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The spatial and temporal trends of Cd, Cu, Hg, Pb and Zn in Seine River floodplain deposits (1994–2000)

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Abstract

Fresh floodplain deposits (FD), from 11 key stations, covering the Seine mainstem and its major tributaries (Yonne, Marne and Oise Rivers), were sampled from 1994 to 2000. Background levels for Cd, Cu, Hg, Pb, and Zn were established using prehistoric FD and actual bed sediments collected in small forested sub-basins in the most upstream part of the basin. Throughout the Seine River Basin, FD contain elevated concentrations of Cd, Cu, Hg, Pb and Zn compared to local background values (by factors > twofold).

In the Seine River Basin, trace element concentrations display substantial downstream increases as a result of increasing population densities, particularly from Greater Paris (10 million inhabitants), and reach their maxima at the river mouth (Poses). These elevated levels make the Seine one of the most heavily impacted rivers in the world. On the other hand, floodplain-associated trace element levels have declined over the past 7 years. This mirrors results from contemporaneous suspended sediment surveys at the river mouth for the 1984–1999 period. Most of these temporal declines appear to reflect reductions in industrial and domestic solid wastes discharged from the main Parisian sewage plant (Seine Aval).

Keywords: Seine River; Metallic elements; Greater Paris; Particulate fraction; Temporal trends

1. Introduction

Trace elements in surface waters have a strong affinity for the solid phase, especially the <63-μm fraction (Horowitz, 1991, 1995; Thomas and Meybeck, 1992). Over the years, numerous trace element surveys have been performed, using a variety of solid-phase sampling media, including suspended sediment (collected by centrifugation, filtration, or traps), bed sediments, dredged sediments, and/or fresh floodplain deposits (FD). Since 1984, all these approaches have been employed in the Seine River Basin, either in routine water-quality monitoring (RNB, 2001), or in

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specific studies (Cossa et al., 1994; Garban et al., 1996; Roy et al., 1999; Ollivon et al., 2002; Carpentier et al., 2002; Meybeck et al., 2004), to monitor and assess the environmental status of this river basin. These multi-sample, multimedia studies have provided a means to determine, at numerous locations within the basin, the spatial and temporal trace element trends covering a 15-year period.

The major objectives of this study were to: (1) better define the spatial and temporal trends in trace element (Cd, Cu, Hg, Pb and Zn) concentrations in Seine River Basin FD since 1994; (2) to identify areas of substantial anthropogenic impacts; and (3) to compare the temporal variations detected in the FD with those identified in contemporaneous suspended sediment surveys carried out by the national river monitoring program (RNB, 2001). An initial comparison was made using a multi-element index in a companion paper (Meybeck et al., 2004). This time, additional comparisons were used to identify the pros and cons for each sampling media (FD versus suspended sediments).

2. Characteristics of the Seine River basin

The Seine River drains most of northwestern France (65,000 km^2) and is 900 km long at Poses, the last lock before the estuarine section of the system (Fig. 1). The estuarine section drains an additional

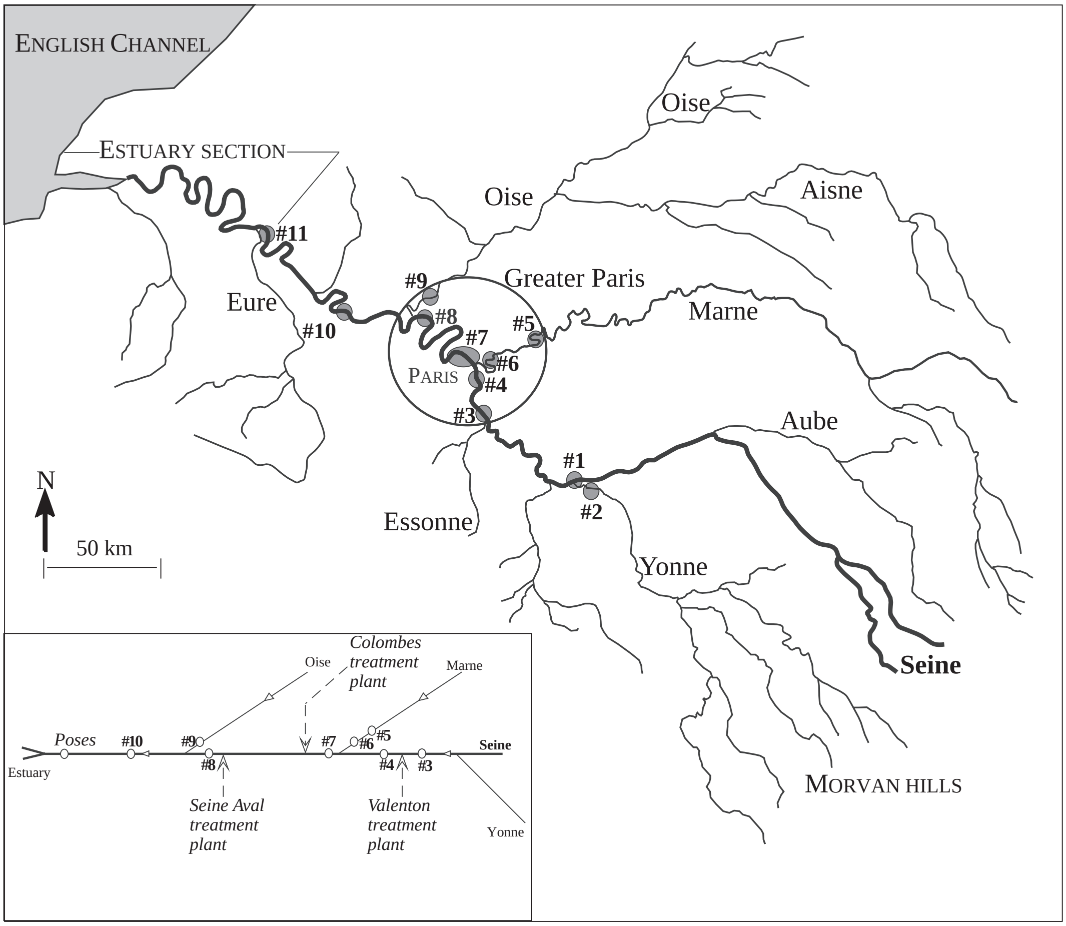

Fig. 1. Map of the Seine River Basin, showing the main tributaries and the locations of the key stations. Numbers correspond to the key stations described in Table 1. The river mouth station is Poses (#11).

7500 km^2 and includes the Eure River and the Seine–Eure confluence (Fig. 1).

Relief, geology, climate, and discharge variations are very homogeneous throughout the Seine River Basin (Meybeck, 1998; Meybeck et al., 1998). The underlying bedrock is ~93% sedimentary of which 78% is chalk and limestone; clays, sandy clays, marls, loess, and sand represent an additional 15% (Thibert, 1994). Silicate rocks (7%) are limited to the upstream Morvan hills (Fig. 1).

Four major tributaries have been sampled (Fig. 1, Table 1): (i) the Yonne River (station #2, stream order 5, draining 11,250 km^2) meets the Seine River at Montereau (station #1); (ii) the Marne River (stations #5 and 6, stream order 6, draining 13,160 km^2) meets the middle Seine River just upstream of Paris (station #7); (iii) the Oise River (station #9, stream order 7, draining 16,900 km^2) meets the Seine River just downstream of Conflans (station #8, stream order 8 as far as Poses); and (iv) the Eure River (stream order 6, draining 7000 km^2) joins the Seine River in the estuarine section. Hence, the Eure River typically is studied separately from the other rivers in the Seine River Basin (Meybeck et al., 2004).

Average annual Seine River runoff is moderate (6.7 L s^{-1} km^{-2} at Poses), ranging from 5 to 10 L s^{-1} km^{-2}. The Seine River and its major tributaries have similar hydrological regimes; all display high winter flows (Meybeck et al., 1998, 1999). In Paris, minimum summer flows used to be as low as 40 m^3 s^{-1}. Through the regulated release of water from 3 upstream (~200 km) reservoirs, summer flows now average 80–90 m^3 s^{-1}. The reservoirs have not substantially impacted the maximum discharges at Poses which can reach 1000–2000 m^3 s^{-1} (Meybeck et al., 1998).

Due to very low relief and moderate rainfall, concentrations of suspended particulate matter (SPM) tend to be very low throughout the Seine River Basin (Meybeck et al., 1999). At Poses between 1984 and 1999, daily SPM concentrations range from 5 to 10 mg L^{-1} during summer low flows and up to 300 mg L^{-1} during winter high flows. During the 1984–1999 period, the long-term average daily discharge-weighted SPM concentration is 21 mg L^{-1}, but has ranged from 20 (1991–1992) to 60 mg L^{-1} (1994–1995).

In the Seine River Basin, only high flows generate substantial SPM transport. This results from the multiple locks that regulate flow in the middle and lower Seine, the Oise, and part of the Marne Rivers. Hence, mechanical erosion and subsequent transport are very limited throughout the Seine River Basin (Meybeck, 1998; Meybeck et al., 1998, 1999); typical annual sediment yields are ≤10 t km^2 y^{-1}. The Seine River Basin is a typical example of a fluvial system affected by multiple and extensive anthropogenic activities. As the Seine River is characterized by very low SPM,

Table 1
Geographical characteristics of the different key stations

Rivers	Station					Survey		
	#	Name	Stream order[(a)]	D[(b)] (p km^{-2})	KP[(c)] (km)	Media	Sample period	*n*
Upper Seine	1	Montereau	5	38	305	FD	1994–2000	4
Lower Yonne	2	Montereau	5	38	306	FD	1994–2000	6
Middle Seine	3	Corbeil	6	51	236	FD	1994–2000	3
	4	Ivry	6	101	211	FD	1994–2000	9
Lower Marne	5	Esbly	6	62	250	FD	1994–2000	3
	6	M.-Alfort	6	172	210	FD	1994–2000	10
Central Seine within Paris	7	Pont Neuf to Puteaux	7	210	210 to 170	FD	1994–2000	11
Lower Seine	8	Conflans/S	7	252	132	FD	1994–2000	2
Lower Oise	9	Conflans/O	7	101	132	FD	1994–2000	2
Lower Seine	10	Mantes	8	252	92	FD	1994–2000	7
	11	Poses	8	242	0.5	FD	1994–2000	8
						SPM	1984–1999	245

(a) Stralher stream order; (b) Population density; (c) Kilometric point upstream of the river mouth as assigned by the Service de Navigation de la Seine (SNS); *n*: number of samples. FD: Fresh deposited flood sediments (Piren Seine Program, Meybeck, 1998; Meybeck et al., 1999, 2004; Horowitz et al., 1999); SPM: Filtered suspended particulate matter, regular monitoring at Poses (RNB, 2001). Station location is in Fig. 1.

overall water quality is sensitive to the multiple inputs of SPM-associated constituents derived from such sources as Parisian sewage effluents, intensive agriculture, and/or major industrial activities.

Landuse within the Seine River Basin is mixed and can be divided into 4 major categories: (1) open fields and forests with localized agriculture upstream of Montereau; (2) Champagne vineyards in the center of the basin; (3) intensive agriculture between Montereau and Greater Paris; and (4) heavy industry (e.g. chemicals, petrochemicals, automobile manufacturing) between the Oise–Aisne and the Seine–Essonne confluences, and the Seine estuary (Meybeck et al., 1998).

Population density in the Seine River Basin averages 250 p km^{-2} but ranges from as low as 15 p km^{-2} in the upstream part of the basin to more than 1800 p km^{-2} in Parisian peri-urban areas. Until 1988, there was a substantial upstream-to-downstream urbanization gradient in the Seine River mainstem. Most Parisian wastewater (~90%) is treated and discharged from the Seine Aval (formerly Acheres) plant which had a total connected equivalent population of 8.1 million at the time of the study; mean effluent discharge during dry days is 27 m^{3} s^{-1} (Fig. 1). It is the world's second largest wastewater treatment facility after Chicago. The oldest part of the system is a network of combined sewers that discharge untreated effluent directly to the river during rainy days. Wastewater treatment now occurs at two additional facilities in and around metropolitan Paris. The Valenton (established in 1987; between stations #3 and #4) and the Colombes (established in 1998; between stations #7 and #8) Plants, with 1.2 and 0.9 million connected equivalent populations, respectively, discharge to the Seine River (Fig. 1). Major industrial sources of trace elements in the basin (automobile factories, metal-plating facilities) are located within and downstream of Paris.

More detailed descriptions of the multiple anthropogenic impacts in the Seine River Basin can be found in Meybeck et al. (1998), Meybeck (2002), and Bordès-Pages and Dugény (2004). Although the morphologic and hydrologic characteristics of the Seine River Basin are relatively homogeneous, differences in population density, agricultural land-use, and the location of numerous industrial facilities superimpose a variety of temporal and spatial patterns on the dissolved and sediment-associated trace element concentrations and distributions within the basin.

3. Materials and methods

3.1. Sampling surveys

Under the Piren Seine program, a collaboration between the University of Paris VI and the U.S. Geological Survey led to the development of a new approach to performing SPM surveys for assessing water quality. It entails the collection and subsequent chemical analysis of superficial (0–5 cm deep) freshly settled floodplain deposits [(FD); Meybeck, 1998; Horowitz et al., 1999; Meybeck et al., 2004]. Since 1994, FD have been collected after winter high-flow events at 11 key sites (Fig. 1). Due to sampling difficulties (hydrological variations, absence of flood deposits), some key locations within the basin have to be represented by multiple stations, separated by 1–2 km (Table 1). Paris (#7, Table 1) is the most complex of these sites as it represents a 30-km river segment between 6 stations. FD are manually collected by the same operator, from the surfaces of river banks, stairs, and levees, either as dried material a few days after peak discharge and/or ~10 cm under water, immediately after peak discharge. These deposits are short-lived, and are generally destroyed between major consecutive floods. This type of sample tends to integrate flood events over 1- to 3-week periods, and probably is more temporally representative than several local individual SPM samples collected during a single high-flow event. One of the goals of this study was to compare the chemical results from these FD samples with those generated from filtered suspended particulate matter (SPM) collected by the National Basin Network (RNB, 2001; run by the French Ministry of the Environment, and the Seine Basin Water Authority), collected 12–24 times per year at Poses between 1984 and 1999.

3.2. Analytical procedures

The fresh FD were freeze–dried prior to analysis. FD mineralogy was characterized by X-ray diffraction (XRD) on a Siemens D5000 diffractometer, using CuKα radiation (step size = 0.04° 2θ; counting time = 2.8 s/step, between 2.5° and 70° 2θ) and equipped with a diffracted-beam graphite monochromator designed to minimize the fluorescence effect. The grain size distributions of the solid material were determined by laser diffraction (Malvern Mastersizer) between 1 μm and 1 mm.

Total chemical analyses of the FD samples were performed using flame AAS (Cd, Pb), ICP-AES (Cu, Zn), and cold vapor AAS (Hg) following an HNO_3/HF/$HClO_4$ digestion (Horowitz and Elrick, 1985; Elrick and Horowitz, 1986; Horowitz et al., 1989). Analytical precision and bias were monitored using various standard reference materials (e.g., USGS MAG-1, QLO-1, SGR-1; NIST 1646 a, 2709, 2711) and sample analytical duplicates that were digested and analyzed contemporaneously with the FD samples at a ratio of 1 : 5. Analytical precision was better than ± 10%, except near the detection limit, where it could reach ± 100%; no bias was detected. Replicate FD samples also were collected at selected key stations (Meybeck et al., 2004). The RNB SPM- and bed sediment-associated chemical data were generated using a variety of analytical procedures; reported analytical errors were on the order of ± 10% (Cossa et al., 1994).

4. Results

4.1. Mineralogy and major element composition of floodplain deposits since 1994

All the Seine River Basin FD samples have similar mineralogies; calcite and quartz are dominant. Some phyllosilicates (kaolinite and mica-type) and traces of plagioclase also are present. This reflects the composition of the local bedrock and agrees with the mineralogies calculated from additional chemical data from the same samples (Meybeck et al., 2004).

The FD samples collected at most of the sites display a bimodal grain-size distribution; the first mode ranges from 5- to 10-μm, corresponding to the clay assemblage, whereas the second ranges between 25- and 35-μm, probably corresponding to a calcite/quartz assemblage (plus some feldspars). The limited variations in grain-size distributions and mineralogy facilitate intercomparisons of FD-associated trace element concentrations throughout the basin; they also have produced a limited and consistent major element composition for all FD samples. Average Ti ranges between 0.18% and 0.23%, average Al ranges between 2.2% and 4.0%, and average Ca ranges between 13.4% and 14.7% (Table 2). Between 1994 and 2000, interannual major element variability is ≤ ± 15% and does not display any marked temporal trends.

4.2. Establishing temporal trends in floodplain deposit-associated trace elements since 1994

Temporal trace element trends for the 1994–2000 period were established at each station when 6 or more samples were available. If not, then an average trace element concentration was determined and the site only was used to establish spatial (upstream/downstream) trends (see next section). Hence, temporal trends have been established for Paris, for the lower Marne River, and for Poses. Enrichment ratios were calculated using Eq. (1):

$$[X/\mathrm{Al}]_{\mathrm{sample}}/[X/\mathrm{Al}]_{\mathrm{background}} \quad (1)$$

where: X = trace element concentration in the sample or the background average Al = concentration of Al in the sample or the background average.

Normalization to Al was selected because FD-associated Al concentrations only display very limited variations throughout the Seine River Basin. Natural background levels were established on the basis of chemical data from prehistoric samples, and bed sediments collected in small forested upstream watersheds in the basin (Meybeck, 1998; Thevenot et al., 1998; Horowitz et al., 1999; Meybeck et al., 2004, Table 2).

4.2.1. Temporal trends for Paris and the lower Marne River

The Paris segment of the Seine River (station #7) does not display very well-defined temporal trace element trends. Cd, Cu, and Hg concentrations vary by a factor of 2 between 1994 and 2000, but are very scattered during the period. Cd enrichment ratios range between 2.6 and 6.4, Cu enrichment ratios between 2.8 and 8.1, and Hg enrichment ratios range between 6.9 and 68.1; thus the Paris segment is highly enriched in Hg. No statistically significant temporal trends could be detected for these trace

Table 2
Medians of selected major and trace element concentrations in the natural background according to Meybeck (1998), Thevenot et al. (1998) and Horowitz et al. (1999) and in flood deposits collected at various stations in the Seine River Basin from 1994 to 2000

River	River station and number		Cd ppm	Cu ppm	Pb ppm	Zn ppm	Hg ppm	Ca %	Al %	POC %
	Natural geochemical Background	*Median*	*0.22*	*15*	*20*	*60*	*0.03*	*n.a.*	*3.30*	*n.a.*
		s.d.	*0.005*	*5*	*3*	*10*	*0.015*		*0.05*	
Seine	Montereau (#1) $n=4$	Median	1.25	85	94	230	0.15	13.40	2.75	3.10
		s.d.	0.42	37	39	67	0.23	1.6.	1.05	1.69
Yonne	Montereau (#2) $n=6$	Median	0.50	19	69	170	0.14	11.30	3.05	2.20
		s.d.	0.38	5	22	17	0.85	0.28	0.66	1.71
Seine	Corbeil (#3) $n=3$	Median	0.60	27	54	140	0.17	14.00	2.15	2.50
		s.d.	0.15	5	4	20	0.02	n.a.	0.38	0.60
Seine	Ivry (#4) $n=9$	Median	0.80	68	86	240	0.32	14.00	4.00	4.10
		s.d.	0.12	22	15	57	0.77	0.32	0.58	1.02
Marne	Esbly (#5)+M. Alfort (#6) $n=13$	Median	0.60	35	45	130	0.15	15.60	2.80	1.97
		s.d.	0.27	9	16	44	0.06	2.75	0.86	0.73
Seine	Paris (#7) $n=11$	Median	1.00	69	110	280	0.39	14.70	4.00	3.57
		s.d.	0.17	17	31	52	0.29	1.26	0.97	0.98
Seine	Conflans (#8) $n=2$	Median	1.70	85	125	343	0.67	14.70	3.43	3.85
		s.d.	0.01	11	21	53	0.12	n.a.	0.04	0.64
Oise	Conflans/Oise (#9) $n=2$	Median	0.95	34	45	200	0.29	n.a.	2.95	2.60
		s.d.	0.07	6	6	42	0.02	n.a.	0.35	0.28
Seine	Mantes (#10)+Poses (#11) $n=15$	Median	1.90	83	110	350	0.58	13.60	3.40	3.50
		s.d.	2.04	41	46	139	0.59	1.03	0.97	1.57

n = number of samples; s.d. = standard deviation; n.a.: non available.

elements during the 1994–2000 period. Only Pb and Zn concentrations seem to decline in this segment during this period. The Pb enrichment ratio declines from 12.6 to 2.5 whereas the Zn enrichment ratio declines from 7.9 to 2.4.

In the lower Marne River (stations #5 and #6), no trace element concentrations seemed to decline during the 1994–2000 period. In fact, trace element concentrations are essentially stable during the period (Table 2). The lower Marne River segment has a high population density (~230 p km^{-2}); however, concentrations and subsequent trace element enrichment ratios at these sites are lower than those displayed in the Paris segment, especially for Hg. This probably occurs because the various anthropogenic sources outlined previously are more moderate (e.g., limited industrialization, limited combined sewer overflows, and efficient wastewater treatment at the Seine Aval plant; Fig. 1).

4.2.2. Trends for the whole basin (Poses, station #11)

The material collected at Poses represents the integrated runoff from the entire 65,000 km^2 Seine River Basin. Between 1994 and 2000, Al and Fe concentrations display no significant correlations with annual SPM loads (at the 99% confidence limit); this would appear to indicate a chemically stable supply of background material. The relatively constant mineralogical assemblages in the same samples lends support to this view. On the other hand, FD-associated particulate organic carbon (POC) concentrations do display a somewhat greater level of variability; about 5% between 1994 and 1997, but declining to only 1.9% between 1999 and 2000.

With the exception of one of the four samples collected between 1997 and 1998 which probably represents an outlier (Fig. 2), FD-associated trace element concentrations display a significant decline at Poses between 1994 and 2000. The temporal trend for Cd (enrichment ratios decline from 14.3 to 7.5) indicates a significantly marked and regular decline from 1994 to 2000 (Fig. 2). The Cd decline is more marked and more regular than for Cu, Hg, Pb, and Zn. Cu concentrations decline by a factor of 3 whereas the enrichment ratios decline from 9.2 to 6.0. Hg concentrations decline by a factor of 2. Despite this decrease, Hg is one of the most enriched FD-associated trace elements in the group (enrichment ratios range from 46 in 1994 to 16 in 2000). The temporal trend in Pb concentrations also is

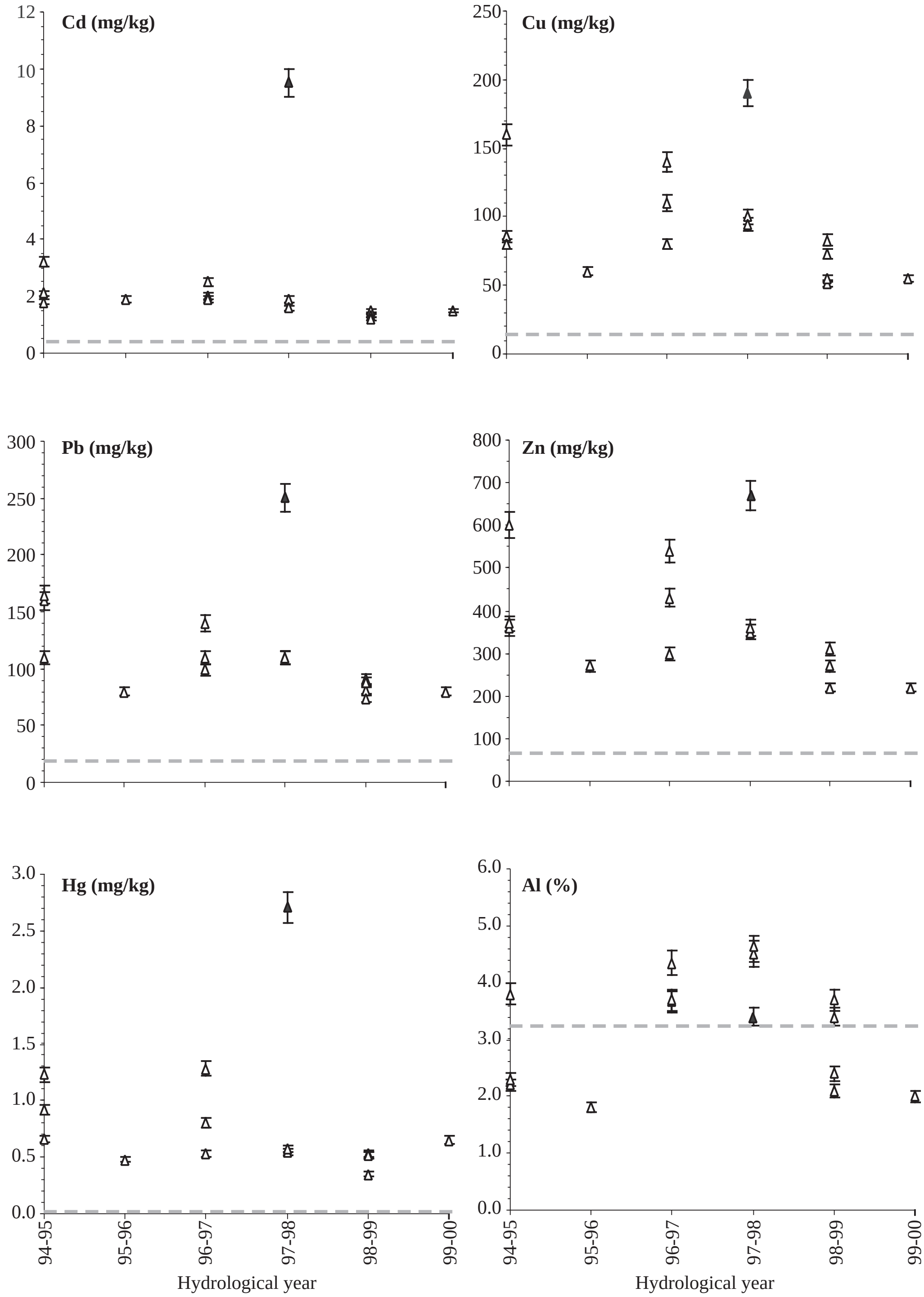

Fig. 2. Temporal trend for Cd, Cu, Pb, Zn and Hg contents (mg/kg) and Al (%) in flood deposits (FD) at Poses between 1984 and 2000 (hydrological years). The high contents, measured in one of the 97–98 samples (▲) are attributed to a sampling error. The dashed grey line represents the geochemical background level (see Table 2 for references).

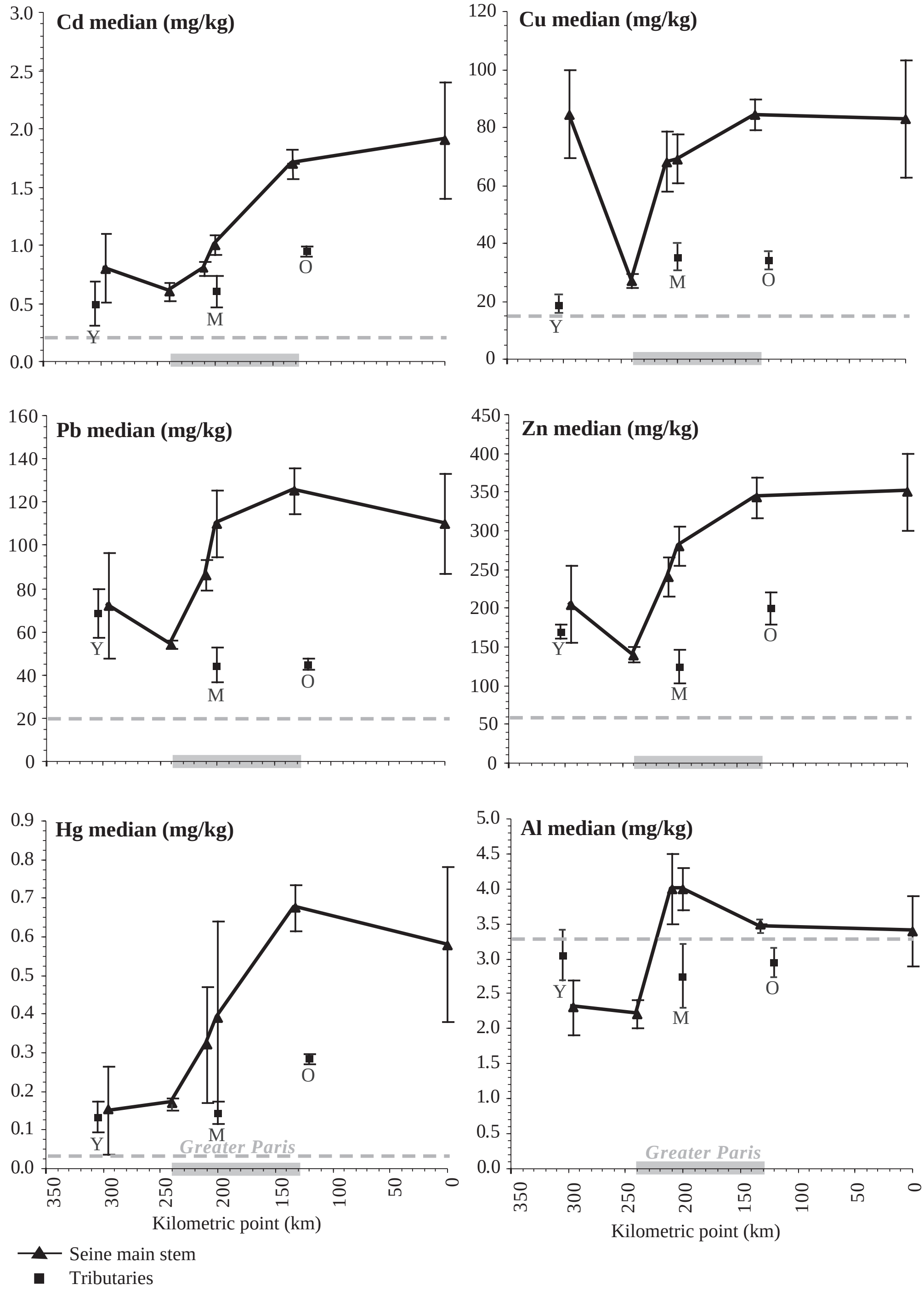

Fig. 3. Longitudinal variations of trace element concentration medians (mg/kg) and Al (%) in flood deposits along the Seine main course (▲) and its tributaries (■; Y = Yonne, M = Marne, O = Oise) for the 1994–2000 period. Kilometric point (KP) is according to the river mouth, Poses (KP = 0). Error bars represent the standard deviation between samples at a station for the studied period. The dashed grey line represents the geochemical background level (see Table 2 for references).

marked (enrichment ratios decline from 11.5 in 1994 to 6.6 in 2000). Finally, even though the enrichment ratios decline from 9.0 in 1994 to 6.0 in 2000, Zn displays the most complex/irregular temporal trend in the group. It should be noted that, despite the statistically significant temporal declines in concentration and enrichment factors for FD-associated Cu, Cd, Pb, Hg, and Zn displayed at Poses, Seine River particulates still are highly enriched in these constituents relative to natural background levels.

4.3. The longitudinal profiles of trace element concentrations in flood deposits throughout the Seine River Basin

The average concentrations for FD-associated trace elements for the 1994–2000 period for the various Seine River Basin sampling sites are provided in Table 2. These concentrations exceed natural background levels by factors ranging from 2- to 10-fold. Longitudinal profiles for the Seine River mainstem and its 3 major tributaries (Yonne, Marne, and Oise Rivers) have been established from Montereau (kilometric point KP=305) to Poses (KP=0.5). As a result of the substantial interannual chemical variability noted previously in the discussion of temporal trends, trace element longitudinal profiles are based on 6-year (1994–2000) median concentrations; the error bars represent intersample temporal variability (the standard deviation for the 1994–2000 period) at each station.

The FD-associated longitudinal profiles for Cd, Hg, Pb, and Zn are all similar (Fig. 3). All display an upstream-to-downstream increase, with maximum concentrations at the most downstream station at Poses. Even in the most upstream area of the Seine mainstem, trace element concentrations are higher than natural background levels. The most marked variations occur in the Cd and Hg profiles, median concentrations increase by factors of 2 and 4, respectively, between Montereau (KP 305) and Poses (KP 0.5). The Cu profile differs because the concentration at Montereau is very high (85 ± 30 mg kg^{-1}), and not substantially different from the one observed at Poses (83 ± 40 mg kg^{-1}). As population density around Montereau is relatively low (38 p km^{-2}), the only potential local sources of Cu are residual (as this source has been limited since the early 1990s) material from local industries and/or possibly the presence of nuclear plant cooling towers located upstream.

The largest longitudinal increase in FD-associated trace elements occurs within the Parisian reach of the Seine River Basin (between KP 211 and 170; Fig. 3). This increase probably is related to either: (1) population density, which more than doubles in this reach (from 101 p km^{-2} at KP 211 to 252 p km^{-2} at KP 170); and/or (2) the outfalls of several medium-sized sewage treatment plants and combined sewer overflows that discharge here (Fig. 1). Further, this reach also is situated downstream of nearly all the confluences of the medium-sized peri-urban streams in the basin (Stralher order between 3 and 5) such as the Yerres, Orge, Yvette, and Bievre Rivers. All these streams are strongly impacted by high population densities (respectively, 269, 340, 465, 830, and 1820 p km^{-2}; Meybeck et al., 2004).

The median FD-associated trace element concentrations for the 3 major Seine River tributaries all are lower than for the mainstem Seine (Fig. 3). Therefore, it is unlikely that these tributaries have a significant impact on the already elevated FD-associated levels in the mainstem Seine. The lack of a detectable dilution effect in the mainstem Seine, due to the inflow of lower concentration material probably results from the current spatial scale of the sampling program.

5. Discussion

5.1. The Seine River Basin, a 'hot spot' of trace element contamination?

When addressing the general question “Is the Seine River Basin impacted by elevated trace element levels?”, the answer is not clearcut. In upstream forested stream catchments, the trace element concentrations of surficial fine-grained sediments are very similar to those found in prehistoric samples, and probably can be used as background values. On the other hand, each sub-basin or river reach can have its own enrichment level, and spatial trend, and these may differ from one constituent to another. Most current findings confirm those reported in earlier studies (Horowitz et al., 1999; Meybeck, 1998, 2002). As the regular SPM surveys at Poses did not begin until 1983, it is difficult to estimate the maximum trace element enrichments that probably occurred downstream of Paris in the 1970s (Avoine et al., 1986).

The maximum enrichments reported for Seine River particulates by these authors for the 1976–1982 period were: 24 for Cd, 3.5 for Hg, 330 for Cu, 195 for Pb, and 1100 for Zn. These enrichment levels are among the highest reported for fluvial particulates on all continents, including medium-sized rivers (10,000–100,000 km^2) affected by large cities and/or by mining and smelting. Cd and Hg levels in the Seine River Basin are extremely high relative to local background levels and in comparison with other elevated levels recorded in Europe and elsewhere. Maximum Cd and Hg concentrations reached, respectively, 52 and 10 $\mu g\ g^{-1}$ in the Scheldt in Belgium (Zwolsman et al., 1996), 34 and 17 in the Rhine (Germany) around 1971 (Malle, 1990), 36 and 8 in Rotterdam Harbor (De Groot et al., 1976), and 21 and 7.6 in the Elbe (Müller and Forstner, 1974, quoted by De Groot et al., 1976). Seine Cd levels compare to those reported for the Kanal Polski (42.4 $\mu g\ g^{-1}$) and the Row Slaski (25.3 $\mu g\ g^{-1}$), both tributaries of the Oder River in Poland (Samecka-Cymerman and Kempers, 2003), to China's Grand Canal (44.5 $\mu g\ g^{-1}$; Liu, 1993), and to the Yamuna River, a Ganges tributary (112 $\mu g\ g^{-1}$ at one station; Singh et al., 1999). The maximum Seine River levels for Cu, Pb, and Zn only are exceeded in rivers markedly affected by mining, smelting, or metallurgical industries such as Lake Coeur d'Alene, Idaho (Cd = 56, Pb = 1800, and Zn = 3500 $\mu g\ g^{-1}$; Horowitz et al., 1993), the Upper South Tyne (Pb = 6000, Zn = 1500 $\mu g\ g^{-1}$; Macklin, 1996), China's Grand Canal (Cu = 1890, Pb = 7730, Zn = 3680 $\mu g\ g^{-1}$), the Scheldt estuary (Cu = 271, Pb = 334, Zn = 1341 $\mu g\ g^{-1}$; Zwolsman and Van Eck, 1999), the Meuse River (Belgium–Netherlands) (Cu = 67, Pb = 1400, Zn = 8000 $\mu g\ g^{-1}$; Rang et al., 1986), the Kanal Polski (Cu = 361, Pb = 172, Zn = 811 $\mu g\ g^{-1}$; Samecka-Cymerman and Kempers, 2003).

Although FD-associated trace element levels in the Seine River have declined between 1994 and 2000, they still are very high compared to other French rivers such as the Loire (Grosbois et al., 2001) and Rhône (Santiago et al., 1994), and in comparison to current levels in the Rhine River, particularly for Cd and Hg, where trace element concentrations peaked in the 1960s and 1970s (Van der Weijden and Middleburg, 1989). More details of the trace element history (long-term spatial and temporal trends) of the Seine River Basin are likely to evolve in the future as a result of ongoing floodplain coring and chemical analyses, along the lines of similar programs in the Rhine (Middlekoop, 1997) and the Meuse (Rang et al., 1986) Rivers.

5.2. Decline in trace element impacts in the Seine River Basin

Since the early 1980s, there appears to have been a marked, albeit not necessarily constant decline in sediment-associated trace element concentrations in the Seine River Basin. This is especially detectable at Poses. This improvement could be related to increases in the proportion of relatively unimpacted detrital material transported into the system, especially during high-flow years. However, the lack of substantial variation in the major element composition of the Poses' sediments would argue against this view. The temporal decline also could be attributed to a generalized reduction of trace element inputs from both domestic and industrial sources. One of the most marked examples of this type of reduction can be observed in the trace element concentrations of treated solid wastes discharged from the Seine Aval plant (Fig. 1). As it represents the connected equivalent of 8 million people (i.e., more than 60% of the total population of the basin), it is considered highly representative of the changes in POC and trace element concentrations of domestic wastes throughout the basin. The temporal FD-associated POC decline observed at Poses, probably can be linked to improvements in the efficiency of Parisian wastewater collection and treatment because summer algal production, a small fraction of the annual supply of POC, has not substantially declined during this period (Billen et al., 1994; Garnier et al., 1995, 1998).

Besides dealing with domestic wastes, the Seine Aval plant also deals with inputs from various small- and medium-sized industrial sources. The composition of treated sewage sludges generated at the facility has been determined monthly since 1980, then weekly since the mid 1990s by the sewage treatment authority (SIAAP). Since the trace element content should not be affected by the treatment, the average annual trace element concentrations of the treated dry sludges can be used to evaluate trace element trends in the raw sewage. Over the past 20 years, trace element concentrations in treated solid wastes have declined, particularly as a result of actions jointly undertaken by SIAAP and the Seine Basin Water Authority (AESN) so that the dry sludge could be used for agricultural purposes (Fig. 4). Note that the rate of Cd decline is faster, and the rate of Hg decline is slower, than for the other trace elements evaluated in this study. This tends to mirror the patterns observed at Poses. The marked decline for all trace elements that occurred in 1994 probably resulted from the presence of excessive amounts of bentonite used during the tunnel drilling and construction of the new Paris Metro (Meteor Line), and not to a specific reduction in trace element sources (M. Gouzailles, SIAAP, pers. comm.). It is interesting to note that the decline in FD-associated trace element levels in the Seine River Basin (especially at Poses) mirrors a sharp reduction in metal use, and the generation of related wastes, in numerous plating workshops in and around metropolitan Paris (M. Lassus, AESN, pers.com.).

5.3. Spatio–temporal trends: a comparison of sampling media

The national river monitoring program for the Seine River Basin (RNB, 2001) has maintained a

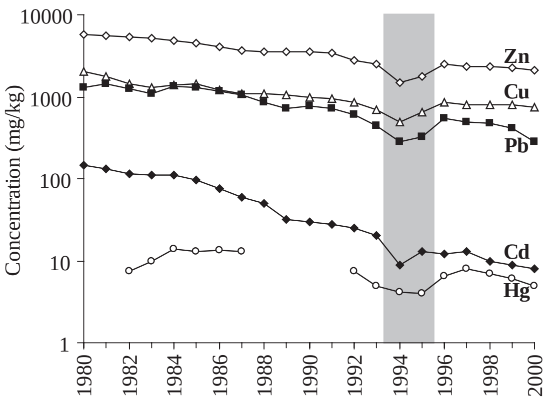

Fig. 4. Temporal variations of trace element contents (mg/kg) in treated solid wastes, from the Seine Aval treatment plant (8 million people; SIAAP, 2001; see Fig. 1 for location). The shaded period represents the metro line construction.

SPM survey at Poses since 1983; sampling occurs from 12 to 24 times per year. For the 1994–2000 period, these data (discharge-weighted averages based on 245 samples) can be compared with that generated from the 15 contemporaneous FD samples collected at this site. The discharged-weighted average SPM-associated trace element concentrations have been calculated for each water year (September–August) to establish SPM-associated chemical fluxes (Thomas and Meybeck, 1992). In turn, these fluxes were determined from a daily SPM flux database (Idlafkih, 1998; Meybeck et al., 1998), assuming constant chemical levels between samples (Thomas and Meybeck, 1992).

The grain-size effect for the two sampling media may be minimal because floodplain deposits consist of suspended matter that settled naturally (due to decreases in water velocity from obstacles like levees, stairs, islands, etc.). A comparison of the major element and POC concentrations for both media for the 1994–1999 period indicates that Al levels were constant for both, but higher in the SPM ($4.47 \pm 0.27\%$) than in the FD ($3.40 \pm 0.97\%$). Further, SPM-associated POC ($2.37 \pm 0.30\%$) also was constant for the period, and lower than in the FD samples. However, unlike the Al pattern, FD-associated POC displayed a marked decline (from 5.6% in 1994–1995 to 1.9% in 1999–2000) for the same period. Hence, because the major element chemistry of both media are not entirely consistent, it would appear advisable to use only enrichment factors, as previously calculated, to compare SPM- and FD-related chemical trends (Fig. 5).

All the enrichment factors for both sample media are in the same range. They show similar temporal declines for all the trace elements under discussion. However, some outliers should be addressed. All the 1997–1998 FD-associated trace element concentrations appear to be outliers because they fall well outside the concentration ranges for all the other samples; hence, this group of samples (data) probably is not representative of annual fluxes, and may correspond to a deeper and more heavily impacted sediment layer, possibly corresponding to an earlier period (mid 1980s). This indicates that the use of trends identified using FD-associated trace element concentrations must be used with caution, especially if they were determined with a limited number of

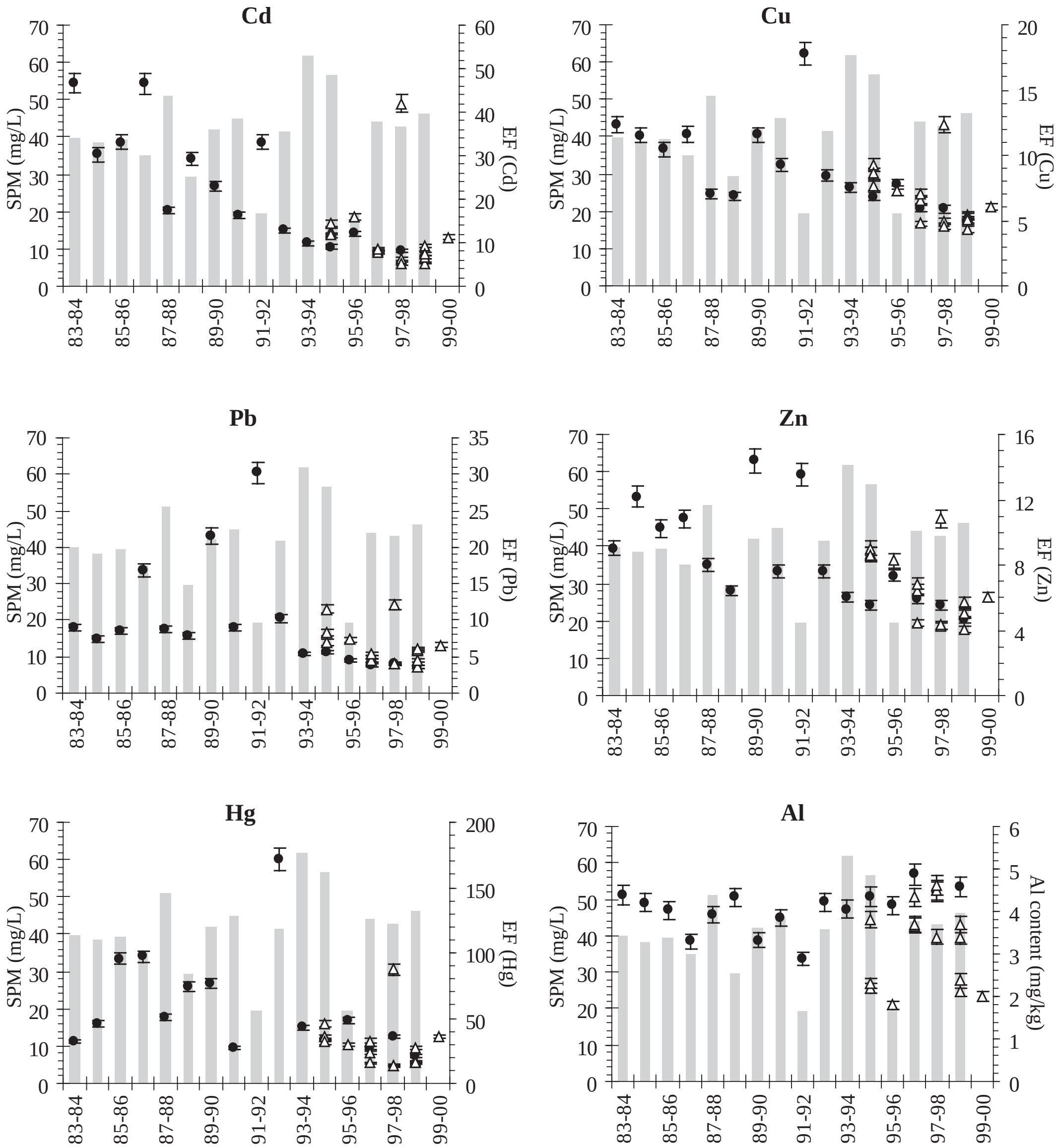

Fig. 5. Temporal trend for discharge-weighted suspended particulate matter (SPM) concentration (vertical bars, mg/L), for Cd, Cu, Pb, Zn and Hg enrichment ratios (ER; see text for calculations) and Al content (%) in SPM (●) and flood deposits (△; FD) at Poses between 1984 and 2000 (hydrological years). The 10% error bars correspond to analytical errors.

samples. An elevated SPM-associated Hg enrichment (~171) was noted in 1992–1993 and also may be questionable for this period, as a result of reporting and/or analytical errors (Meybeck et al., 2004).

A closer look at some of the interannual variations also reveals the influence of annual SPM loads (Fig. 5) on trace element concentrations and enrichment ratios. Trace element variations appear to be linked to variations in discharge-weighted SPM concentrations. Lower enrichment ratios, especially for Cu, Pb, and Zn, often are associated with higher SPM loads, and vice versa. This probably results from variations in dilution levels associated with greater or smaller amounts of detrital material containing near-background trace element levels. However, there does not appear to be a significant correlation between annual SPM and trace element concentrations.

The Seine River Basin Authority and the French ministry of the Environment prefer to sample bed sediment for evaluating fluvial trace element levels. In the Seine River Basin, samples are collected once a year, at up to a maximum of 40 sites. The results from these surveys mirror those from both SPM and FD; there has been a steady decline in trace element levels at Poses since the mid 1980s. These bed sediment surveys also confirm the general downstream increase in trace element levels detected using the FD samples, especially when using a metal pollution index (Meybeck et al., 2004). However, bed sediment-associated trace element concentrations display much greater interannual variability than the FD samples. As the entire bed sediment sample is used, rather than a limited grain-size range, they tend to contain substantially higher concentrations of coarse material than is typical in SPM (filtered or trapped) or FD samples (Idlafkih, 1998; Horowitz et al., 1999). This higher percentage of coarse material likely is the cause of the greater degree of interannual variability than that detected in the other types of sample media.

The pros and cons for the various sample media used to evaluate trace element levels in the Seine River Basin are summarized in Table 3 (Idlafkih, 1998; Horowitz et al., 1999; Meybeck et al., 2004; Thevenot et al., 1998). All three types of sample media (SPM, FD, bed sediments) produce similar annual temporal trace element trends. However, it would appear that FD surveys can provide information on a finer spatial scale, while using fewer samples, than would be required for SPM surveys. On the other hand, SPM surveys, particularly those intended to determine fluxes, probably can provide finer temporal details than could be achieved using FD samples. However, finer temporal detail only can be achieved using SPM separated by filtration (sediment trapping would not be appropriate) of a large number of individual samples. Hence, the choice of an appropriate sample media may well depend on the specific goal(s) of the survey, as well as the available financial and human resources.

Table 3
Summary of pros and cons of different Seine River solid material surveys

Sampling media	Pros	Cons
Filtered particulate matter survey	Allows fine temporal analyses Suited for flux calculation Can be performed at any discharge flow Punctual temporal contamination well identified Provides information on filter feeder exposure to contaminants	Sensitive to short-term discharge variations. Sampling frequency dependent (12–24/year for large river basins) Vertical and lateral composite samples can be needed Does not integrate time
Trapped particulate matter survey	Allows temporal analyses with special calculation conditions Suited for flux calculation Temporal variations integrated Can be performed at any discharge flow Large quantity obtained for analyses	Grain-size bias possible according to discharge conditions and sites (unfit for high water velocity) Secured site needed
Fresh flood deposit survey	Allows fine spatial analyses Time integration of the high flow event Only a few samples needed to describe spatial and year to year variations Non-expensive and easy sampling method	Sensitive to punctual contamination Sampling after floods only Suitable sampling site needed Awareness of sample representativity (caution to punctual anthropogenic sources)
River bed sediments	Easy to establish at moderate cost Large quantity of material retrieved Provides information on benthos exposure to contamination	Integrates long and undetermined period of records Very dependant on grain size No short term analysis possible

6. Conclusions and perspectives

Based on the trace element concentrations associated with a variety of solid-phase sample media, the Seine River Basin probably was among one of the most anthropogenically impacted basins in the world in the early 1980s (Meybeck et al., 2004). Subsequently, there has been a marked decline in Cd, Cu, Pb, and Zn, and a moderate decline in Hg in the mainstem Seine River, especially at the river mouth at Poses. Second order variations, especially for Cu, Pb, and Zn, appear to be related to seasonal hydrological variations and/or the drilling of a new Paris Metro line (Meteor line).

This marked temporal reduction in sediment-associated trace element levels in the Seine River Basin probably can be related to a contemporaneous decline in the trace element levels from both industrial and domestic sources as reflected in the treated sludges from the main Paris sewage treatment plant (Seine Aval).

There appears to be a major upstream–downstream (lower to higher) trace element concentration gradient in the Seine River Basin. This gradient remains substantial, despite the overall temporal reduction in numerous anthropogenic trace element sources. The most substantial increase in the gradient appears to take place in the 40 km river reach encompassing Greater Paris (between KP 210 and 170). However, specific finer-scaled spatial variations in trace element impacts are difficult to detect using just fresh floodplain deposits because the Seine River Basin drains such a large area (65,000 km^2).

Sediment-associated trace element levels in the lower Oise and Marne Rivers are lower than those found in the Seine River mainstem; further, there has been little or no substantial change in concentrations between 1994 and 2000.

The sediment associated trace element temporal trends observed at the mouth of the Seine River Basin at Poses, based only on 15 FD samples collected over a 7-year period, closely match the trends determined from bimonthly SPM samples. Hence, when resource limitations preclude the maintenance of a full SPM survey, limited FD surveys may be adequate to establish valid annual temporal trends. However, additional caution must be used when performing FD surveys because only a limited number of samples represent each hydrological year.

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