate matter (SPM; Cossa et al., 1994; Idlafkih, 1998) that were collected and analyzed as part of additional surveys.

Chemical analyses for all trace elements, Al, Fe, Mn, particulate inorganic and organic carbon were performed using existing analytical procedures (Horowitz and Elrick, 1985; Elrick and Horowitz, 1986; Horowitz et al., 1989). These analyses provide total ($\geq$95%) concentrations for the constituents of interest. Based on the concomitant analyses of a variety of reference materials and duplicate samples, analytical precision was better than $\pm$10% except near the reporting limit; no bias was detected.

4. The metal pollution index presentation

4.1. Definition

The MPI is based on the concentrations of Cd, Cu, Hg, Pb and Zn, some of the most commonly analyzed toxic trace elements in most aquatic environments. These five selected trace elements appear quite sensitive to anthropogenic influences (e.g. population density, industrialization, urbanization). Data on other toxic elements from regulatory surveys performed within the Seine basin by the French Ministry of the Environment (RNB, 2001), such as As, Cr, Ni, Sb, and Se either were generally not available or were viewed as less reliable or both; hence, they were not included in the MPI which aims to be applied in most types of surveys.

The MPI is a combination of elemental pollution indices (PI) defined as :

$$\mathrm{PI} = [(\mathrm{Me})\ \text{measured} - (\mathrm{Me})\ \text{calculated background}] / [(\mathrm{Me})\ \text{calculated background}]$$

where (Me) = metal concentration

The calculated background concentrations used in the determination of the PI are considered to represent those levels of Cd, Cu, Hg, Pb, and Zn derived from atmospheric fallout and local soil and rock weathering, without any direct anthropogenic contribution. Background concentrations were determined for each sample, based on their inferred mineral and organic phases, observed with X-ray analyses (clays and other aluminosilicates, carbonates and quartz) and organic matter. Once the calculated background levels and the PI are established, the MPI is calculated as follows:

$$\mathrm{MPI} = \mathrm{PI}\ (\mathrm{Cd}) + \mathrm{PI}\ (\mathrm{Cu}) + \mathrm{PI}\ (\mathrm{Pb}) + \mathrm{PI}\ (\mathrm{Zn}) + 1/8\ \mathrm{PI}\ (\mathrm{Hg})$$

Note the lower weight attributed to the PI (Hg) in the Seine basin. This reduced weighting is based on several factors. First, Hg is the most impacted trace element by human activities in the basin (Horowitz et al., 1999; Grosbois et al., in prep). Second, Hg concentration can be difficult to determine, and samples are readily contaminated during collection and analysis as observed in some data obtained in the early 1980s (Grosbois et al., in prep). Third, the MPI was originally designed to describe general trace element contamination on a scale from 0 to 100. A non-weighted PI (Hg) would have produced a MPI close to 500 at the basin outlet at Poses if some of the maximum concentrations determined in the 1980s had been included. As weighted, the mercury pollution indices PI (Hg) remains close to the other trace elements pollution indices. Hence, the determination of the MPI for each sample requires four steps:

- determination of the theoretical background trace element levels in the four solid fractions (clays and aluminosilicates, carbonates, organic matter and quartz);
- determination of the four phases in each sample, from their respective Al, POC, and PIC concentrations;
- calculation of the pollution indices (PI) for the five trace elements;
- combination of the individual PI into the MPI for each sample.

As constituted, the MPI can be mapped, averaged in space and time or be examined at fine temporal scales.

4.2. Determination of theoretical background trace element concentrations

This step determines the theoretical background trace element level in each sample from (1) the percentage of the natural mineral and organic phases in each sample without any additional anthropogenic input and (2) the theoretical background trace element composition in each phase.

To evaluate this latter composition, two types of information were used. The first source is the trace element composition of non-impacted fine-grained bed sediments from small, monolithogenous and low-population density forested areas of the Seine River Basin (Horowitz et al., 1999): (i) forested watersheds (<1 p km^{-2}); (ii) agricultural watersheds (<10 p km^{-2}) ; and (iii) rural watersheds (<10–40 p km^{-2}). The first two subgroups have similar trace element chemistries, with the exception of Cu and Cd, which are somewhat elevated in several agricultural areas. The third group already appears to be slightly affected by human activities, especially for Cd and Hg. The forested basins samples were mixed by similar lithology to produce six composite samples representing the following basin lithologies: chalk, marl, limestone, sand and clays, quartz sand, and crystalline rocks.

The second source to evaluate the trace element composition of the four phases uses samples having extreme mineralogical assemblages and limited anthropogenic influence (Table 1i). This latter source includes a clay-rich sample (DM2), a quartz-sand sample (CSD36B), and a detrital carbonate-rich sample (CSD44). The chemical composition of organic-rich samples is based on material collected in forest catchments; however, their organic matter content did not exceed 30%. Hence, the values for background trace element concentrations for this fraction are somewhat uncertain.

Once the theoretical background concentrations for each mineral and organic fraction were established (Table 1ii), they were compared to trace element average values for shales, carbonates, sandstones, and organic matter compiled from various sources (Rosler and Lange, 1972; Martin and Meybeck, 1979). These comparisons indicate that the theoretical background concentrations established for the Seine River Basin fall within acceptable ranges. These local background levels are also similar to those reported for fine-grained bed sediments from relatively unaffected areas with a similar lithology in the US and Canada (Horowitz et al., 1999). The background trace element concentrations associated with each of the four mineral and organic phases are assumed to be constant throughout the Seine River Basin.

Then, the calculation of mineral and organic percentage of each sample is based on the PIC, POC and Al concentrations in each sample.

i. The percentage of calcite is based on PIC using the stoichiometric conversion factor because, in this basin, there is essentially calcium calcite (the Mg-PIC correlation is insignificant). Hence,

$$\%\ \text{calcite} = (\%\ \text{PIC}) \times 8.33$$

ii. The percentage of organic matter (OM) is based on soil organic carbon (SOC) assuming a 40% carbon content in SOC. Since there are

Table 1
(i) Examples of typical contents in river samples used as background references; (ii) Theoretical background trace element contents (mg/kg) of the four main detrital components in the Seine Basin; (iii) Prehistoric background levels; (iv) Seine river background levels

	Cd	Cu	Hg	Pb	Zn
i- Flood deposits used as background references[a]					
CSD44	0.1	46	0.1	27	76
DM2	0.1	6	0.06	16	35
CSD36B	0.1	5	0.04	10	25
ii- Theoretical contents of the four main fractions					
Clays + Al-silicates	0.2	20	0.05	20	50
Carbonates	0.2	8	0.01	15	60
Quartz	0.08	6	0.01	10	20
Organic matter	0.4	25	0.15	5	150
iii- Prehistoric background levels[b]					
Calculated	0.2	14	0.04	16	66
Measured	0.3	14	0.02	24	100
iv- Seine Basin background level[c]					
Estimated	0.22 ± 0.05	15 ± 5	0.03 ± 0.015	20 ± 3	60 ± 10

[a] Mineral assemblage for these three reference samples: CSD44 with 12% clays + Al-silicates, 73% carbonates, 2% organic matter, and 13% quartz; DM2 with 40% clays + Al-silicates, < 1% carbonates, 9% organic matter, and 50% quartz; CSD36B with 5% clays + Al-silicates, 7.5% carbonates, < 1% organic matter, and 86% quartz.

[b] 5000-year-old deposits at Bercy excavation in Paris (Horowitz et al., 1999) with a mineral composition of approximately 56% carbonates, 3% quartz, 1% organic matter and 40% of clays + Al-silicates calculated from the Al, PIC, and POC concentrations (Al = 45 000 mg/kg).

[c] in Thevenot et al., 1998, 2002; Horowitz et al., 1999; Meybeck et al., 1999; established for Al = 30 000 mg/kg.

other sources of organic matter in the river (e.g. urban wastes, algae blooms), the SOC has been differentiated from POC in flood deposits. A correlation with Al was established with POC contents in headwaters of the basin where both population densities and algae blooms are limited [% SOC = 1.3 × (% Al), $r^2 = 0.74$, $n = 50$]. Hence,

$$\% \text{ OM} = (\% \text{ SOC}) \times 2.5$$

iii. In all flood deposits, the percentage of aluminosilicates was based on the concentrations of $Al_2O_3 + Fe_2O_3 + TiO_2 + MgO + Na_2O + K_2O + (SiO_2)_{clay}$ with the $(SiO_2)_{clay}$ representing the silica bound to aluminosilicates. However, Si was not determined in any of the samples; therefore, its concentration was estimated based on the relation $(SiO_2)_{clay} = 2.14 \times (2.7\% \text{ Al})$. The 2.14 factor converts Si into SiO_2, and the Si/Al weight ratio normally reported in river particulates as 3 (e.g. Martin and Meybeck, 1979), was reduced to 2.7 to account for locally derived quartz. In the analysis from regulatory surveys Ti, Mn, Mg, Na and K concentrations are not available; therefore, the percentage of aluminosilicates is based solely on the concentration of Al. This decision is supported by the excellent correlation between Al and % Fe_2O_3 + % TiO_2 + % MnO + % Na_2O + % K_2O + % MgO ($r^2 = 0.83$; $n = 105$). Hence in those samples,

$$\% \text{ aluminosilicates} = (\% \, Al_2O_3) \times 1.196$$

In this simplified scheme, trace elements contributions from heavy minerals and iron oxides are attributed to the aluminosilicate fraction.

iv. The percentage of quartz was estimated from the difference between the sum of the previous fractions and 100%. Since the trace element concentrations associated with the quartz fraction are quite low, the imprecision of the quartz estimates are unlikely to substantially affect the estimated theoretical background trace element concentrations in each sample. Hence,

Table 2
(i) Variations of mineral and organic phase percentages in Seine river flood deposits; (ii) natural trace element contents in Seine river flood deposits and forested stream sediments ($n=165$)

	Minimum	Median	Maximum
i- Mineral and organic percentages in the flood deposits			
% clay + Al-silicates	5	28	69
% carbonates	0	30	74
% organic matter	0.9	5.6	14.2
% quartz	0	36	90
ii- Calculated natural trace element contents in flood deposits			
Cd (mg/kg)	0.10	0.17	0.22
Cu (mg/kg)	7	11	18
Pb (mg/kg)	11	14	16
Zn (mg/kg)	25	48	66
Hg (mg/kg)	0.01	0.03	0.06

$$\%\ \text{quartz} = 100 - (\%\ \text{calcite} + \%\ \text{OM} + \%\ \text{aluminosilicates})$$

As calculated, the mineral and organic assemblages for the FD samples display a surprising basin wide range, particularly for the aluminosilicates (5–69%); this occurs even though the Seine basin has a relatively homogeneous lithology, and probably results from substantial local background variations in the type of detrital input (Table 2i). This wide range in calculated mineral and organic composition tends to confirm the need to determine background concentrations, not only for each station, but also potentially for each sample.

Combining the percentage of the four phases to the background trace element concentrations associated to each phase gives the background trace element composition of each FD sample. These calculated trace element background concentrations can be relatively variable (e.g. up to two to three-fold for Cd, Cu, Pb and Zn, and six-fold for Hg; Table 2 (ii), particularly for those coming from small drainage areas. However, at most key stations, draining larger areas (5000–65 000 km^2), the calculated trace element background concentrations in FD tend to be homogeneous, remaining relatively similar from 1 year to the next. Thus, the variability displayed by trace element concentrations in FD is mostly a result of various anthropogenic inputs through time.

The calculated background concentrations in FD can be compared to those measured on two prehistoric alluvial samples from Bercy (5000 years BP; C. Le Royer, pers. com.; Table 1 iii), which is located within Paris a few kilometers downstream from the Seine–Marne confluence. The calculated mineralogical composition of the Bercy material is close to the calculated composition of most present day samples except for the concentration of organic matter, which almost certainly has declined (by oxidation and bacterial action) since its deposition. Further, the calculated trace element concentrations for the Bercy samples are reasonably close to the measured ones (Table 1iii). These background levels also are close to the basin wide levels proposed by Horowitz et al. (1999), and by Thevenot et al. (1998, 2002); Table 1iv) which also included an analysis of prehistoric levels in an estuarine core (Avoine et al., 1986).

4.3. MPI accuracy and intrasite variability in flood deposits

In the PIREN-Seine surveys, analytical duplicates generate similar MPI (Table 3). This is not surprising since analytical precision is quite good. MPI spatial variability also has been evaluated at several stations with sampling duplicates (Table 3). The differences in MPI for two samples collected contemporaneously a few meters apart are not significant at Esbly on the Marne River (1994), nor at Mantes (1999) and Puteaux (1997) on the Seine River (Table 3). Further, during a single flood event in January 2000, the MPI established at Ivry on two samples, one collected at the peak and the other on the falling limb of the hydrograph, are nearly identical (13.1 and 13.9, respectively).

However, the MPI from duplicates can be affected by grain-size differences. When duplicates contain coarse silt and sand-sized quartz particles, MPI reproducibility can decline (e.g. the Aisne at Choisy; Table 3).

At the Denouval station (#32), downstream from the major Seine–Oise confluence, and the

Table 3
Metallic pollution index values for sampling and analytical duplicates

River	Station (#)	Date	Sample description	MPI	% clay+OM
Sampling duplicates					
Aisne	Choisy #30	16.01.1994	very coarse sand	0.3	6
			fine silt	5.3	26
Marne	Esbly (near #8)	16.01.1994	coarse sand	4.3	13
			fine silt	5.8	34
Seine	Ivry #6	07.01.2000	fine; upper bank	13.1	36
			fine; lower bank	13.9	44
Seine	Puteaux #15	03.01.1997	fine silt	15.2	54
			fine silt	15.8	53
Seine	Mantes #21	03.04.1999	heterogeneous	22.7	24
			homogeneous	21.8	27
Seine	Denouval #32	12.01.2000	left bank (fine)	37.5	19
			middle bank (fine)	25.4	30
			right bank (fine)	18.4	41
Seine	Poses #22	20.01.1994	surficial	37.4	25
			deeper	52.0	42
Analytical duplicates					
Eure	Downstream Chartres #29	25.03.2001	silt	21.2	44
				20.3	44
Seine	Corbeil #5	04.06.2001	silt	8.9	32
				8.6	32
Stream	Forest	31.05.2001	silt	4.1	33
				2.6	32
Marne	Chartreves #33	26.06.2001	silt	1.2	9.5
				1.8	9.4

#: station numbers (see locations in Fig. 1).

Seine-Aval wastewater treatment plant, three samples were collected contemporaneously (Table 3). The first, on the left bank, has the highest MPI (37.5); the second, collected from the middle island, has an intermediate MPI (25.4); and the third, collected from the right bank, has the lowest MPI (18.4). The left bank sample is strongly influenced by effluents from the Seine-Aval plant because lateral mixing is incomplete. However, the middle island sample appears to reflect conditions in the Seine River mainstream. Lastly, the right bank sample appears to reflect incomplete lateral mixing between the Seine River and the less impacted Oise River.

An unexpected difference between two samples collected contemporaneously occurred at Poses during the 1994 flood (MPI = 52 and 37). This significant difference was attributed, a posteriori, to differing Cd levels that resulted from collecting the two samples from different depths within the floodplain deposits.

As a rule, FD samples were collected with the intention of limiting grain-size variability. However, the regular particulate surveys performed outside the PIREN-Seine program are likely to collect more heterogeneous samples with a concomitant increase in inter- and intrastation noise'. Based on the foregoing, it would appear that correctly sampled FD and the associated calculated MPI are capable of accurately reflecting site-specific spatial and temporal variations in particulate-associated trace element concentrations. Furthermore, this technique appears to work at both homogeneous (e.g. well-mixed mainstream sites) as well as heterogeneous sites (e.g. incompletely mixed sites at or near confluences).

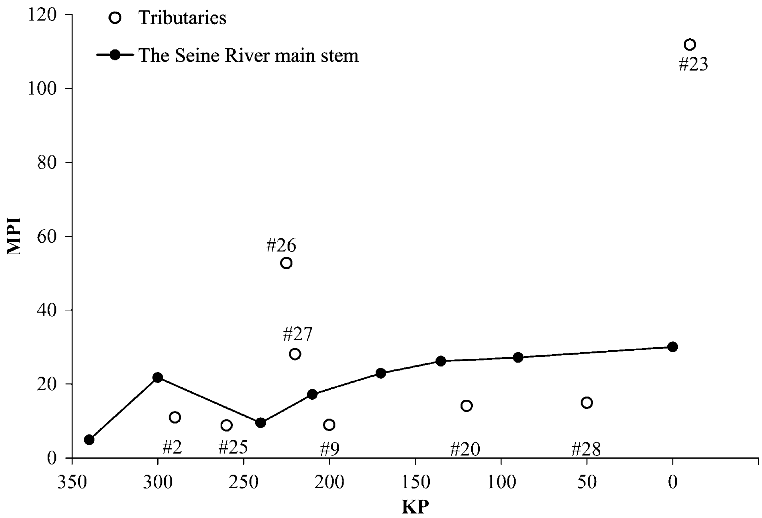

Fig. 2. Longitudinal upstream-downstream changes in MPI in the Seine river basin using floodplain deposits (averages for 1994–2000). Stations in the mainstream (●): Seine at Bray (KP=340, #24), Montereau (KP=300, #1), Corbeil (KP=240, #5), Ivry (KP=210, #6), Paris (KP=170, #10 to #16), Conflans (KP=135, #17), Mantes (KP=90, #21) and Poses (KP=0, #22). For tributaries (○): Yonne (#2), Loing (#25), Orge (#26), Yerres (#27), Marne (#9), Oise (#20), Epte (#28). The Eure (#23) is discharged directly into the upper estuary. KP : kilometer point from the river mouth (#22).

5. Spatial analysis of the MPI from flood deposits (1994–2001)

5.1. Spatial distribution of the MPI throughout the basin

Longitudinal variations of the MPI can be established for FD sampled at 16 key stations on the Seine mainstream and its major tributaries from 1994 to 2001. This profile extends over 340 km from the Bray station downstream of the Seine–Aube confluence (#24, kilometric point KP=340) to the river mouth at Poses (#22, KP=0) and the Eure at Léry (#23; Fig. 1). As the concentrations of Cd, Cu, Hg, Pb and Zn, on which the MPI is based, display markedly smaller year to year intrastation variability relative to interstation variability, the MPI for each station have been averaged over the 1994–2000 period (Fig. 2).

On the upper Seine mainstream, from Bray (#24) to Montereau (#1, KP=300), the MPI increases, respectively, from 5 to 22, indicating a marked anthropogenic impact. As population density and land use are very similar between these two locations, two industrial sources appear to be the cause of the increase: (1) a metal industry located in Montereau, 1 km upstream of the sampling point; and (2) the Nogent sur Seine nuclear power plant which may have released trace elements from its cooling towers until the mid 1990s. The Montereau industries also may have affected the Yonne river just upstream with its confluence with the Seine river.

Downstream from the Montereau confluence, the average MPI declines to 9.5 ± 0.7 at Corbeil (#5) due to a spatial dilution effect. Below Corbeil, the Seine enters in Greater Paris and the MPI increases to 17 ± 4 at Ivry (#6). This increase probably is related to the direct overflow of some combined urban sewers into the Seine river during heavy rainstorms and of inputs of two contaminated periurban tributaries, the Orge river (#26; MPI$=53 \pm 19$) and the Yerres river (#27; MPI$=28 \pm 4$).

The Marne river at Maison-Alfort (#9) is markedly less contaminated (MPI$=9 \pm 4$) than the Seine mainstream just upstream of their confluence (station #6). However, the influence of the Marne on the Seine mainstream can not be observed because from the Seine–Marne confluence to Chatou (# 16; Fig. 1), the Seine is much impacted by Greater Paris and gradually becomes more impacted as the average MPI increases to 23 ± 8. This increase probably results from major combined sewer discharges and mirrors previously reported trace element patterns displayed in bed sediment profiles (Garban et al., 1996; Thevenot et al., 1998).

Downstream of Paris, MPI spatial patterns in the area in and around the Seine–Oise confluence are complex (#17 Seine at Conflans, #20 Oise at Conflans, #32 Seine at Denouval, and #21 Seine at Mantes; Fig. 1) due to incomplete lateral mixing of the mainstream and inflows from the Oise River on the right bank plus effluents from the Seine-Aval wastewater treatment plant on the left bank, already observed with the intra-station distribution of the MPI at Denouval (#32, Table 3). Despite efficient particulate retention ($\geq$90%) at the Seine-Aval plant, the remaining SPM released in the treated waste water is not likely to be much less contaminated than the SPM of the untreated sewage water (M. Gouzailles, SIAAP, pers. com.), heavily impacted by trace elements (MPI = 165 in July 2000).

Thirty kilometer downstream from Denouval, the three water masses (Seine-Aval effluent, mainstream Seine, and Oise Rivers) gradually mix. As a result, the MPI at Mantes (#21; Fig. 1) displays an intermediate value (27 ± 7) and at the river mouth station at Poses (#22; Fig. 1), the MPI only increases slightly (30 ± 5). This would appear to indicate that anthropogenic impacts in this final river reach are relatively minor.

5.1.1. The MPI distribution relative to Strahler stream orders

Strahler stream orders are commonly used in the Seine River Basin to study water quality issues (Billen et al., 1994; Meybeck, 1998; Meybeck et al., 1998; Meybeck, 2002). In order to explain the MPI spatial distribution, seven stream order groups have been detailed: (A) pristine monolithogenous forest catchments (stream orders 1–2) for the Bercy deposits and the six composite samples; (B) small rural and periurban streams (stream orders 1–3); (C) medium tributaries (stream orders 4–5); (D) central Seine within Greater Paris (stream order 7); (E) large tributaries (stream orders 6–7); (F) the Seine downstream of Paris (stream order 8); and (G) a specific group for the lower Eure (#23, stream order 6). The MPI values increase with increasing stream order but not regularly (Fig. 3):

- In group A, the median MPI is between 0.2 and 2, representing the geochemical background for the Seine river basin. One sample with an MPI of 4 has been excluded from this group. It corresponds to the crystalline catchments in the Morvan hills (7% of the Seine catchment) and the current trace element reference values for aluminosilicates is inappropriate.
- The group B present very low MPI (2–5), corresponding to a very limited anthropogenic impact. Although, periurban influences can be observed in a few group B streams (Ecole, MPI = 11.8; Ru de Gazeran, MPI = 13.6; Maldroit, MPI = 15.7) due to a high population pressure throughout their basin and cities upstream of the sampling stations.
- In group C, low MPI (5–10) are characteristic of medium-sized tributaries in which the metal contamination is well established although still low such as the lower Grand Morin (#42; MPI = 8 ± 2), the upper Essonne (#34; MPI = 8.5 ± 1.5), the lower Aisne (#30; MPI = 5.3 ± 0.2), the upper Thérain (#38; MPI = 4), the upper Seine at Bar (#43; MPI = 5.6 ± 0.9), the lower Loing (#25; MPI = 8.8 ± 2.9), the Aube (#35; MPI = 3.8), and the upper Vesles (#36; MPI = 7.7).

  However, in this group C, some MPI values can exceed those found in the mainstream Seine River (group D). Elevated MPI have been calculated for the Vesles below Reims (#37; MPI = 36.7), the Therain below Beauvais (#39; MPI = 12), the lower Yerres (#27; MPI = 22–33), the Meauldre below Trappes (#40; MPI = 38), the Ru de Gally below Versailles (#41; MPI = 25–46) and the Orge river (#26; MPI = 10–82). The Meauldre and Ru de Gally sites are directly influenced by treated domestic sewage and urban runoff since the headwaters for both are heavily urbanized. The

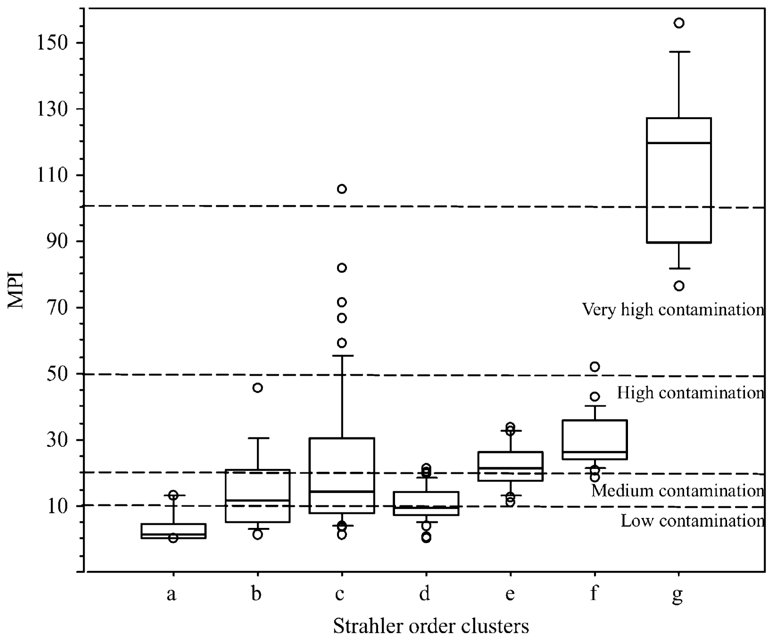

Fig. 3. Statistical distribution of MPI based on floodplain deposits (1994–2000) in 7 clusters of Strahler stream orders. (a) pristine monolithogenous forest catchments (stream orders 1–2); (b) small rural and periurban streams (stream orders 1–3); (c) medium tributaries (stream orders 4–5); (d) central Seine within Greater Paris (stream order 7); (e) large tributaries (stream orders 6–7); (f) the Seine downstream of Paris (stream order 8); and (g) a specific group for the lower Eure (#23, stream order 6). MPI scale: 0–2 = no significant contamination, 2–5 = very low contamination, 5–10 = low contamination, 10–20 = medium contamination, 20–50 = high contamination, 50–100 = very high contamination, > 100 = extremely high contamination.

MPI for the Orge have markedly declined from 1995, when it exceeded 52 to 2001 (MPI = 10), probably because of the gradual collection of waste waters and their treatment outside this watershed.

- As the stream order increases, exposures to various anthropogenic impacts, particularly those linked to urbanization and industrialization, increase. Hence, it is not surprising that the MPI increases from approximately 10 to 20; such levels are characteristic of medium contamination in the middle Seine (group D) and the large tributaries (group E) upstream of their confluence with the Seine mainstream.
- Finally, the lower Seine (group F) presents elevated MPI (21–52) reaching a maximum at the most downstream station at Poses (MPI = 26–52), characteristic of high contamination.
- The Eure River (group G), although characterized by a medium population density (65 p km^{-2}), always is the most impacted of all the Seine River tributaries with an MPI ranging from 77 to 156. This is much higher than MPI observed in the lower Seine at Poses or at Mantes. This is essentially due to very high Pb levels, attributed to a local industrial source (probably a battery plant). Such extreme MPI values, exceeding 100, i.e. very high contamination level, only are exceeded by the average MPI for the untreated sewage composite from the Seine-Aval plant (MPI = 165 in 2000).

On the basis of the FD survey since 1994, the following scale of MPI can be defined: MPI < 2 for a non-impacted station, 2 < MPI < 5 for a very low contaminated station, 5 < MPI < 10 for a low contaminated station, 10 < MPI < 20 for a medium contaminated station, 20 < MPI < 50 for a highly contaminated station, 50 < MPI < 100 for a very highly contaminated station, MPI > 100 for an

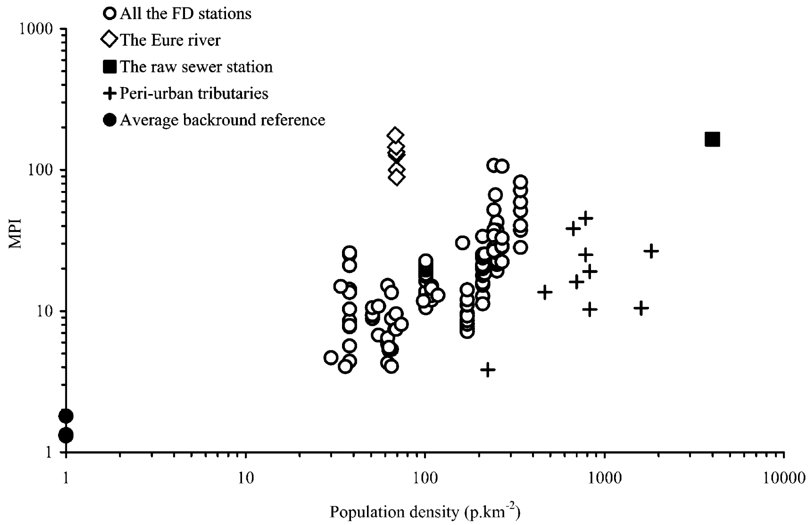

Fig. 4. Relationship between MPI in flood deposits (1994–2000) and population density. (○) = All the FD stations, (●) = the background samples, (■) = the raw sewer station, (+) = peri-urban tributaries, (◇) = the lower Eure river (#23). Same contamination scale than Fig. 3.

extremely contaminated station such as untreated waste waters.

5.2. The MPI distribution within a population gradient

The previous analysis of MPI according to stream orders reveals the possible importance of population density on metal contamination, already tested in prior studies (Billen et al., 1994; Meybeck, 1998; Horowitz et al., 1999). In the Seine River Basin, population densities range from less than 1 p km^{-2} for the forested watersheds to more than 1800 p km^{-2} for some periurban basins. Most stations on the Seine river and its tributaries are characterized by population densities ranging from 15 to 270 p km^{-2}. As an extreme case, if the circa 2500 km^2 main Parisian sewer system (Seine Aval), serving a population of 10 million is viewed as an urban basin, then the population density approaches 4000 p km^{-2} with a MPI of 165.

The MPI for forested catchments (representing the background level) and the Seine-Aval sewer particulates (maximum anthropogenic impact) could be viewed as the two water quality end-members for population density impacts in the Seine River Basin. As a result, most of the analyzed FD samples fall on the general theoretical mixing line when MPI is plotted against population density (Fig. 4). However, two exceptions should be noted: (1) the Eure at Léry (#23) has a population density approximately 65 p km^{-2} and an average MPI of 112 ± 24, approximately 10 times higher than would be expected from the general MPI-population density relationship. These results are confirming an additional contamination, probably an industrial origin; (2) some periurban streams present lower than expected MPI. Some or all the wastewater generated by the populations, upstream of these sampling points, are treated and/or discharged outside their watersheds and treated sludges usually are dispersed on agricultural land. Further, for some of these stations, population density is extremely difficult to assess because their headwaters actually are the outlets of treated wastewater from upstream urban centers.

Although the stream order approach provides a reasonable first-order description of the spatial MPI distribution and the overall trace element impacts in the Seine River Basin, mostly linked to changing population densities, it does not sufficiently account for second-order variations which appear to be linked to specific urban sewage treatment or to industrial discharges.

5.3. Trace element sensitivity to the MPI variations

In the Seine River Basin, anthropogenic impacts on trace elements concentrations can be evaluated by plotting their concentrations against MPI. A first group of trace elements (As, Be, Co, Li, Sr, V) and most major elements (e.g. Al, Ca, Fe, K, Mg, Mn, and Na) do not correlate ($r^2 < 0.3$) with the MPI (e.g. lithium, Fig. 5a). As such, they are unlikely to be affected by anthropogenic impacts, or the anthropogenic sources for these elements are different from those affecting the concentrations of the five MPI trace elements. A second group of trace elements (Ba, Cr, Ni, and Se) display limited correlation ($0.4 < r^2 < 0.6$) with the MPI. Such elements may be affected by some anthropogenic impacts. The last group (Cu, Cd, Hg, Pb, Zn, Ag, P and Sb) display strong correlation ($r^2 > 0.8$) with the MPI (Fig. 5b,c). The presence of the first five is hardly surprising since they are incorporated in the MPI; however, it should be borne in mind that their respective individual weights in the MPI only are 0.24 (Cd, Cu, Pb and Zn), and 0.04 (Hg). Since the MPI in the Seine basin, with the exception of the Eure, are strongly correlated with Ag, Sb, and P, these constituents probably have similar origins to those for the five MPI constituents. As such, the concentrations of these non-MPI constituents should increase substantially with increasing MPI, as well as with increasing stream order and population density.

6. Temporal analysis of the MPI (1981–2000)

The MPI has been designed to compare most types of particulate metal contamination surveys. Fine temporal MPI variations are here presented using sediment traps during the 1994–1995 hydrological year (Idlafkih, 1998), filtered suspended particulate matter (RNB, 2001), bed sediments (RNB, 2001) and flood deposits.

6.1. Seasonal variations of the MPI during the 1994–1995 hydrological year

The 1994–1995 water year was notable because of the marked differences between the high (up to 2000 $m^3 s^{-1}$) and low (140 $m^3 s^{-1}$) flows at Poses (Idlafkih, 1998). During this period, Idlafkih collected SPM with traps on the Seine river at Morsang (#4), at Chatou (#16), at Poses (#22), on the lower Marne river at Annet (#7) and on the lower Oise river at Mery near Beaumont (between #18 and #20; Fig. 1) (Idlafkih et al., 1997; Idlafkih, 1998). For such a wet year, the composition of river particulates is very variable (e.g. organic matter ranges from 5 to 50%) and the natural metal background may reflect this variability. The MPI were calculated for these sites from trapped sediment analyses ($n = 20$ at each station). Since the period of trap setting and retrieval is synchronous for all the stations, the seasonal variability can be checked.

At all the stations, the MPI present the highest values during the low flow period (Fig. 7). This marked seasonal variation is amplified from the less contaminated station (Marne at Annet) to the most contaminated station (Seine at Chatou and Poses). The Chatou station is more scattered probably as a result of the influence of two major Parisian combined sewer overflows injected some 10 km upstream during summer rainstorms.

This marked seasonal variation can be interpreted by a greater dilution with detrital SPM during the high flow period than during the low flow period (respective SPM fluxes being 100 and 1 kg/s). However, SPM contamination and transport processes are more complex than just a dilution of urban pollution inputs. During the summer (low flow), contaminated particles may settle between Paris and Poses until they are resuspended and carried at the next important flood (Chesterikov et al., 1998). The use of the tracer ^{10}Be confirms this mechanism and the residence times of SPM may exceed 6 months during the low flow summer periods (Bonté and Mouchel, 2002).

6.2. Temporal decline of the MPI in the Seine river basin (1981–2000)

Temporal trends have been performed with samples collected at the river mouth at Poses (#22). Various types of particulates have been collected: (i) a SPM survey starting in 1983 using filtered matter within the national RNB river quality net-

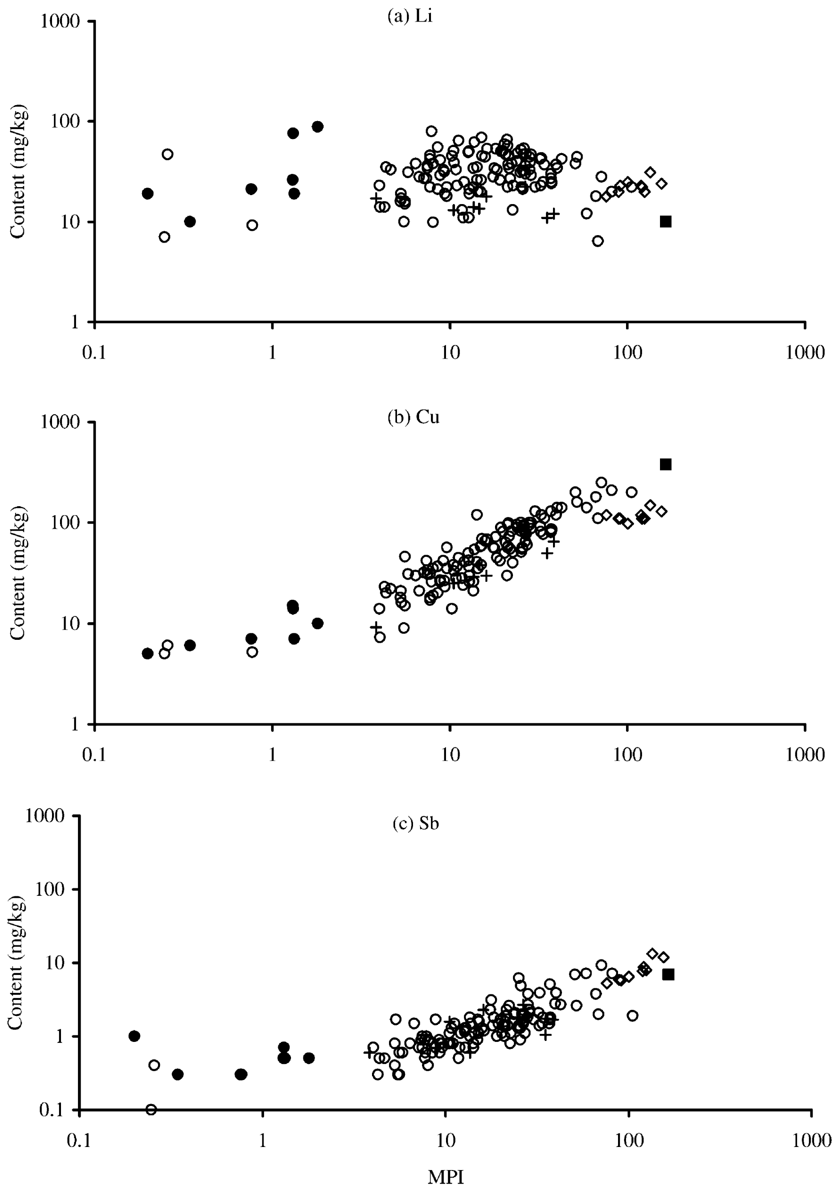

Fig. 5. Relationship between trace element concentrations (mg/kg) and the MPI in flood deposits (1994–2000) (a) Li, (b) Cu, (c) Sb. Same symbols and contamination scale than Fig. 4.

work; (ii) a bed sediment survey starting in 1981, within the same RNB network; (iii) academic and pilot SPM studies from 1990 to 1995 (Cossa et al., 1994; Idlafkih et al., 1997; Idlafkih, 1998); and (iv) the PIREN-Seine FD survey starting in 1994 (Horowitz et al., 1999; Grosbois et al., in prep).

The average annual MPI for SPM at Poses has been calculated by hydrologic year (October to September) on the basis of the averaged annual

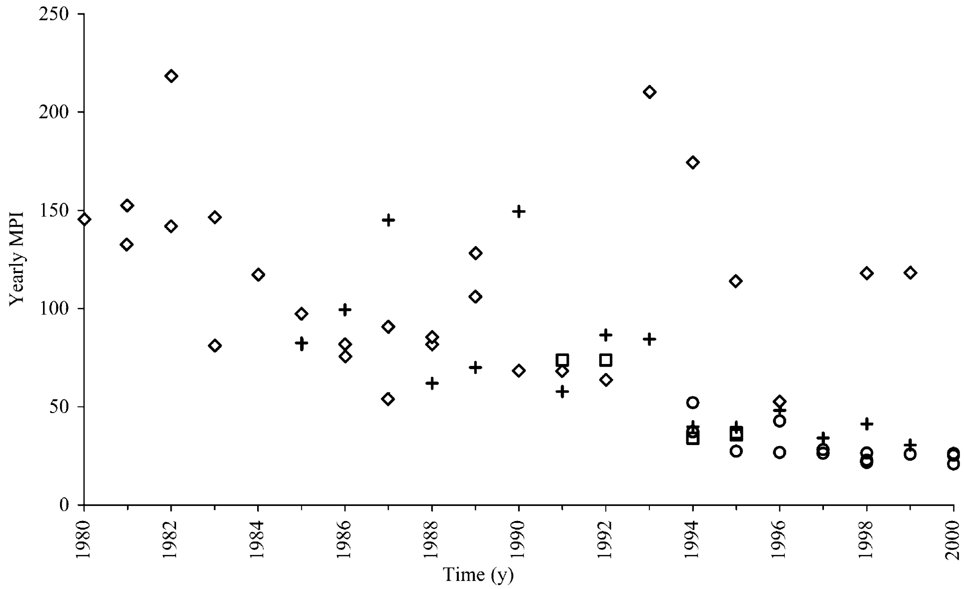

Fig. 6. Yearly MPI trends (1980–2000) at the Seine River mouth (Poses, #22) based on different types of sample media : (+)= filtered SPM (RNB, 2001); (◇)=bed sediment, (RNB, 2001); (□)=filtered SPM, pilot studies (see text for references); (○)= flood deposits (this study). Same contamination scale than Fig. 3.

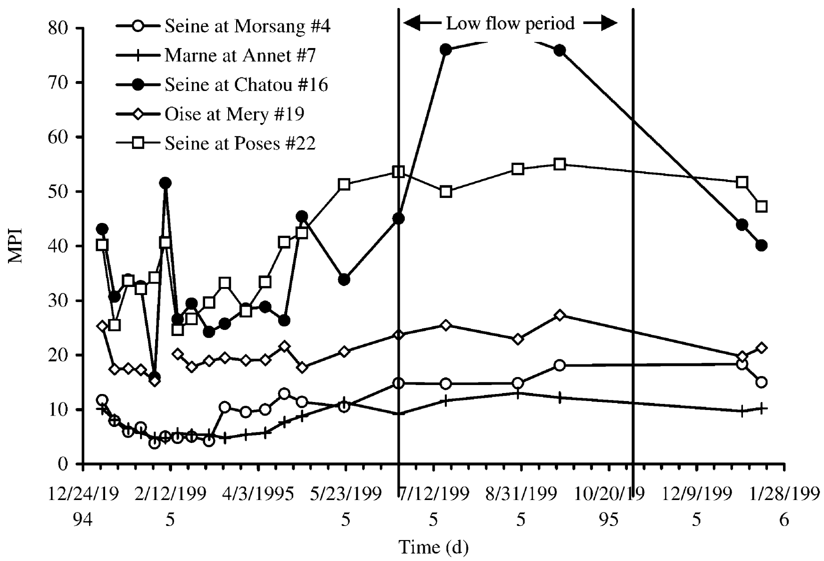

Fig. 7. Seasonal MPI variations in trapped suspended particulate matter during the 1994/1995 hydrological year at five stations: the Seine at Morsang (○; #4), at Chatou (+; #16) and at Poses (+; #22), the lower Marne at Annet (◇; #7), the lower Oise at Mery (◇; between #18 and 20). Same contamination scale than on Fig. 3.

elemental concentrations weighted by the SPM loads for the period around each analysis (based on daily SPM fluxes). The calculated MPI for different sample types are very consistent at Poses (Fig. 6). Annual MPI values have declined since the early 1980s from 150 to 30 in the late 1990s. The MPI based on the 1981–2000 bed sediments data are the highest and the most scattered of all the various sample media. Two MPI peaks calculated for SPM (1987 and 1990) are due to very high Hg levels, which may represent analytical outliers (Grosbois et al., in prep). Such MPI peaks would have been much greater if Hg had not been weighted. After 1990, the SPM and FD surveys generate similar MPI: from 1995 to 2000, the average value for the SPM survey is 39 ± 8 whereas the average value for the FD survey is 27 ± 7.

This general decline of the MPI appears to have resulted, at least in part, to a substantial decline since 1980 by a factor 10 (Cd), 5 (Pb, Zn, Cu) and 2 (Hg) in metal concentrations collected at the Seine-Aval plant, the biggest point-source of the Seine basin, (M. Gouzailles, pers. com, 2000; Grosbois et al., in prep.). The average MPI in the particulate matter from untreated sewage at the Seine-Aval plant decreased from 1500 in 1980 to 250 in 2000, i.e. a seven-fold reduction in the overall metal contamination from 8M people and from the connected industries, among which numerous small plating workshops. However, Greater Paris was not the only anthropogenic source in the basin. The RNB bed sediment survey shows in the early 1980s elevated MPI (from 30 to 50) at stations #3, #18 and #9. All these stations are located upstream of Greater Paris (Fig. 1). Since 1985, the MPI for these mid-basin stations have also displayed a general decline from 40 to 10. After 1997, a slight increase can be noticed but it may not be significant.

The bed sediment trend at Tolbiac (#10, Fig. 1) within Paris, was somewhat unexpected. From 1981 to 1984, MPI levels were extremely high (150–250). These are substantially higher than contemporary values for Poses (Fig. 6) and even exceed those for untreated sewage collected at the Seine-Aval treatment plant. These excessive MPI could result from the overflow of numerous combined sewer, locally contaminated by multiple plating industries at that time. These industrial sources were markedly reduced since 1980 (C. Lassus, AESN, pers. com.). Bed sediments at Tolbiac are sampled in a sheltered area and may correspond to a permanent contamination hotspot not representative of the Parisian reach for which a decline of contamination has been observed on flood deposits.

7. Conclusions and perspectives

The metal pollution index (MPI) appears to be a robust indicator of anthropogenic impacts in the Seine River Basin. The MPI is calculated from the concentrations of five key trace elements (Cd, Cu, Hg, Pb, and Zn) in conjunction with a limited amount of ancillary data (Al, PIC, and POC). The ancillary data are used to characterize four major mineral and organic phases with associated background trace element concentrations.

The MPI can be used to determine spatial (e.g. longitudinal profiles) as well as temporal trends (seasonal and yearly). At most of the sampling sites in the Seine River Basin, the MPI can be related to population density and/or stream order, but specific local industrial sources, sewage effluents and their evolutions should be carefully considered for a finer spatial analyze. Year to year MPI variations on flood deposits are generally low ($\pm 20\%$); therefore, a minimum of 5 years probably is needed for temporal trend analysis. However, year-to-year MPI variations for bed sediments are much scattered than those associated with floodplain deposits; hence, a minimum of 10 years probably is needed for trend analysis based on such sampling. MPI can be applied on previous regulatory surveys (filtered samples, bed sediments), performed since the early 1980s, in the Seine River Basin. It allows a first general assessment of the metal contamination throughout this basin. Although, the MPI has declined from 150 in the early 1980s to 30 in the present situation. The present contamination of the Seine river at mouth remains very high (MPI $\sim$ 30), compared to the upper part of the basin: the impact of Paris megacity, with its 10 million people, on this riverine system is still important despite continuous efforts in metal decontamination over the last 25 years.

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References

Aston S, Bruty D, Chester R, Padgham R. Mercury in lake sediments: a possible indicator of technological growth. Nature 1973;241:450–451.

Avoine J, Boust D, Guillaud JF. Flux et comportements des contaminants dissous et particulaires dans l'estuaire de la Seine. Rapp P-v Reun Cons Int Explor Mer 1986;186:392–411.

Billen G, Garnier J, Hanset Ph. Modelling phytoplancton development in whole drainage networks : the river strahler model applied to the Seine River system. Hydrobiologia 1994;289:119–137.

Bonté P, Mouchel JM. Flux et temps de séjour des particules dans le Bassin de la Seine. Piren-Seine. Rapport de synthèse 1998–2001, Sisyphe, Université Paris 6, 2002, p. 77.

Chapman D. Assessment of the quality of the aquatic environment through water, biota and sediment. London: Chapman and Hall, 1992. p. 550.

Chesterikov A, Thevenot D, Mouchel JM, Poulin M, Garban B, Ollivon D. Le fleuve dans la ville. In: Meybeck M, de Marsily G, Fuster E, editors. La Seine en son bassin, fonctionnement ecologique d'un systeme fluvial anthropise, 1998; pp. 301–344.

Cossa D, Meybeck M, Idlafkih Z, Bombled B. Etude pilote des apports en contaminants par la Seine. Agence de l'Eau Seine-Normandie/Ministère de l'Environnement, Ifremer-Nantes, R. int. Del/94.13, 1994; p. 151.

Elrick K, Horowitz AJ. Analysis of rocks and sediments for arsenic, antimony and selenium by wet digestion and hydride generation atomic absorption. Varian instruments at work, AA-56, 1986; pp. 1–5.

Forstner U, Wittmann GTW. Metal pollution in the aquatic environment. New York: Springer-Verlag, 1981. p. 110–197.

Garban B, Ollivon D, Carru AM, Chesterikov A. Origin, retention and release of trace metals from sediments of the river Seine. Water Air Soil Pollut 1996;87:363–381.

Grosbois C, Meybeck M, Horowitz AJ, in prep. Spatio-temporal distribution of Cd, Cu, Hg, Pb and Zn (1984–2000) in the Seine river particulate matter. Submitted to Sci Total Environ.

Guerrini MC, Mouchel JM, Meybeck M, Penven MJ, Hubert G, Muxart T. Le bassin de la Seine : la confrontation du rural et de l'urbain. In: Meybeck M, de Marsily G, Fustec E, editors. La Seine en son bassin, fonctionnement écologique d'un système fluvial anthropiséElsevier, 1998. p. 42–83.

Horowitz AJ. A primer on sediment-trace element chemistry, 2nd ed. Chelsea, MI: Lewis Publishers Inc, 1991. p. 136.

Horowitz AJ. The Use of Suspended Sediment and Associated Trace Elements in Water Quality Studies. Wallingford, UK: IAHS Press, 1995. p. 58 (Int. Ass. Hydrol. Sci. Special Pub. No. 4).

Horowitz AJ, Elrick K. Multielement analysis of rocks and sediments by wet digestion and atomic absorption spectroscopy. Varian instruments at work, AA-47, 1985; pp. 1–7.

Horowitz AJ, Elrick KA, Hooper RP. The prediction of aquatic sediment-associated trace element concentration using selected geochemical factors. Hydrol Process 1989;3:347–364.

Horowitz AJ, Elrick KA, Demas CR, Demcheck D. The use of sediment-trace element geochemical models for the identification of local fluvial baseline concentrations. In: Peters N, Walling D, editors. Sediments and stream water quality in a changing environment: trends and explanationInt. Ass. Hydrol. Sci. Pub, 1991. p. 339–348 (No. 203).

Horowitz AJ, Meybeck M, Idlafkih Z, Biger E. Variations in trace element geochemistry in the Seine River Basin based on floodplain deposits and bed sediments. Hydrol Process 1999;13:1329–1340.

Idlafkih Z. Transport des ions majeurs, éléments nutritifs, carbone organique et des métaux en trace particulaires (Al, Fe, Mn, Cd, Cu, Hg, Pb, Zn) dans un fleuve anthroPIé : la Seine. Importance des crues. Comparaison avec le Rhin moyen. Thèse de Doctorat, 1998. Univ. Paris 6, p. 303.

Idlafkih Z, Meybeck M, Chiffoleau JF, Cossa D, Fich A. Comportement des métaux particulaires (As, Cd, Cu, Hg, Pb, Zn) dans la Seine à Poses en période de hautes eaux (1990–1995). Int. Ass. Hydrol. Sci. Publ., 1997; 243: pp. 45–58.

Martin JM, Meybeck M. Elemental mass-balance of material carried by major world rivers. Mar Chem 1979;7:173–206.

Meybeck M. Man and river interface : multiple impacts on water and particulates chemistry illustrated in the Seine River Basin. Hydrobiologia 1998;373–374:1–20.

Meybeck M. Riverine quality at the anthropocene: propositions for global space and time analysis, illustrated by the Seine River. Aquat Sci 2002;64:376–393.

Meybeck M, de Marsily G, Fustec E, editors. La Seine en son bassin, fonctionnement écologique d'un système fluvial anthropisé. Paris: Elsevier, 1998. p. 749.

Meybeck M, Idlafkih Z, Fauchon N, Andreassian V. Spatial and temporal variability of total suspended solids in the Seine Basin. Hydrobiologia 1999;410:295–306.

Müller G. Schwermetalle in den Sedimenten des Rheins—Veranderungen seit 1979. Umschau 1971;79:778–783.

RNB 2001. Réseau national de bassin (Surface water quality network). Ministère de l'environnement-Agence de l'Eau Seine-Normandie. Aggregated data can be found at www.eau-seine-normandie.fr (Banque de données de qualité des eaux).

Rosler HJ, Lange H. Geochemical tables. Elsevier: Amsterdam, 1972. p. 468.

Salomons W, Forstner U. Metals in the hydrocycle. New York: Springer-Verlag, 1984. p. 63–99.

Thevenot D, Meybeck M, Chesterikov A, Chevreuil, M. Métaux: sources multiples et accumulation. In: Meybeck M., De Marsily G., Fustec E. editors, La Seine en son bassin, 1998; 391–437.

Thevenot D, Meybeck M, Lestel L. Métaux lourds : des bilans en mutations. Piren-Seine, Rapport de synthèse 1998–2001, Sisyphe, University Paris 6, 2002; 78.

Thomas R. The distribution of Hg in the sediment of Lake Ontario. Can J Earth Sci 1972;9:636–651.

Turekian K, Wedepohl KH. Distribution of the elements in some major units of the earth's crust. Geol Soc Am Bull 1961;72:175–192.

Wedepohl KH. Composition and abundance of common sedimentary rocks. In: Wedepohl KH, editor. Handbook of Geochemistry. New York: Springer-Verlag, 1969. p. 250–271.