Historical perspective of heavy metals contamination (Cd, Cr, Cu, Hg, Pb, Zn) in the Seine River basin (France) following a DPSIR approach (1950-2005).

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Abstract

The Driver-Pressures-State-Impact-Response approach is applied to heavy metals in the Seine River catchment (65 000 km²; 14 million people of which 10 million are aggregated within Paris megacity; 30 % of French industrial and agricultural production). The contamination pattern at river mouth is established on the particulate material at different time scales: 1930-2000 for floodplain cores, 1980-2003 for Suspended Particulate Matter (SPM) and bed-sediments, 1994-2003 for atmospheric fallout and annual flood deposits. The Seine has been among the most contaminated catchments with maximum contents recorded at 130 mg.kg^{-1} for Cd, 24 for Hg, 558 for Pb, 1620 for Zn, 347 for Cu, 275 for Cr and 150 for Ni. Today, the average levels for Cd (1.8 mg.kg^{-1}), Hg (1.08), Pb (108), Zn (370), Cu (99), Cr (123) and Ni (31) are much lower but still in the upper 90% of the global scale distribution (Cr and Ni excepted) and well above the natural background values determined on pre-historical deposits. All metal contents have decreased at least since 1955/65, well before metal emission regulations that started in the mid-1970's and the metal monitoring in the catchment that started in the early 1980's. In the last 20 years, major criteria changes for the management of contaminated particulates (treated urban sludge, agricultural soils, dredged sediments) have occurred. In the mid 1990's, there was a complete shift in the contamination assessment scales, from sediment management and water usage criteria to the good ecological state, now required by the 2000 European Directive. When comparing excess metal outputs, associated to river SPM, to the average metal demand within the catchment from 1950 to 2000, the leakage ratios decrease exponentially from 1950 to 2000 for Cd, Cr, Cu, Pb and Zn, meanwhile, a general increase of the demand is observed: the rate of recycling and/or treatment of metals within the anthroposphere has been improved ten fold. Hg environmental trajectory is very specific: there is a marked decontamination from 1970 to 2000, but the leakage ratio remains very high (10 to 20 %) during this period. Drivers and Pressures are poorly known prior 1985; State evolution since 1935 has been reconstructed from flood plain cores analysis; Impacts were

maximum between 1950 and 1970 but remained unknown due to analytical limitation and lack of awareness. Some Responses are lagging 10 years behind monitoring and have much evolved in the past 10 years.

Key words: heavy metals; contamination; DPSIR; Seine River; Cd; Cr; Cu; Hg; Pb; Zn.

1. Introduction

The metal circulation of Cd, Cr, Hg, Pb and Zn and its drivers within a medium-sized river basin, the Seine River Catchment, France, is assessed for the past 60 years based on analyses of river particulate matter. The Seine catchment combines most types of Human pressures, except mining activities. It is studied since 1990 within our multidisciplinary PIREN-Seine programme (Meybeck et al., 1998; http://www.sisyphe.jussieu.fr/internet/piren/). Metal budget determination and studies of multiple interactions between metals and Humans are fully detailed for the current period in a companion paper (Thévenot et al., this volume). Within the PIREN-Seine, previous works on metal contamination include combined sewer overflows to the river (Estèbe et al., 1998), urban fallout (Garnaud et al., 1998, Azimi et al., 2003), contamination of aquatic biota (Carru et al., 1996, Chevreuil et al., 1995 and 1996), spatial structure of contamination (Meybeck, 1998), flood deposits contamination (Horowitz et al., 1999, Meybeck et al., 2004) and contamination trends of river particulates over the last 10 years (Grosbois et al., 2006). Other previous studies on heavy metals in the Seine River system concern the distribution of metals between dissolved and particulates phases (Idlafkih et al, 1995), the Hg contamination in the estuary (Chiffoleau et al., 1999; Cossa and Ficht, 1999; Cossa et al. 2002) and Pb isotopes tracing (Roy et al., 1999). A first synthesis on metal contamination is found in Thévenot et al. (1998). We also benefit from the regular environmental surveys (RNB, 2003) from water authorities as the Agence de l'Eau and the Regional Environment Administration (DIREN) for the river survey, and from the Syndicat Interdépartemental d'Assainissement de l'Agglomération Parisienne (SIAAP) for the sewage network of Paris conurbation termed here megacity.

Sources, evolution, fate and regulation of metal fluxes in the basin are here presented through the Driver-Pressures-State-Impacts-Responses scheme, although with a different order, as often used in river basin analysis (von Bodungen et al., 2001; Pirrone et al., 2005; Salomons et al., 2005). River catchments are also used as accounting units for material flow analysis (Baccini and

Brunner, 1991). Other accounting units as cities (Bergbäck et al. 2001; Sörme et al. 2002) and countries (Billen et al., 1983; Bertram et al., 2003) have also been used.

2. The Seine River Catchment

The Seine River catchment (65 000 km² and 497 m^3/s (1983-2003) at the Poses station upstream the estuary) is characterized by low relief and low sediment transport yield (about 10 t.km^{-2}.y^{-1} at most stations), oceanic climate with summer low flows and winter high flows. Detailed information is provided in Meybeck et al. (1998) and Grosbois et al. (2006). The Seine basin currently accounts for 25 % of French agriculture, 25 to 30% of French industrial activity and 23% of French population for only 12% of the French territory and less than 10% of its total water flow and sediment transport. By all accounts, Human pressures on the Seine basin are about twice higher than national averages like for the population density (215 people.km^{-2} for the Seine vs. 109 people.km^{-2} for the French territory).

In addition to these pressures, the basin is characterized by a highly biased population distribution: about 70% of the basin population is concentrated over the Paris megacity including Paris *intra muros* and its suburbs (9.5 Mp, 2,750 km^2), which covers only 4% of the basin area. Most of this urban population is connected to a single waste water treatment plant, the Seine-Aval WWTP, which releases its treated sewage some 70 river km downstream of Paris center (figure 1).

Figure 1

3. Evolution of the state of metal contamination of the Seine River

Two different time scales are considered here (i) the longer term (1930-2000), by floodplain core analyses sampled near the river mouth at Muids and Bouafles (M and B, figure 1) and (ii) immediate past (1983-2003) by the analysis of river suspended particulate matter (SPM) at the

river mouth station. These results are then compared with those monitored on other media e.g., deposited bed sediments and annual flood deposits.

3.1. Long-term evolution of contamination as archived in flood plain sediments (1930-2000)

The long-term evolution of metallic contamination downstream of Paris megacity is reconstructed from the chemical profiles of metals in several flood plain cores collected close to the river mouth, using ^{137}Cs and unsupported ^{210}Pb to date the different sediment horizons. These approaches are now commonly used in environmental archives of estuaries (Valette-Silver, 1993), river floodplains (Middlekoop, 1997) and reservoirs (Audry et al., 2004). Three successive oxbows (cut-off meanders) located on the right bank of the Seine River between 170 and 182 km downstream of Paris, were cored in April 2003, using a Eijkelkamp soil motorised percussion corer (93 mm internal diameter, 100 cm length). Seven sediment cores were sliced in sample increments of 2 cm. Core dating has been realised by ^{137}Cs and ^{210}Pb methods (Le Cloarec et al., this volume).

Profiles of ^{137}Cs in European river sediment cores are expected to witness four events: a first significant occurrence in 1953-54 (Cambray et al., 1989), a first peak in 1959-1960, a maximum peak in 1963-1964 and subsequently a decline as a result of the 1963 Nuclear Test Ban Treaty (e.g. Ritchie et al., 1975; Walling, 1997), then another sharp peak in 1986, corresponding to the Chernobyl accident. All ^{137}Cs profiles observed in the seven cores show the 1954 occurrence and two peaks attributed to the 1963 and 1986 maximum, which allow the core dating, assuming a constant sediment rate between the three key dates. Two cores were chosen for metal analysis, one from Bouafles, the other from Muids (B and M, figure 1), each one with a well documented sedimentation by ^{137}Cs. Samples have been analysed by Instrumental Neutron Activation Analysis (INAA), irradiated with ORPHEE reactor (Laboratoire Pierre Süe, Saclay), for determination of Zn, Co, Cr and As, and by graphite furnace AAS for determination of Pb, Cd and Cu. Samples have not yet been analysed for Hg.

The oldest records of the metal contents in these cores are the 1930's (figure 2). The results from 2 to 4 core slices from the two main cores were averaged to yield 5-year means. In order to facilitate the comparison of the relative contamination for several metals, enrichment factors (EF) of metals have then been determined as the ratio between the average contents in a 5-year period to the natural background contents as determined from pre-historical deposits (4000 BP): Cd = 0.22, Co = 10, Cr = 40, Ni = 16, Pb = 20 and Zn = 60 mg.kg^{-1} (Thévenot et al., 2002; Meybeck et al., 2004), for an average Al content of 33 000 mg.kg^{-1}. EF is very close to 1.0 for the elements which are barely affected by Human impacts as Co for the Seine and can exceed here 100 for Cd, the most sensitive element (figure 2). Since the particulate organic carbon (POC) content and Al contents in core profile –typically ± 30%- are much less variable than metal contents, POC-metal relationships probably plays a minor role in metal profiles. The EF variations are therefore essentially attributed to the changes of metal inputs to the river.

The maximum enrichment sequence is Cd (EF$_{max}$ = 140) >> Pb = Zn (EF$_{max}$ = 25) >> Cr ≈ As (EF$_{max}$ = 5 to 7) >> Co (EF$_{max}$ = 1.8). In the absence of Hg analyses, an estimate of EF for the late 1970's was based on the work of Avoine et al. (1986) in the Seine estuary for the 1976-81 period: Hg reached 7 mg.kg^{-1} for an estimated background of 0.03 mg.kg^{-1}. The enrichment factor for mercury (EF$_{max}$ = 230) comes therefore higher than for cadmium. Similar maximum EF are very rarely reported in the literature: they are generally due to mining and smelting activities as for the Meuse River (Belgium) (Rang et al.,1986) and the Coeur d'Alène Lake in Idaho (Horowitz et al., 1995) or to heavy industrial impacts particularly in estuaries, as in the Scheldt (Zwolsman and Van Eck, 1999) and the Rhine (Malle,1990).

Each element has its specific contamination pattern (figure 2). As and Co which are here among the least influenced by Human pressures present a regular decontamination since the 1930's. Zn and Pb contaminations are nearly constant from 1930 to 1965 and then decline until 2000; they are highly correlated in these 5-year profiles. Both Cr and Cd present a well marked EF maximum in 1965, it declines very sharply for Cd (EF from 140 to 10), and moderately for Cr (EF from 7 to 2). Both Cr and Cd are also correlated in these profiles.

It must be noted that for all metals and As, the contamination levels are currently 2 to 6 times lower in the 2000's than they were in the 1930's.

Figure 2

3.2. Medium-term variations (1983-2003) of SPM contamination at river mouth: influence of hydrology

Metal contamination and metal transport in the Seine basin are surveyed at the river mouth station (Poses) for which monthly analyses of river SPM are performed since 1983 (RNB, 2003; Grosbois et al., 2006) following the methodology set up by the Ifremer (Cossa et al., 1994; Idlafkih et al., 1995). Annual metal fluxes and annual average contents of SPM were calculated for each hydrological year (e.g. September 98 to August 99, referred to as 1999 mean) on the basis of the river TSS fluxes around each analysed SPM samples (Grosbois et al., 2006) and compared to annual water and suspended sediment fluxes (figure 3). All flux figures are then normalized to interannual means for the documented period (1983-2003) in order to facilitate intercomparisons. The average figures for this period are 15.7 $km^3.y^{-1}$ for river flow, 670 000 $t.y^{-1}$ for solid transport, 3.8 $t.y^{-1}$, 480 $t.y^{-1}$ and 1.7 $t.y^{-1}$ respectively for Cd, Zn and Hg fluxes. Cd, Zn and Hg are presented here. The evolution of Cu and Pb from 1983 to 1999 is also discussed in details in Grosbois et al. (2006) with the overall contamination of the whole basin.

A general and continuous decrease of metal content in river SPM is recorded between 1983 to 2003, although much less pronounced for Hg (Grosbois et al., 2006). Despite this decrease, since yearly metal fluxes (e.g. Hg, Zn and Cd) are highly correlated with SPM fluxes, four high metal flux years are associated with high flows (1987/88, 1993/94, 1994/95 and 2000/01). This hydrologic control on metal fluxes is also observed for Cu and Pb. Stocks of contaminated river sediments must be relatively high since very wet years are not associated with marked decrease of metals contents in SPM in proportions to the increase of SPM fluxes (e.g. 1993 and 1994 water years).

These metal contents in suspended particles at the river mouth station can be compared to those of the Bouafles and Muids sediment cores taken slightly upstream the Poses station, i.e. with nearly identical catchment surface and river pollution sources (figure 1). SPM metal contents for 5-

year periods are systematically 20 to 40% higher than those reported for the sediment cores for the 1985, 1990, 1995 and 2000 periods. We suggest these differences can be attributed to the well-known grain size effect (Salomons et al., 1977; Horowitz, 1991): average SPM takes into account low flows particles and minor floods which are characterized by fine particles (10 to 40 µm) whilst flood plain sediments are coarser (50-200 µm). A first analysis of the flooding occurrence at Bouafles and Muids shows that these high flood events occur less than 10 % of the time on average (< 4 weeks/year). Patterns of decontamination over the 1983-2003 period, common to SPM and cores, are very much parallel: although the floodplain sediment is not keeping record of all river particles, it can be used to reconstruct the long term evolution of the riverine contamination.

The evolution of the State of contamination is compared to the one of recent pressures which are directly well documented on the Seine catchment (section 4), then to long-term drivers and pressures which are only known at the nation's level (section 5).

Figure 3

4. Recent evolution of Human pressures: metal emissions from the anthroposphere to the Seine basin (1979-2003)

The long-term record (1930-2003) of environmental contamination of the Seine catchment has been well established with flood plain core patterns. Data on environmental pressures in the Seine catchment are much less documented. Pressure trends are here considered for two major contamination pathways, the atmospheric pathways (emissions and fallout for 1995-2004) and the urban point sources assessed by the 1979-2003 evolution of metal contents in treated sludge from Paris main sewer network that collected a population of 8 million people (now 6.5 million).

4.1. Atmospheric fallout and atmospheric emissions (1989-2004)

Atmospheric fallout has been monitored from 1994 till 2004 on total and /or dry and wet deposits at several stations in the Seine River basin (Azimi et al., 2003; Azimi, 2004). Location and sampling procedures are detailed in our companion paper (Thévenot et al., this volume). The annual measured fallout data (1994-2004) are compared to the official annual emissions (figure 4) as estimated by a specific institution financed by the French Ministry of Environment (CITEPA, 2004). Each fallout station has been attributed a proportional weight to its spatial representativeness (see details in Thévenot et al., this volume) postulating that fallout stations are representative of the overall contamination state of terrestrial mosses (Zechmeister et al., 2003), mapped from the 2000 national survey when circa 150 moss samples were taken in the Seine River basin and its immediate surrounding (Gombert et al., 2004). The spatial average of each metal fallout for the whole Seine basin is determined year per year from 4 to 6 stations with their relative weights assumed to be constant during the period of study.

Total fallout also includes dust that originates either from local sources, i.e. erosion from crop fields in the basin (52% of the Seine basin) or from external sources as far as Sahara dust as discussed in detail by Thévenot et al (this volume). The corresponding inputs of metals associated with aeolian dust would be 0.10, 23, 6.5, 0.011, 5.5 and 17 $t.y^{-1}$ for Cd, Cr, Cu, Hg, Pb and Zn respectively, to be compared with the actual total metal fallout: (average figures: 3.3, 26, 323, 0.76, 209, 1135 $t.y^{-1}$ for Cd, Cr, Cu, Hg, Pb and Zn in 2002): 80 to 98% of metal fallout are thus due to local sources, excepted for Cr.

This estimated total fallout measurement shows high values for Zn, lower values for Pb and Cu, and much lower ones for Cd, all declining since 1995, particularly for Cd, Pb and Zn, less for Cu (figure 4). Fallout decreases could be explained by emission regulations: (i) decrease then ban (year 2000) of leaded gasoline, (ii) reduction of industrial emissions in the 1990's (for example from urban waste incinerators) due to better fume trapping, and (iii) gradual shift from coal burning to nuclear power in the energy sector in the 1970's.

The figures of metal emissions to the atmosphere are estimated by CITEPA from a combination of industrial census, types and sizes of emitters, technical means of metal emission controls. CITEPA emission figures of metals to the atmosphere also decreased between 1989 and 2003 (0.034 to 0.02, 9.3 to 0.43 and 3.0 to 2.0 $kg.km^2.y^{-1}$ for Cd, Pb and Zn respectively) and remain constant for Cu (0.45 $kg.km^2.y^{-1}$). However these estimated emission values are an order of magnitude lower than the atmospheric fallout data (figure 4). This discrepancy is either due to the fact that some major sources of emission are not taken into account or that the highest part of the measured fallout is due to the recirculation of local dusts coming from nearby soils and from former industrial activities and uses (e.g. dust deposition on roofs or from unidentified stocks).

Figure 4

4.2. Evolution of composition of urban waste waters and sewage sludge (1978-2003)

Paris megacity covers an area of 2,750 km^2 with a population of 9.5 million inhabitants. The main Seine Aval wastewater treatment plant (SA-WWTP), is located at Achères some 65 river km downstream of Paris (figure 1) and operated by a specific local authority, the SIAAP. The mean flow of raw sewage was about 25 $m^3.s^{-1}$ during dry weather for the period 1978-2003 and is now 22 $m^3.s^{-1}$ due to new WWTP. The evolution of the composition of sewage received at the SA-WWTP is here estimated by the analysis of treated sewage sludge, on a monthly basis, between 1978 - 1988 and weekly since 1988. The SA-WWTP sewers combine multiple metal sources from atmospheric fallout, roof runoff, street runoff and domestic sewage, connected sewage from industries and from other local sources like hospitals (see Thévenot et al., this volume).

The particulate metals in treated sludge, heated at 200°C during the stabilisation phase, can also be used as a proxy for the contents of particulates released to the Seine River: heated sludge metals content equals 2 times those of fresh treated sewage (dry weight), due to the occurrence of organic matter in treated sewage (about 70 %) and its elimination during sludge treatment (50 %

elimination for dry weight). The load of suspended matter released in the Seine River with treated sewage ranged between 35 000 to 50 000 t.y^{-1} (dry and wet weather combined) until the late 1990's and is now reduced to 25 000 t.y^{-1}. Therefore the decreasing trend in metal contents in sludge (up to 10 fold, figure 5) mimics as well the trend of metal inputs from SA-WWTP to the river. However, the total inputs from SA-WWTP should also take into account the dissolved metals released after treatment (Buzier et al., in press). For Cd, Cu, Pb, Hg, Ni and Zn, an exponential decontamination of Paris sewage is observed, being represented by a linear trend when using a logarithmic scale for contents. The decontamination rate is maximum for Ni and Cd, medium for Pb, Zn and Cu and minimum for Hg. For Ni and Cd, the decontamination rate over the past 25 years is reaching an order of magnitude (see Grosbois et al, 2006, for details).

Figure 5

4.3. General decontamination of the Seine River basin (1974-2003)

The overall decontamination trend of the Seine basin is presented in figure 6 for the past 30 years for Cd, Cu, Hg, Pb, Ni and Zn from various types of river particulates. The first analysis of metal in the Seine catchment was published by Leroy (1972), it concerned total mercury concentration on unfiltered waters, then Chesterikoff et al. (1973) carried out analyses of Lower Seine particulate mercury. In 1974, Cd, Hg, Pb and Zn were monitored by the Agence de l'Eau Seine Normandie on bed sediments of the Oise River suspected to be highly polluted (Lesouef et al., 1979). Bellamie et al. (1980) also reported metals levels in the Seine River network sediments.

Other surveys on the Oise were carried out by Chesterikoff et al. (1973) on deposited sediments and by Dessery (1982) on the fine silt deposited in the storage tank of Mery-sur-Oise drinking water plant. The Oise is a major tributary of the Seine River accounting for 25 % of its drainage area and water discharge. The lower Oise is also under high industrial pressures as for the lower Seine. As a result, the Lower Seine and the Oise displayed similar contamination levels and evolved in parallel over the past ten years (Grosbois et al., 2006). These early Oise surveys are therefore used in figure 6 as proxies for the general contamination of the lower Seine; they also

match the 1976- 1981 estuarine survey made by Avoine et al. (1986). These three data sets represent the highest metal levels monitored on the Seine River/Estuary particulates.

The annual evolution of metal contamination at the river mouth station (Poses) for the 1981-2003 period is presented in figure 6 for 3 types of samples: (i) river suspended matter (SPM) from the regular national environmental survey (RNB, 2003), (ii) annual flood deposits (FD) on river banks (Horowitz et al. 1999, Grosbois et al. 2006) and deposited bed sediments (DS) (RNB, 2003). The background levels of river particulates in the Seine basin (BRG) are also reported and will be discussed further.

The decontamination trend of the Seine River basin since the late 1970's is effective for all the surveyed metals for most documented media. The decontamination rate is faster for Cd and Ni, than for Pb, Cu and Zn, and decontamination is the least effective for Hg. The mean contents in estuarine particulates (1976-1981) are generally coherent with the river SPM and bed sediment annual surveys that started in 1981 and 1983. For these metals, the decontamination is continuous and parallel to the decontamination observed previously in treated sewage sludge (see figure 5).

Pb and Hg patterns in this annual data set should be discussed: during the 1981-2003 period, the maximum documented levels for Pb and Hg in river SPM are observed in 1990-91. At that period, Pb levels in river SPM are very closed to levels measured in treated sludge, around 500 µg.g.$^{-1}$, i.e. 25 times higher than natural background. However the Pb decrease in bed sediments (DS) is continuous. Hg levels in SPM in 1993 could be due to an analytical artefact (Grosbois et al. 2006). The metal contents in annual bed sediments samples are much more variable than average SPM contents based on 12 to 24 samples per year and annual flood deposits samples are also less variable than bed sediments. As previously mentioned, metal levels in SPM (discharge-weighted averages) are generally higher, by a factor 1.2 to 1.4, than those of flood deposits, which are closer to those of bed sediments (e.g. Cu, Ni, Zn) suggesting a grain-size influence. Annual flood deposits, floodplain core particulates and river bed sediments have much similar metal contents.

Although there is a general agreement between these surveys and the environmental archives derived from core analysis some discrepancies are noted: the Zn enrichment factor in core

samples present a slight increase for the 1993-97 period (marked 1995 in figure 2), which is not observed in figure 6 trends.

When comparing figures 5 and 6, the sewage sludge and river particulates contamination trends of metal are parallel. This suggests (i) that the Seine-Aval plant is a major contributor of particulate metals to the Seine and that this contribution is made with a constant mixing proportion (ii) and/or that other metal sources are declining at the same rates as those observed in the Seine-Aval sludge. Despite these trends, the 2000's contamination levels are still very high for Hg, high for Cd, medium for Cu, Pb and Zn. For Ni, the contamination is now close to zero, since metal contents in bed sediments, flood deposits and river SPM at Poses station are now very close to the estimated background values (Thévenot et al., this volume and discussed further). For Co, the contamination has always been very limited.

The State of metal contamination in the Seine River catchment has here been based on two approaches: (i) the comparison of recent surveys, 20 to 30 years, for various media (river SPM, river sediment and flood deposits and (ii) the use of river archives in flood plain sediments. This second approach has the maximum cost/benefit ratio: a dozen analyses of carefully selected samples can provide an overall picture of the contamination levels over 60 years, thus resulting in different contamination trajectories for each metal. These are explained by the retrospective analyses of Pressures and their Drivers over the 1950-2000 period in the next section.

Figure 6

5. Long-term evolution of metal uses and transformation (1950-2000) in France and in the Seine catchment

The decrease of the metal contamination in the Seine river basin is compared to the evolution of the metal uses, established for the past 50 years during which important variations of uses, transformations and metal recycling have occurred.

From 1950 to 2000, the population of the Seine basin increased from 9.5 to 14 Million people (at the Poses station) indicating greater urban pressure. No specific data concerning metal supply and

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consumption are directly available for the Seine Basin: only national statistics are available from National Statistics and survey bodies (INSEE, 1948-2003; FEDEM, 2003; ADEME, 2004). It will therefore be assumed in this section that the Seine catchment captures a constant proportion of the national metal uses, assumed 30 %, to reflect that this catchment is slightly more industrialized than national average. In addition to these estimated metal uses, we carried out a specific study of the overall industrial activity, from 1940 to 2000, within the Seine River catchment.

5.1. General de-industrialisation in the Seine River catchment (1940-2000): the Pb industries example.

The overall trend of industrial use of metals is estimated by the rate of de-industrialization in the Ile-de-France region around Paris, which represents about 2/3 of the total industrial activity in the catchment upstream of the Poses station. The Ile-de-France region lost about half of industrial jobs during the past 40 years, from 1.4 million in 1962 to 666,000 in 1998. One out of four inhabitants in Ile-de-France worked in industry during the 1980's as compared to one out of seven in 1998 (Cadenel and Calzada, 2000). This de-industrialisation is confirmed by the decrease of number of Pb processing industries (refining, foundries, battery manufactures, Pb-oxides, Pb-glass), for the whole basin (figure 7). The number of Pb industries strongly decreased in the last 60 years but this has been accelerated in the 1990's. This trend is mostly marked by the six-fold decrease of industries in Paris *intra muros* and in its nearby suburbs between 1940 and 2000, while the industries number remained nearly stable in the rest of the basin during that period. This trend is compared in the next section with the overall French statistics for metal uses.

Figure 7

5.2. Metal demand variations in France (1950-2000)

The reconstruction of past metal uses for the Seine catchment cannot be directly achieved. Our estimates are the best available figures for the whole French territory from INSEE (1948-2002) and

FEDEM (2003) (figure 8). All total metal demand at the national scale exhibits a continuous growth from 1950 to 1995, excepted for Hg. During this period, the Cd demand has been multiplied by eight, Zn and Pb by three and Cu by four (figure 8). Hg demand peaked in the early sixties; the French Hg demand has dropped by more than one order on magnitude since 1960 (from about 450 t/y to 13 t/y). The recent decrease in Cd demand is also very sharp since 1995 (- 40 %, figure 8). More recent detailed National statistics of metal demand per economic sectors are derived from multiple data sources (figures 9 and 10).

- The detailed account of Cd (figure 9) shows that the overall consumption remains almost constant at 1,100 t from 1975 to the 1990's but, during this period, the consumption pattern shifted from the traditional market area of Cd pigments (stabilizers and coating/plating (about 80% of uses in the 1960's), to the rapidly growing field of Ni-Cd batteries (70 % in 1995). In 1996 the total Cd use reached 1860 t then dropped sharply after 2000. This is due to a decrease of the unitary weights of the Ni-Cd batteries and to technology transfer to Li-ion batteries (Ademe, 2004). Cd in traces associated with other materials (phosphate fertilizers or Zn metal roofs) is not considered in such accounts.

- The dominant uses of Pb has also been very variable (figure 10). From 1950 to the early 70's, the dominant metal uses are found in construction and in cables and, in second position, Pb in batteries. Pb is still used as metal sheets in building, as metal grains in ammunitions and in solders. But, since 1970, it is often replaced by other materials such as PVC or polyethylene, for example for the shielding of cables for electricity and telephone (more than 30% of the Pb uses in the 1950s). Pb oxides pigments important in the past are now mainly used in radiation protection glasses (television, computer monitors) and crystal glass. As for Cd, Pb as traces in other metal uses (e.g. Zn) is not accounted in these figures.

- Cr is now essentially (71% in 1996) used as ferrochrome for stainless steel, 14% for refractory purposes, and 15% as chemical products (Vignes et al. 1998). Only few statistics are available for this metal. The use of Cr in tanneries, once a major source of Cr wastes, is now nearly zero.

- The consumption of Cu increased from 100,000 t in the 1950's to 574,000 t in 2000. Cu is mainly used as metal for electric wires (40% in 2002) and in pipes (30%) (FEDEM, 2003). The comprehensive Cu cycle recently published for several European countries concluded to a current stock increase of about 3 kg Cu per capita per year for France, which is less than in Austria (11 kg), Germany (8 kg), Scandinavia, United Kingdom and Greece (5 kg) (Bertram et al., 2003).

- Hg uses are multiple (Lestel, 2006). Between 1960 and 1980 France consumed around 300 to 400 $t.y^{-1}$ of Hg (Minerais et métaux, 1935-1986), mainly for the chlor-alkali industry in the 2000's: 50% of the French chlorine is still being produced by using the Hg-process, in seven plants, none of them being now situated in the Seine basin. In the 1970's and 1980's several major industrial sources of Hg, as the PUK industry at Villers-Saint-Paul, were identified on the lower Oise (figure 1). This activity resulted in an extreme contamination with Hg contents up to 26 $mg.kg^{-1}$ in Oise SPM (Chesterikoff et al., 1973) and in bed sediments up to 20 $mg.kg^{-1}$ in 1974 (Lesouef et al., 1979) which has been somewhat understated at this period. The Hg-demand for batteries was much lower and has strongly decreased from 18.3 $t.y^{-1}$ in 1990 to 0.34 $t.y^{-1}$ in 1999. France is still using Hg in dentistry (35 $t.y^{-1}$). Hg stock in dental amalgam of the population has been estimated at 240 t (Picot and Proust 1998).

- The annual Zn demand is now around 250-300 10^3 $t.y^{-1}$. The greatest use (48% in 2003, FEDEM) is for iron coating and steel products (galvanizing). There is also a strong demand for a vast range of die-cast products (22%). Zn is also used as brass (12%) and as a chemical product (ZnO, 7%). These traditional applications are stable since 1950 (Gadeau, 1959; Duchaussoy, 1971; Vignes et al, 1998).

The combustion of fossil fuels should be taken into account in the leakage of heavy metals into the atmosphere and from there to soils and aquatic systems, especially for Hg. This source of metals has been downsized by nearly four fold between 1958 and 1996 since the coal consumption in France decreased from 80 $Mt.y^{-1}$ in 1958 to 24 $Mt.y^{-1}$ in 1996 (Vignes et al, 1998).

The EU directives and their application in French regulations have probably been the major drivers of the reduction of metal leaks into the environment since the 1970's as the Directive 76/769/EEC

(now 94/27EEC) on Ni release, the Hg use limitations (total ban of Hg thermometers in 1999), the control of Pb batteries and accumulators (Directive 91/157EEC) etc.

Figure 8

Figure 9

Figure 10

It is very difficult to assess the general Drivers of metal contamination over the time scale (>> 50 years) that is required in a medium/large catchment as the Seine River. (i) General statistics on overall metal uses are not available at the river catchment scale. (ii) Various metals uses should be determined for each metal. (iii) The chemical speciation of wastes and leaks to the environment should be known for each type of use (at least a breakdown of gaseous, soluble and particulate forms). These are some of the key questions that environmental historians are now facing. The reconstruction of past economic and ecological impacts is even more difficult.

6. Past, present and future impacts of metal contamination in the Seine River system (1930-2015)

Within the D.P.S.I.R. scheme of analysis of river systems, the impacts are related to economic activities, Human health and to ecological impacts (von Bodungen et al., 2001). If the contamination of the Seine catchment by heavy metals since the 1930's could be reconstructed from the floodplain cores analyses (see previous sections), impacts have been barely assessed until the late 1970's. In 1979, a regular network of coastal waters quality monitoring (RNO) was established at a national level by IFREMER. It includes an outer Seine estuary station on which mussels (*mytilus edulis*) have been regularly analysed (Claisse, 1989, Cossa and Ficht, 1999; Chiffoleau et al, 1999). In the mid 1980's, the drinking water intakes in the River Seine network were also analysed and archived for total heavy metals by the Ministry of Health; however, this

data set has a restricted access unlike the RNO survey. We are therefore simulating the extreme water quality for total metals on the basis of reconstructed metal contents in river particulates as recorded in cores since 1930. Both mussels metal data and total metals in water intakes are compared to present-day standards. The legacy of past metal contamination is also still impacting the present Seine River system and its management.

6.1. Estuarine mussels contamination (1979-2004)

Total metals in mussels in mg.kg^{-1} dry weight have been monitored in Villerville (figure 1) since 1979 with a frequency of 2.5 analyses per year; metals are reported (RNO, 2005). The Cd and Pb criteria for mussels consumption are currently 5 and 7.5 mg.kg^{-1}, respectively. These criteria values have been exceeded in 14 % and 3 % of samples for Cd and Pb respectively from 1979 to 2004 but no exceedance has been observed for Cu, Zn or Hg. This relative evolution of the mussel contamination is normalized (figure 11) to another Normandy station of the same network, Grandcamp, which is among the 10 % least contaminated stations of France (average metal contents in mussels equal to: Cd = 0.4, Cu = 6, Hg = 0.05, Pb = 0.9 and Zn = 60 mg.kg^{-1} dry weight) (Claisse, 1989, RNO, 2005).

Cd contamination is the greatest. It first decreased between 1979 and 1984. Then, a large maximum is observed between 1985 and 1995 and the nowadays relative Cd content is only twice the reference level. Hg decontamination is effective from 1979 to 1988, then remained stable at 3 fold the reference level. Pb contamination has been variable with relative maximum contamination in 1982, 1990 and 2000. Zn and Cu contaminations are very moderate.

The River Seine inputs are not the only source of contamination at Villerville. Direct sources from tributaries to the estuary like the Eure River (Meybeck et al, 2004) or from Le Havre and Rouen cities and associated industries are important as well (Chiffoleau et al, 1999, Cossa and Ficht, 1999, Cossa et al, 2002). The 1985-1995 maximum of Cd contamination is attributed by these authors to wastes from the phosphor-gypsum industry (phosphate ore is rich in Cd) at Le Havre, which ceased its activities in the mid 1990's. The 1979-1985 and 1995-2002 decline of mussel Cd

is related to the decrease of Cd in river particulates during this period, similar to the general Hg decrease.

The mussel watch site at Villerville is probably not located at the place of maximum estuarine contamination, which is supposedly to be closer to Le Havre, on the estuary right bank (Cossa and Ficht, 1999; Chiffoleau et al., 1999). But Le Havre station was not selected in this comparison with the Seine River inputs because of direct metal release from estuarine industries and harbour activities.

Others surveys of metals contents in river aquatic biota, e.g. fishes, are limited. In the September 1972 profiles of Hg contamination in the Lower Seine and estuary (Chesterikoff et al., 1973) the measured Hg contents in various freshwater fishes of different ages ranged between 0.16 to 0.5 mg.kg^{-1}, i.e. reaching the 1972 threshold for Human consumption (0.5 mg.kg^{-1}) set by the Ministry of Health.

Figure 11

6.2. Reconstructed total metals concentrations in drinking water intakes (1930-2000)

Before the development of Atomic Absorption methods in the 1970's, metal analysis was very tedious, little reliable due to sampling contamination, and detection limits were very high. This explains the total absence of data on metals in the Seine catchment before this period (P. Leroy, personal communication). Since the mid 1980's, the record of total metal in unfiltered river waters for water intakes of Paris megacity drinking water plants is centralized by the Ministry of Health at a local level (Région Ile-de-France). Yet, due to confidentiality, these data have a restricted access.

A tentative reconstruction of total metals contents in unfiltered waters has therefore been made by multiplying the 5-year average excess contents of metals in floodplain cores by a correction factor of 1.4 to take into account the finer fraction in suspended sediments (see section 3). These excess contents are then associated with different levels of suspended matter concentration: 20 mg/L, 85

mg/L and 150 mg/L, which respectively correspond to the percentiles 50 %, 95 % and 97 % of SPM in the Seine River downstream of Paris and in the Oise River (Meybeck et al., 1998). For instance, the reconstructed average total metals for the highest SPM levels encountered at flood stage, i.e. 150 mg/L, reached 90 µg/L for Pb, 70 for Cu, 250 for Zn, 6.4 for Cd and exceeded 1.0 µg/L for Hg in the 1975-80 period (figure 12 A). This Hg value can be compared to the direct analysis of total Hg downstream of Paris, which reached 1.0 µg/L in 1971 for 60 mg/L of SPM and 0.4 to 0.75 µg/L for only 25 mg/L of SPM in 1972 (Chesterikoff et al., 1973; Leroy, 1972). Although we have not yet the level of Hg contamination prior 1971, it is very likely that it was also similar to the 1971 level when considering the evolution of Hg uses during this period. If the Oise levels for Hg in sediments for the early 1970's are converted into total Hg on unfiltered floodwaters, they correspond to a level of 3 µg/L for major floods (SPM > 150 mg/L). The addition of dissolved metals at flood stage would increase the estimated total metals levels by 5 to 20% according to the dissolved/particulate metal ratio during floods (Cossa et al., 1994, Thévenot at al., this volume).

The French criteria for total metals in raw water prior to the treatment for drinking water (Min. Health, R 1321. 1-68) are currently: 5 µg/L for Cd, 50 for Cr, 1.0 for Hg, 50 for Pb and 5000 for Zn. When the simulated total metal concentrations during floods (SPM = 150 mg/L) are normalized to these present criteria (standard exceedance SE, figure 12 B), exceedance levels were reached at least 9 days per year on the average before 1965 for Pb, Zn, Cu and from 1955 to 1970 for Cd and Cr and probably for Hg prior to 1970. As the metal contents in floodplain cores are actually 5 year averaged values, reconstructed metal concentrations for individual floods and at shorter periods may have much more exceeded our current drinking water criteria: total metal concentrations at 5.2 µg/L for Cd, 1.0 for Hg, 20 for Pb have been likely in the past when considering maximum recorded levels (see table 5).

In the 1970's, the drinking water companies have been probably aware of such water quality issues for Hg in the Oise River and in the Central Seine (Leroy, 1972). Therefore, they have constructed and used water storage basins at Orly (1972) on the Seine and at Mery-sur-Oise (1980) to settle the contaminated river particles during few days and decrease the total contents in metals and in persistent organic pollutants.

6.3.   The present and future legacy of the Seine River contamination

The past contamination of the river sediments is still impacting the current ecological state, river and agriculture uses. Yet this question remained poorly addressed until today.

The Seine River Port Authorities (SNS and VNF) are presently facing major problems concerning the disposal of dredged sediments from the river, from estuaries and also from river harbours, as the Port de Gennevilliers, which are several times more contaminated than river sediments. Most of these metals were generated from past Human activities, sometimes several decades ago. These sediments, once dredged, are now qualified as 'wastes' according to the current French and EU regulations.

The ultimate depository of these contaminated sediment is the outer estuary and the Baie de Seine, in the English Channel. According to our estimates, from 1935 to 2000, the Seine River proper (i.e. without the direct estuarine tributaries, the Risle and the Eure, both highly contaminated for Pb and other metals) has carried a total excess amount of 18 000 t for Pb, 875 t for Cd, 12 500 t for Cu, 8 900 t for Cr, 50 000 t for Zn and 1 000 t for As (Horowitz et al 1999, Grosbois et al. 2006). The excess Hg load between 1975 and 2000 is estimated to 60 t. If the industrial period prior 1935 is considered and if the direct inputs to the estuary from the Risle and Eure Rivers and from Rouen and Le Havre cities are taken into account, these values should be doubled. The finest contaminated sediments are now probably dispersed into the whole English Channel, which is a highly dynamic marine system, and, from there, to the North Sea.

The Lower Seine floodplain sediments show contamination levels that exceed the current criteria for agricultural soils in the top 30 cm (see further on table 2). The ancient sites of Paris sewage land disposal in the vicinity of the Seine-Aval WWTP, which have been fertilised by the city wastes for one hundred years before any metal control was done (< 1970's), are also now subject to food cropping restrictions.

Metal contamination Impacts are still very difficult to establish. There is no "mussel watch" for freshwater species, nor a fish contamination programme, as established since 1979 for the coastal zone. Impacts on Human Health are also poorly documented. When addressed, e.g. on drinking water resources, they may be of restricted access. Retrospective analyses suggest that maximum impacts had occurred in the 1950's and 60's at a time of very limited analytical capacity and negligible environmental concern. The contamination archives in flood plain sediments of the Lower Seine suggest a possibility of present metal contamination of related crops. The sediment contamination legacy results in increasing cost for the maintenance of navigated reaches in the next decade, and perhaps further. The societal Response to metal contamination gradually developed since the late 1970's.

7. Societal responses to metal contamination (1950-2005)

Two administrations are specially devoted to the Seine River protection (i) the Seine River Basin Agency (Agence Financière de l'Eau Seine Normandie, AFBSN, then named Agence de l'Eau Seine Normandie, AESN), established in 1964 and operational a few years later, and (ii) the river basin administration depending from the Ministry of Environment (Mission Déléguée de Bassin Seine Normandie, then DIREN de bassin), established a few years later. They jointly published a synthesis of water quality issues in the 1970's (MD-BSN/AFBSN, 1976) in which the metal contamination of the Seine River particulates was not at all addressed. The responses are therefore relatively recent. They are here studied through (i) collection and treatment of waste waters from industries and from Paris megacity, (ii) through the development of environmental surveys and research, (iii) the evolution of regulations.

7.1. Improvement of industrial processes (1952-2002): the Pb example

Many industrial sectors using metals have been very efficient in the last 30 years to recycle their metal-containing wastes, to change metal-related processes etc. As a result, the metal emissions into the environment have been much reduced. Although there is very little statistical information available over this period, an example of waste treatment is here given for Pb industries.

A corpus of 161 manufactures present on the Seine River catchment and concerned by Pb handling has been established. They were active between 1970 and 2003, either in Pb processing such as batteries manufacturing, or as by-product discharged during the process (for example plating). The cumulative curves of newly installed equipment in this corpus (figure 13, curve C) show that the equipment number increased 4-fold in the 1970's then 2.5-fold in the following 20 years. In addition to this quantitative trend, treatments were upgraded in the 1990s by combining several types such as neutralisation, settling and biological treatments. This evolution shows the rapid changes between 1968 and 1978 and then, a steady development of equipment until today.

In the mid-1970's, the River Basin Agency (AESN) gradually launched an important preventive action on industrial pollution abatement (C. Lassus, pers. com.), particularly targeted to metal plating industries and automobile industries, as the edition of Good Practice manuals and lectures in technical schools.

Figure 13

7.2. Collection and treatment of urban sewage (1950-2000)

The history of the sanitation of Paris megacity is well documented from the archives of the SIAAP. The sewage collection, gradually developed over a century (Barles, 2005), is now completed for more than 90 % of the population since the early 1980's. About 1.1 10^6 $m^3.d^{-1}$ of urban sewage are currently collected (figure 13, curve A). Meanwhile, a great number of industries, particularly the small ones, have been connected to the urban sewage network.

There has been a marked lag between the collection rate and the treatment rate: in the 1950's and early 60's, about 85 % of collected sewage was not treated, with special mention to particulate matters that carry a great share of metals in sewage waters. This discrepancy has been reduced to 15 % between 1966 and 1978 due to the development of the SA-WWTP (Achères II, III and IV phases, figure 13, curve B). With the construction of two other WWTP (Valenton I_A in 1987 and I_B, and Colombes in 1998), followed by the reduction of untreated overflows during storms (figure 13, VIII), the proportion of untreated waters is currently reduced to a few percents on an annual basis. Sewer types must also be considered. Originally the Parisian sewers network was conceived some 100 years ago as a combined network accepting street runoff during rainstorm. It was eventually developed, after World War II, as a separate network in suburban Paris. Until 1960, the annual overflow of the three major combined sewers (CSOs) was about 350 $hm^3.y^{-1}$ into the Seine River without any treatment during rainstorm, then gradually reduced to 250 in the 70's, 150 in the 80's, 50 in the 90's and less than 10 since 2000. Storm water retention ponds were also constructed for a total volume of 454,000 m^3 in 2005. Therefore, the contamination pulse resulting from the storm weather overflow is greatly decreased and a greater share of storm sewer waters is treated. In other periurban sites, such settling ponds have not yet been dredged since their construction in the 1970's, and the management of these contaminated sediments remains open. In addition, the Total Suspended Solids retention of urban waste waters has been improved: in 2001, clariflocculation has been installed in the SA-WWTP, improving the treatment of sewage during wet weather. The overall total metal abatement in Paris sewage treatment works has been gradually improved in the last decades and is currently the following: 76 % for Cu, 70 % for Zn and 49 % for Pb (see discussion in Thévenot et al., this volume).

7.3. Evolution of environmental monitoring and of reference contents for metal contamination in the Seine basin particulates (1971-2005)

The development of long-term environmental surveys for the heavy metal contamination in various media like water and particulate matter is a good indicator of the concern of National and River

Basin authorities (Chapman, 1996). Since 1979, the metal monitoring has been gradually developed on various media, from atmospheric fallout to estuarine mussels (figure 14 A). Groundwaters surveys are not addressed here. So far these different types of surveys, that essentially concern the particulate matter, were interpreted separately.

In 1971, few total metals started to be monitored at the main water intakes of Paris. "Total metals" on unfiltered waters are still analysed at the request of the Ministry of Health since they are used as water quality criteria for the drinking water industry, as established in 1989 and revised in 2001. Yet their use in metal contamination assessment is very limited since they are very sensitive to hydrologic condition and SPM levels (Horowitz, 1991; Cossa et al., 1994, Idlafkih et al., 1995, Chapman, 1996). Since 1981, the metal contents are analysed annually at selected stations on bed sediments within the National River Basin Network (RNB, 2003), and river SPM is analysed since 1983 at the river mouth, which allows direct flux estimates (see figures 3 and 6).

In the Seine catchment, most metal surveys are carried out on particulate media (river SPM, bed sediments, flood deposits, soils and sludge) yet their interpretation depends on the reference levels chosen for the Seine catchment particulates. These references levels have greatly evolved since the first estimated "normal contents" published in 1979 by three administrations in charge of the Seine River surveillance (Lesouef et al., 1979). Since then these reference values have been decreased at three occasions (table 1), by the River Basin Agency AFBSN-AESN (1979, 1988), and within the PIREN-Seine scientific programme: by a factor 25 for Hg, 10 for Cd, 2 to 3 for Zn and Pb (figure 6).

These reference contents can also be compared to those developed by the Agence de l'Eau Artois Picardie (AEAP, table 1) for the Artois-Picardie basin, adjacent to the Seine and characterized by very similar sedimentary rocks from the Paris Basin (chalk and limestone). Hg and Cd "reference levels" set up by the AEAP in this basin are also much higher than those based on prehistorical deposits and on present day forested streams (Avoine et al., 1986; Meybeck et al., 2004). As the content of particulate matter in clay-sized particles must also be considered, analyses of Al or grain-size determinations should be provided with the reference level (see table 1).

Finally it must be noted that the official reference level (blue-green limit of colour-coded quality) currently used in France was established by the national SEQ-Eau system versions 1 and 2 as one tenth of the green-yellow limit at which an effect is found on the biota (SEQ-Eau, 2003) (see further on table 3). These theoretical blue-green levels can be extremely low and some of them (Cd, Cu, Hg and Zn) are actually below the natural contents found in most bedrock types, excepted pure quartz sands. If these blue-green levels are considered, the 5000 years old sediment samples collected on the Seine basin (Avoine et al., 1986; Meybeck et al., 2004) would not be qualified as pristine for Cd, Cu by the SEQ-Eau but as already impacted by Human activities (green colour code)! Contamination scales are discussed further (section 8.2). The SEQ-Eau reference values for particulate metals should now be revised and take into account the influence of lithology on geochemical background (Horowitz, 1991).

Table 1

7.4. Evolution of regulations related to particulate metal management (1970-2004)

The anthroposphere generates important modifications of particulates fluxes in river systems (Meybeck and Vörösmarty, 2005) as recycling treated urban sludge, dredging river channels and settling in reservoirs. This circulation of solids within the anthroposphere is sometimes underscored in metal contamination assessment. It is now regulated by multiple criteria and guidelines, which reflect the interactions between societies and environmental issues.

Urban sludge

The sewer sludge reuse in agriculture was first regulated in 1985 by national AFNOR reference criteria on "the use of urban sludge as fertilisers and soil conditioners" (French NFU 44-041; AFNOR, 1985). In the late 1980s, France has adopted the Council Directive 86/278/EEC for the sewage sludge used in agriculture. As the initial transposition of this directive was considered insufficient by the Commission in 1995, it was completed by the adoption of the Enforcement Order of 8 January 1998, which made the AFNOR NFU 44-041 standard compulsory for sludge

reuse in France. Between 1970 and 2004, the acceptance criteria have therefore been divided at least by two for the majority of the metals (table 2). Since March 2004, there is an additional criterion for the 'compost material' (French NFU 44-095 standard; AFNOR, 2002) on "organic soil improvers such as composts, containing essential substances to agriculture, standing from water treatment". Compost products made from sewage sludge (e.g. combining sludge and green wastes) will therefore have to meet the NFU 44-095 standard. As an example for Cd: in 1998, the sludge standard decreased from 40 to 20 mg.kg^{-1}, in December 2000 to 15 mg.kg^{-1} and in December 2003 to 10 mg.kg^{-1}. Compost material is now at 3 mg.kg^{-1}.

When comparing the sludge criteria evolution (table 2) with the decontamination trend of Paris megacity sludge produced by the SIAAP (figure 5), it appears that the recommended criteria levels for agricultural reuse have always been met since 1985, when they were established for Cr, Cu, Pb and Hg. For Cd, the recommended criteria exceeded by a factor two during two years and it was very close for Pb and Zn in the mid 1980's. Then, the SIAAP managed to have a wider margin of sludge use for all metals until January 1998 when the regulatory standard was established at levels very close to the sludge content for Cu, Zn and Hg. For Cd the general decrease of the sludge contamination is nearly parallel to the regulation (figure 5) so that the SIAAP had never faced difficult issues related to its enormous amount of produced sludge (now 61,000 t.y^{-1} of heated sludge).

Dredged sediments in the river network

The Seine River is the most navigated river of France and it is an obligation of the Port Authorities (SNS) to maintain the river bed for navigation. The quantity of dredged sediment in the Seine basin ranged between 60 000 and 180 000 t/year for the last fifteen years, i.e. around 15 % of the long-term suspended sediment transport at Poses.

Until the late 1990s, French regulations were not clear about the management of contaminated dredged materials extracted from rivers, unlike for marine and estuarine sediments. In 1995, French Inland Navigation Services (VNF) established its own directive, which was used as a decision tool for dredged sediment management. Two threshold metal contents (VNF1 and VNF2)

were set leading to three classes (table 2): (i) [Me]<VNF1 for clean sediments that can be used for any purposes, i.e. could be released in the river without restriction, (ii) VNF1 ≤ [Me] ≤ VNF2 for medium contaminated sediments that can be used for any purpose except land disposal for crop culture and (iii) [Me]>VNF2 for highly contaminated sediments that need to be treated before any other use or alternatively stored in landfills designed for hazardous waste. It must be noted that the VNF recommendation for "clean sediment" (VNF1) is based on the criteria for an agricultural use of soils (table 2).

More recently, in 2003, a new directive has been established by VNF according to the European regulation (2003/33/EC Council Decision of 19 December 2002): (i) a risk study is now compulsory before any dredging project; (ii) the sediment analysis should be coupled to a toxicity risk assessment. Thus, an ecotoxicological approach is now applied, based on the Mean Probable Effect Concentration Quotient.

Dredged sediments in the coastal zone

The coastal sediments annually dredged in France from estuaries and harbours exceed one million tons per year (dry weight). They are managed by a different administration than for river sediment, which has to consider the international conventions on European Regional Seas pollution, OSPAR and Barcelona (Alzieu, 1999). The two-level criteria (L1 and L2, table 2) proposed in 1996 by France to the Oslo-Paris convention (OSPAR) are generally different and more restrictive than the VNF ones for Cd, Hg and Zn (table 2).

Table 2

Standards, guidelines and criteria for metal contamination management are produced at multiple levels: River catchment, National, European and Regional Seas treaties. They also concern several ministries, Environment, Health, Industry, Transport, Agriculture, Sea, and few institutional and/or private stakeholders, as the greater Paris waste management authority (SIAAP) and the drinking water industries, each having their own logics. The management targets, are also very

much limited by the evolution of technical and scientific knowledge as exemplified by the marked decrease of metal reference contents in sediments over the last 30 years and the occurrence of non-operational blue-green metal threshold in the French SEQ-Eau scale. So far, this kind of Responses is mostly triggered by the stepwise application of E. U. environmental regulations rather than based on environmental quality targets.

8. Discussion

The application of the Driver-Pressure-State-Impact-Response to the metal contamination, now advocated by the European Environment Agency, is actually very complex and mobilizes information and data from multiple sources, located in a dozen of administrations and authorities. Such integration is not yet achieved. Our attempt to apply D.P.S.I.R. to the Seine catchment on a long term scale shows that (i) the Lower Seine has been one of the world's most contaminated rivers, (ii) information on contamination state was not available before 1970, (iii) contamination state has markedly been improved from 1950 to 2000 while the demand for metals in France was steadily growing, Hg excepted, (vi) information on drivers and pressures was not collected prior to 1980, these can only be reconstructed on the basis of careful environmental history analysis. The Responses are relatively recent and they followed the development of metal analyses in environmental samples and of metal contamination awareness in the late 1960's. The attempt to make a DPSIR analysis also revealed the lack of integrated vision from most actors including the Ministry of Environment established in 1971. Then we are comparing the excess metal outputs from the River Seine catchment to the estimates of metal uses on this area for a 50 year period through a specific indicator, the leakage ratio. Finally we briefly compare the Seine with other contaminated rivers and estimate the per-capita release of metal from the catchment to the basin outlet from 1930 to 2000.

8.1. Development of metal contamination awareness

The contamination awareness is here analysed through three criteria: (i) the development of environmental surveys (figure 14, curve A), (ii) the development of scientific research (figure 14; curve B) and the development of regulations (figure 14, curve C).

Prior to 1968, the analyses of metals in rivers were very limited by the available techniques as colorimetry and polarography. From 1968 to 1972, Atomic Absorption methods were developed and the first study published on metal contamination in the Seine catchment has been done by P. Leroy from the Paris drinking water public institution (Service de Contrôle des Eaux de Paris, now CRECEP). It dealt with total mercury on unfiltered river samples after permanganate digestion analyzed by Flameless Atomic Absorption (Leroy, 1972). Leroy made several longitudinal profiles in 1971 on about 100 km in the central reach of the Seine, from Corbeil upstream of Paris to Conflans, upstream of the Seine-Oise confluence (figure 1). He made two important observations: (i) Hg was associated with SPM, (ii) total Hg concentration was the highest downstream of Paris sewage overflow sites and when sediments were resuspended. According to his data set, the combination of these total Hg and SPM levels gives a range for maximum Hg associated with the particulates between 9 and 17 mg.kg^{-1}. His conclusion was that the Seine was actually contaminated, even if the level of contamination could not be assessed since the background reference value in river particulates was not determined either in the Seine catchment or in other rivers. In the paper discussion, the director of the public institution in charge of the drinking water supply for Paris did not realize either the severity of such contamination and referred to a "possible contamination from ancient pressures". Leroy's work was confirmed by Chesterikoff et al. (1973), who found Hg contents in SPM up to 26 mg.kg^{-1}, qualified as "a very serious issue".

From 1968 to 1980, private and public institutions of mega Paris have been continuously checking total metal concentrations at their water intakes on the Seine, Marne and Oise rivers (A. Montiel, pers. com.). Although this information has not been made public, it was communicated to the Agence Financière de Bassin Seine Normandie (AFBSN, now AESN).

The first River Seine survey of metal contamination, completed at a national level in 1971, also concerned total Zn, Pb, Cu and Cd on unfiltered waters (MDB-SN/AFBSN, 1976). Due to differences in analytical protocols, contamination during sample treatment and very high detection limits with colorimetric methods, the resulting concentrations were greatly variable and could not be exploited (A. Montiel, SAGEP then CRECEP, pers. com.). The limit of total metal analysis is well known (Horowitz, 1991)/

In 1975, a first laboratory intercomparison exercise was set up prior to the second "National Inventory of the degree of pollution of surface waters" ("INP") coordinated by the French Water Authorities in 1976. Total metals were then measured by Atomic Absorption methods. This second inventory was also limited to the protection of aquatic resources prior to drinking water treatment, which have been the main objectives of metal surveys from 1971 until the mid 1990's. Meanwhile, numerous tests were commissioned by the AFBSN on deposited sediments in the Seine River Basin (Bellamie et al., 1980; Chesterikoff et al., 1973) in order to better describe the state of contamination with a standard approach. In 1979, Lesouef et al. published the first paper on Cd, Hg, Pb and Zn contents of sediments ("the sediment, a contamination memory") on which the first regular survey of river sediments was based in 1981 (Robbe et al., 1984). This awareness phase of metal contamination took about 10 years (1970-1980) until the regular monitoring was set up on deposited sediments.

In 1978, the SIAAP also started its regular metal monitoring in treated sludge, probably the oldest monitoring of its kind in France. At the same moment, the national network for coastal waters quality (RNO) was established by the ISTPM and CNEXO, now united as Ifremer, and metal analyses in estuarine mussels were undertaken since 1979 (Claisse, 1989). In 1983, suspended matter quality was also regularly analysed at the Poses station by the Service de Navigation de la Seine (SNS) for the AESN. This completed the metal survey as it exists today (see details in Grosbois et al., 2006).

In the late 1980's, the regional administration of the Ministry of Environment in charge of the Seine Basin (Délégation de Bassin, now located at the DIREN Ile de France) took the initiative to contact the National Centre for Scientific Research (CNRS). As a result, several scientific teams were

clustered into the Piren-Seine multidisciplinary programme in 1989, funded by a dozen of public and private institutions of the Seine Basin and backed by the AESN. The Piren-Seine scientists developed a second stage of metal surveys in the catchment on sediments and biota (Carru et al., 1996; Chevreuil et al., 1995 and 1996; Garban et al., 1996) flood deposits (Idlafkih et al., 1995; Idlafkih, 1998; Horowitz et al., 1999), urban runoff (Estèbe et al., 1998), atmospheric fallout (Azimi et al., 2003) and, since 2004, on floodplain cores (Bonté et al., in preparation). In parallel, numerous studies on the metal distribution in the Seine estuary were realized within the Seine-Aval programme (Cossa and Ficht 1999; Chiffoleau et al. 1999, Cossa et al. 2002). The dredged sediment analysis is also recorded by the SNS since the 1990's. The Seine catchment is also part of two important national surveys of metal contamination in terrestrial mosses (Gombert et al., 2004) and in soils (Baize, 1997).

The publication rate of scientific papers on metals in the Seine Basin is presented on figure 14B. Before 1990, there has been very few published papers on metal contamination for two reasons: (i) environmental scientists actually working on the contamination were not enclined, or even authorized, to publish their results in scientific journals, and data remained as reports like those of CEMAGREF (Bellamie et al., 1980) and Institut d'Hydrologie Climatique (IHC, Univ. Paris 6) (ii) prior to 1990, river geochemists at the French CNRS were not pushed nor funded to work on systems under high anthropogenic pressures and preferred to focus on near-pristine rivers. The publication rate on Seine metal is therefore clearly linked to the Piren-Seine programme established in 1989. As a result, scientific publications lagged 10 to 15 years behind the awareness period.

The analysis of the few dozen of national regulations and assessment tools concerning the metal contamination also shows a major lag (figure 14 curve C, a to f). Regulations were developed since the mid 1970's with few bench marks, like the development of contamination scales (SEQ-Eau system; Oudin, 1999) and the application of European Directives. The French metal governance has been accelerated in the last 10 years, principally in connection with the 1988-1990 European work on a good ecological state adopted in 2000 and which has been translated into French regulations in 2005 (Water Framework Directive MEDD, 2005).

The metal contamination issue and its governance in France shows the following succession: (i) decline of contamination, (ii) issue awareness decade in 1970-80, (iii) start of environmental surveys in 1980 and the development of the regulation since the 1980's privileging the drinking water use, (iv) acceleration of concern after the mid 1990's and change of issue vision including environmental contamination and various users needs. When the important national regulation measures were taken in the mid 1980's, the level of metal contamination had already been much decreased (see section 3).

Figure 14

8.2. Various visions of metal contamination in particulate matter

Two types of metal contamination approaches have been developed in the past twenty years in France: (i) the construction of standards, criteria and/or guidelines for the protection of drinking water resources and for the management of particulate matter found in freshwater sediment, coastal sediments, agricultural soils and treated urban sewage sludge (table 2), which have been discussed previously and (ii) the construction of metal contamination scales for the freshwater sediments (table 3).

Before the construction of the national water quality assessment system (SEQ-Eau) in the mid 1990's (Oudin, 1999), there was no national scale for assessing the contamination of river, lakes, reservoirs and canal sediments. Each River Basin agency (Agence de l'Eau) developed its own approach, which was very much depending on Basin management policies. For instance, the Artois-Picardie Basin (AEAP, 18200 km², north of the Seine catchment) has a heritage of severe contamination resulting from mining and industrial activities. AEAP has therefore targeted its metal scale in the early 1990's to dredged sediment management, not to an ecological capacity (table 3): the first level (L_1, table 3) was set up as 6 times its "basin background reference", thus separating the "non-contaminated and negligible contamination" states (see table 1, AEAP 1990's) from the "probable contamination" level, while the second level (L_2) was identified as the "established contamination" (Noppe, 1996). Meanwhile, in the Seine Normandie Basin (AESN) located in an identical geological setting but lacking any mining pressure, a relative index of contamination (I)

was proposed based on the natural background levels (C_n) established by Pereira-Ramos (1988) (table 1, AESN 1988) as $I = C_m/C_n$, with C_m = measured metal content. Five levels of I were proposed although not qualified: < 2, 2-4, 4-8, 8-16 and > 16 (Pereira-Ramos, 1988) and then a polymetallic index of contamination was based on Cd, Cr, Cu, Hg, Pb and Zn with equal weights.

In the mid 1990's, the national scale for a Good Ecological State was established for total metals concentration within the SEQ-Eau, mainly based on European guidelines for potable waters existing in the mid 1990's (Oudin, 1999). This was then revised and completed for particulate metals in 2003 (SEQ-Eau, 2003), with a five colour scale: blue for pristine, green for some contamination without any ecological or Human health impact, yellow with some impact, orange with important impact and red for extreme impact (table 3).

Such a new scale was very different from most existing scales in French Basins. For instance in the Artois-Picardie scale, Cd, Cu, Hg, Pb levels below the L_1 level that was originally qualified as "negligible contamination" were then qualified in the maximum impact range (red scale by the SEQ-Eau)! The contamination state based on the AEAP scale is always minimized compared to the SEQ-Eau ecological capacity scale, excepted for Cd during the 1950-1975 period for which both scales are in the black range. This discrepancy is maximum for the most recent period, 1995-2000, for all compared metals (Pb, Zn, Hg, Cd, Cr, Cu) and reaches 2 to 3 colour range: many stations qualified as "black" by the SEQ-Eau are qualified as 'green' by the former AEAP scale.

The SEQ-Eau approach is a great improvement: it keeps the sediment management concern and adds another scale based on ecotoxicological values. It also gives to water quality stations a continuous quality index generally from 0 to 100 which can be spatially averaged. Yet most river basin and national administrations report the overall quality using the simplified colour code in five categories for their general communication, particularly for mapping and for general statistical analyses. Yet, some colour limitations remain in the present SEQ-Eau scale: (i) the Orange-Red limit can be very far from the highest values actually observed (which can be ten times higher at some stations), e.g. a 2 fold decrease of Hg contamination from 0.6 to 0.3 mg/kg cannot be shown by a shift in colour code. (ii) the Blue-Green limit is conventionally set up as 1/10 the Green-Yellow limit. SEQ-Eau scale modifications have been made in our decision support system, SEQUAMET

(de Pontevès et al., 2005), targeted to metal contamination assessment in the Seine catchment: we have therefore proposed the addition of another level of contamination coloured in black, which correspond to twice the Orange-Red limit of the SEQ-Eau (table 3). We have also split the Yellow category into two subcategories for Cd, Hg and Pb (Y1 and Y2, table 3). Finally the Blue-Green limits of Cd, Cr, Cu, Hg and Zn of the SEQ-Eau, set up as 1/10 of the Green-Yellow limit for Cd, Cr, Cu and Hg, were replaced by a specific estimates of the Seine natural background for different rocktypes based on subpristine sediments (Meybeck et al, 2004; Grosbois et al., 2006)

Table 3

8.3. Comparing the metal demand and metal leaks to the River Seine (1935-2000)

The excess metal loads in river can be pro-rated to the circulation and use of metals within the basin and to the erosion of metal stocks, particularly found in construction and dumps. This last point is discussed in Thévenot et al. (this volume). It is difficult to establish the exact metal demand for the Seine basin territory for two reasons: (i) metal demand statistics are only available for the whole French territory, (ii) when some regional statistics happen to be known they refer to administrative regions that do not coincide with the hydrographical boundaries.

As a first estimate, the Seine basin metal demand has been taken to be 30% of the national demand for all metals and periods. These values are available only for the industrial demand including the construction sector but they do not include other demands. The average demands (t.y^{-1} for the Seine basin) is established at 5-year intervals since 1950 (see section 5.2 and figure 8). The excess load of metals (t.y^{-1}) transported by the river (table 4) is determined following four steps: (i) from 1930 to 1980, the average contents in river SPM are those established from the dated cores multiplied by a correction factor of 1.4 to take into account the finer grain size of SPM compared to alluvial cores (see section 3.2), (ii) the background contents of metal are then substracted and the resulting "excess contents" per period of 5-year are multiplied by the long term average of river SPM flux at Poses (700,000 t.y^{-1}, Meybeck et al 1999) to determine the excess metal flux at Poses, (iii) dissolved metal fluxes at Poses are added on the basis of the excess

metal flux assuming dissolved/ total metal proportions of 10% for Cd, 10% for Cr and Hg (estimations),15% for Cu, 12% for Pb and 20 % for Zn. These proportions are here estimated for an average SPM of 45 mg/L (see Thévenot et al., this volume, for further discussion), and are considered as constant between 1930 and 2000, (iv) the retention of contaminated particles in reservoirs, floodplain and dredged material depositories is then added (this correction is minor, from 3 to 6% of the mass of excess particulate metals only) (Thévenot et al., this volume).

The ratio between the "total excess metal load" (table 4) and the metal industrial demand is termed here the "leakage ratio" (LR). It has greatly varied over time, by one to two orders of magnitude and can be interpreted as an indicator of anthroposphere leaks to the hydrosphere.

The leakage ratio has evolved in parallel for Cd, Cu, Pb and Zn according to an exponential decrease and it is metal-specific (figure 15). The leakage is now less than 1 % for Cd, 1‰ Cu and Pb, while it exceeded 10% for Cd and 1 % for Pb in the 1950's. It is difficult at this stage of our research to decipher these differences and trends which are due to (i) differences in the forms of metals in SPM (i.e. as metals, oxides or others) (ii) evolution of metal-using industries and their processes, (iii) controls of metal emissions and (iv) chemical properties of metal.

Hg leaks are very different from all others: they are always high during the documented period 1980 to 2000, increasing from 6 to 27%, meanwhile there was a continuous decrease of Hg demand. The Hg trends suggest a long-lasting contamination and/or a specific transfer mode of this metal, which should be further investigated.

Table 4

Figure 15

8.4. Was the Seine among the most contaminated rivers?

The metal contamination issue has only been a major concern since the late 1970's for multiple reasons: (i) In 1972 the UN Conference on the Environment at Stockholm informed the global water-management community of metal impacts on human health as for the Minamata desease (Hg) and Itaï-Itaï desease (Cd), (ii) in the late 60's the development of Atomic Absorption

Spectrometry allowed for the multimetal analyses at low detection limits and at very low cost per sample.

The maximum metal levels ever recorded in the Seine particulates are presented in table 5. All of them are comparable to the maximum levels found in the Meuse and the Rhine (Middlekoop, 1997) and Scheldt (Zwolsman and Van Eck, 1999), which are also characterized by relatively low transport of particulates compared to other big rivers (Meybeck and Ragu, 1996) and by very high pressures from big cities, industries and mines (the latter being absent on the Seine catchment).

Although the Seine catchment contamination is markedly improving, it is still among the 10 % most contaminated rivers of the world (table 5) for Hg, Cd and to a lesser degree for Pb, Zn and Cu but not for Cr and Ni. Many world rivers draining volcanic rocks have higher particulate Ni contents than the Seine.

Table 5

8.5. Evolution of excess loads of metals prorated to the Seine basin population (1935-2000)

The excess loads found in the river (table 4) can be normalized to the total basin population as determined from the national census and expressed in g metal per capita per year (figure 16).

The decontamination of river particulates has occurred although the population was increasing by more than 50% in the last 60 years. As a result, the evolution of per capita leaks is even faster than metal decontamination in the river. The highest per capita loads are always observed for Zn, the lowest for Cd and Hg. The general order of per capita excess metal throughout 70 years of record is the following (Hg figures are not yet available prior 1983):

1930-1950 Zn >> Pb > Cu > Cr >> As > Cd = Co

1955-1970 Zn >> Pb > Cu = Cr >> Cd > As > Co

1975-2000 Zn >> Pb ≥ Cu > Cr >> Cd > Co ≥ Hg

Figure 16 illustrates these variations of per capita excess loads. The maximum per capita leaks are observed decades ago: in 1935 or before for Cu and Co, 1940 for Pb and As, 1955 for Zn, 1960 for Cd and 1965 for Cr. Since there is a lack of regular Hg analyses in river sediments prior to 1983, we have used for the 1980 period the average Hg content in the upper estuary SPM established between 1976 and 1981 (Avoine et al., 1986), and for the 1970 period an estimated Hg content of at least 10 mg.kg^{-1} from Leroy (1972) and Chesterikoff et al. (1973).

Since their maximum levels, the per capita leaks have decreased 30 times for Cd, 10 for Pb, 6 to 7 times for Cu, Cr and Zn, and a ten-fold decrease of Hg per capita loads is likely between 1970 and 2000. These trends illustrate the marked changes of human pressures on the aquatic environment combining de-industrialization, metal-recycling and changes of industrial processes.

Figure 16

9. Conclusions

The Seine catchment is combining very high pressures and very limited dilution power because its low river suspended matter. As a consequence, the Seine Basin is structurally fragile and its river course, downstream of Paris megacity, has been and still is, among the world's most contaminated rivers. The D.P.S.I.R analysis reveals the following:

(i) Each metal, Cd, Cu, Hg, Pb, Ni and Zn, has its specific driver evolution, contamination level, probable ecological and economical impacts, and management criteria rules and should therefore be addressed separately in any analysis.

(ii) The Seine river sediments have been among the most contaminated ones ever recorded for Hg and Cd, and to a lesser extend to Zn and Pb; As, Cr and Ni contaminations have been limited.

(iii) While the metal demand per capita has much increased since the 1950's, excepted for Hg and a recent decline for Cd -both due to environmental regulations, the contamination level in the river Seine, as reconstructed from core analysis, has markedly decreased since that period: as a result

the leakage ratio (excess river load/metal demand) has dropped by one order of magnitude for all metals but Hg.

(iv) Metal decontamination started 20 years prior to the major environmental regulations that were developed in the late 70's. From 1960 to 1980 decontamination was mostly due to major changes in the industrial activities over the Seine catchment. The 1980-2000 decontamination combines changes in metal uses constrained by environmental regulations (e.g. Cd and Hg) and wastes outputs reduction from industrial and domestic sources.

(v) Before 1970 there was a near-total lack of awareness about metal contamination due to the "analytical darkness" prior to the common use of atomic absorption analysis. More than 10 years of preliminary studies in the 1970's were needed before a regular monitoring was established (1979-1983) first in sewage sludge then on river sediments. Yet the contamination of freshwater biota has never been monitored unlike for the estuarine and marine species started in 1979.

(vi) From 1971 to the mid 1990's the major concern about metal contamination was the protection of drinking water resources as for other French river basins, not the ecological capacity (patrimonial value). In the mid-1990's the national system of water quality assessment (SEQ-Eau) completely changed this attitude and included a good ecological state.

(vii) The metal contamination criteria are produced by multiple public institutions (six Ministries) and have greatly evolved over the last 20 years: they are now 5 to 10 times more constraining. The reference and the natural background levels have also much evolved. As a result some sediments once considered as harmless for the aquatic biota or crops are now qualified as wastes. The river metal contamination was among the least documented issue in the Dobris European Environmental Assessment (Stanners and Boudreau, 1995). The Seine river was not identified as severely polluted: the "Paris station" selected to comply with the EU "exchange of information" directive since 1976 and confirmed in 2005 by the Ministry of Environment is located 65 km upstream the actual impact of Paris, downstream the Seine-Aval WWTP and much less documented than the river mouth station.

The consideration of a longer time scale, here 60 years, is necessary. In most rivers it can only be realized from sediment archives in floodplains, lakes and estuaries, already advocated since a

long time (Meybeck and Helmer, 1989; Valette-Silver, 1993). This approach is very promising and should be coupled with the reconstruction by environmental historians of past metal demand and uses, metal-containing wastes, regulations, since only the very recent period (1985-2005) is well documented. The development of isotopic analyses, like for Pb, to trace the various metal sources in impacted river basins is also promising (Roy et al., 1999), particularly if pressures trajectories are also documented.

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Tables

Figures

Table 1: Evolution of natural reference levels (mg.kg-1) for particulate metals in the Seine catchment (AESN and Piren-Seine) and for the Artois-Picardie catchment (AEAP) of similar geology.

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Al	Ref
AESN 1979	ND	1-2	ND	ND	0.5-1	ND	20-50	100-200	ND	(a)
AESN 1988	5	0.75	25	12.5	0.1	ND	30	100	ND	(b)
AEAP 1990's	5	1.0	30	15	0.2	10	40	100	ND	(c)
SEQ-Eau 2003	10	0.09	3.6	2.7	0.07	12	10	14	ND	(d)
Piren-Seine 1998	5	0.35	50	15	0.03	17	25	80	45000	(e)
Piren-Seine 2002	6	0.22	40	15	0.015-0.05	16	20	60	33000	(f)

(a) Lesouef et al. (1979); (b) Pereira-Ramos (1988); (c) "levels of no or negligible contamination" in Noppe (1996); (d) national blue-green levels SEQ-Eau version 2 (2003); (e) Thévenot et al. (1998 geochemical background); (f) Thévenot et al. (2002 geochemical background).ND : non determined.

Table 2: Evolution of national and river basin metal contamination criteria (mg.kg^{-1}) for particulate metals in France: urban sludge reuse in agriculture, dredged river, sediments disposal, soil standard for crops, dredged coastal sediment.

				Cd	Cr	Cu	Hg	Pb	Ni	Zn
Urban sludge criteria & standard	Criteria	1970's: NFU 44-041		40	2000	2000	20	1600	400	6000
	Criteria	1986's: 86/278/EEC (a)	max	40		1750	25	1200	400	4000
			min	20		1000	16	750	300	2500
	Standard	1998: 97-1133 (b)		10	1000	1000	10	800	200	3000
Compost	Standard	2004: NFU 44-095 (c)		3	120	300	2	180	60	600
Dredged river sediment	Quality guidelines	1998 VNF1(d)		2	150	100	1	100	50	300
		1998 VNF2 (d)		6.4	250	300	3	367.5	150	500
		2004 VNF (e)		2	150	100	1	100	50	300
Ploughed soil	standard for crops (f)			2	150	100	1	100	50	300
Dredged coastal sediment		1996 (g)	L_1	1.2	90	45	0.4	100	37	276
			L_2	2.4	180	90	0.8	200	74	552

(a) Council directive 86/278/EEC on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture; (b) Decree of 8 December 1997 and Enforcement Order of 8 January 1998 for agricultural use of urban sludge; (c) Enforcement Order March 18, 2004; (d) 1st VNF sediment quality recommendations for dredged sediment management; (e) 2nd VNF sediment quality guidelines for dredged sediment management for which an ecotoxicological approach is taken into account along with criteria and procedures for the acceptance at landfills ; (f) Baize (1997); (g) Alzieu (1999).

		Cd	Cr	Cu	Hg	Pb	Ni	Zn
Artois-Picardie Basin (< 1995) (a)	(G-Y) L$_1$	6	180	90	1.2	240	60	600
	(O-R)L$_2$	18	540	270	3.6	720	180	1800
National SEQ-Eau (1996) (b)	(B-G)	0.09	3.6	2.7	0.07	10	12	14
	(G-Y)	0.85	36	27	0.7	23	20	140
	(Y-O)	3	43	40	0.85	37	40	330
	(O-R)	5	50	110	1	50	200	1200
Seine catchment: SEQUAMET (2005) (c)	(B-G)	0.3		22	0.05	25		80
	(G-Y$_1$)	0.85		30	0.2	30		140
	(Y$_1$-Y$_2$)	1.5			0.7			200
	(Y$_2$-O)	3		40	0.85	37		330
	(O-R)	5		110	1	50		1200
	(R-BL)	10		220	2	100		2400

(a) in Noppe (1996); (b) SEQ-Eau (1996); (c) de Pontevès et al. (2005); colour codes as for SEQ-Eau: B = Blue code; G = Green; Y = Yellow; O = Orange; R = Red; BL = Black

Table 4: Excess loads of metals (t.y⁻¹ for 5-year averages) carried in the Seine river system and basin population in millions (1930-2000) (no significant excess is noted for cobalt).

Date	Pb	Cd	Cu	Cr	Zn	As	Hg	Population
1930	467	6	385	130	1368	17		9.1
1940	504	13	309	136	1293	24		8.7
1945	422	9	277	106	1025	22		9.2
1950	462	19	332	193	1365	21		9.5
1955	520	28	396	244	1562	17		10
1960	424	34	314	246	1294	19		10.2
1965	404	34	247	278	1321	19		10.5
1970	339	27	217	196	975	14		11.2
1975	274	19	191	135	690	9	7	11.5
1980	216	12	175	131	732	8	4.9	12.8
1985	188	8	162	165	614		1.8	13
1990	271	4	113	106	489		1.5	13.4
1995	113	2	107	69	393		1.9	13.5
2000	70	1	74	66	294		0.8	14

Table 5: Maximum levels (mg.kg^{-1}) recorded in the Seine River particulates compared to the upper decile (C90) of the global river distribution

	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Ref.
Lower Seine Historical maximum (1935-05)	39 (a)	275 (a)	347 (a)	26 (b)	150 (c)	558 (a)	1317 (a)	a; b; c
(date)	(1960)	(1965)	(1965)	(1972)	(1976/81)	1960	(1960)	
Seine maximum in dredged sediments (1996-2004)	9	117	172	24	34	278	575	d
Seine maximum downstream of Paris (i)	130 (h)	900 (h)	570 (i)			340(h)	1620 (i)	e
Present Lower Seine (mean 2000/03)	1.8	123	99	1.06	31	101	370	f
Global rivers (top 10 percentile)	0.9	142	55	0.18	80	46	176	g

(a) Cd, Cr, Cu, Pb and Zn, Bonté et al. (in prep) in floodplain cores; (b) Hg in SPM, Chesterikoff et al. (1973) ; (c) Ni : in estuarine sediments, Avoine et al. (1986); (d) recorded in dredged sediment analysis (SNS database); (e) about 50 km downstream of Paris Center; (f) data from RNB (2003); (g) Meybeck (2006); (h) surface sediments at the Pecq, 1991 (Garban et al., 1996); (i) in a core at Chatou (Thévenot et al., 1998).
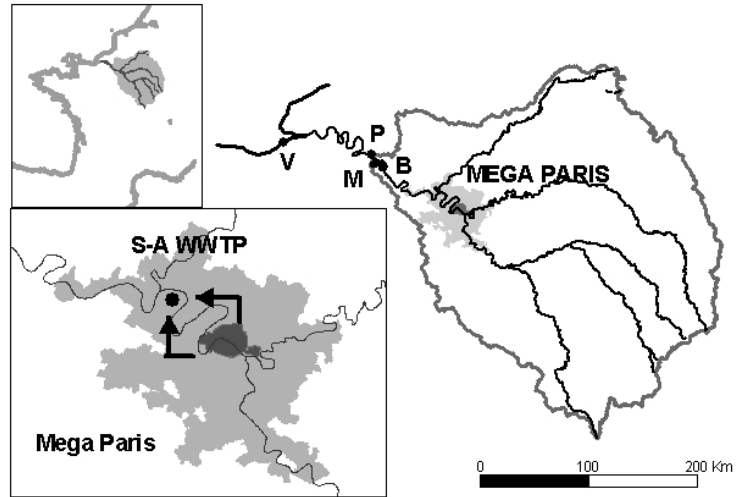
Figure 1: General presentation of the Seine river basin

P = Poses (river mouth station); M = Muids and B = Bouafles (floodplain core location); V = Villerville (mussel watch); S-A WWTP: Seine-Aval, Paris megacity main waste water treatment plant
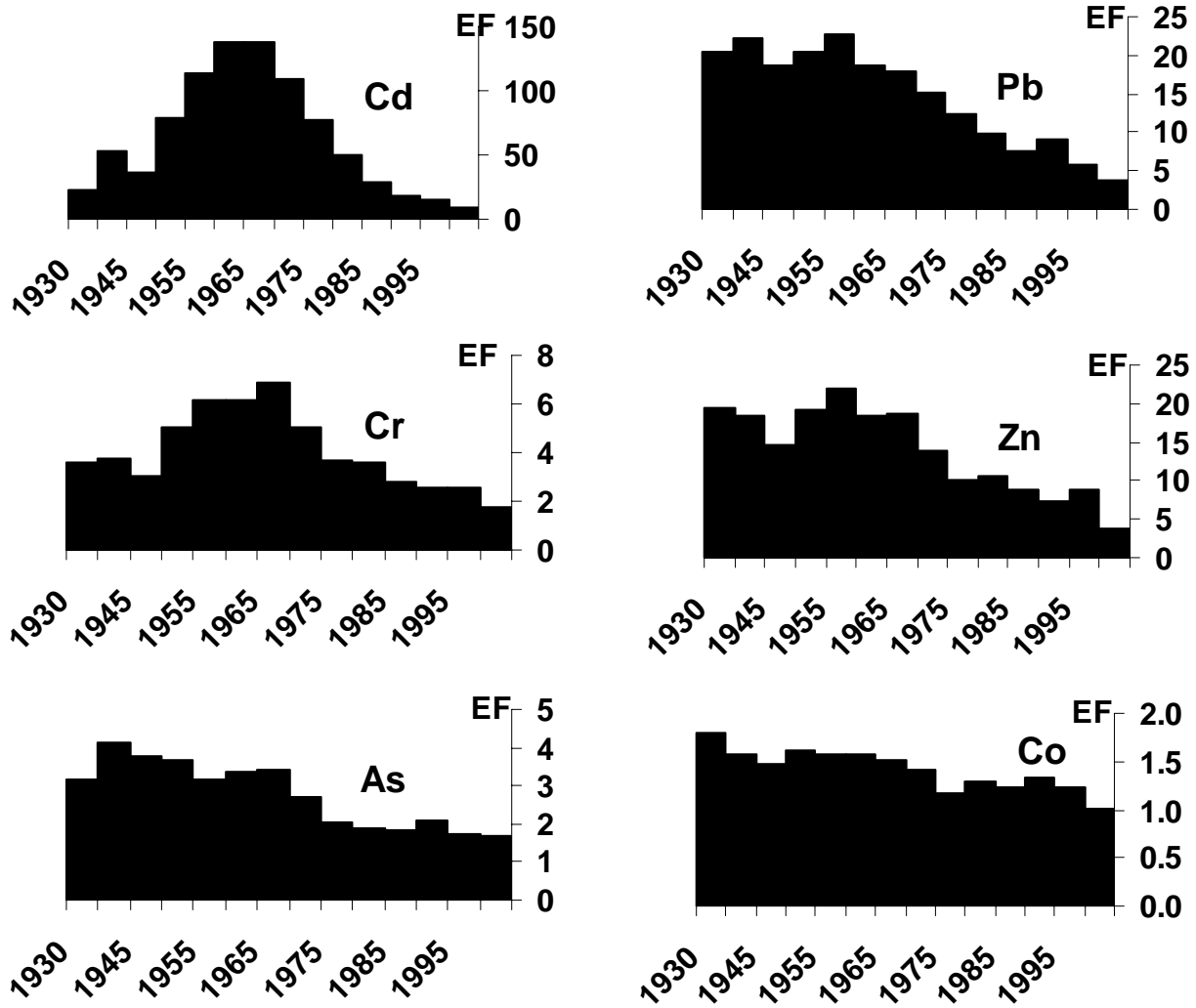
Figure 2: Five years average temporal profiles of five metal enrichment factors (EF) in Seine floodplain cores downstream of Paris megacity (EF = 1 for natural background contents).
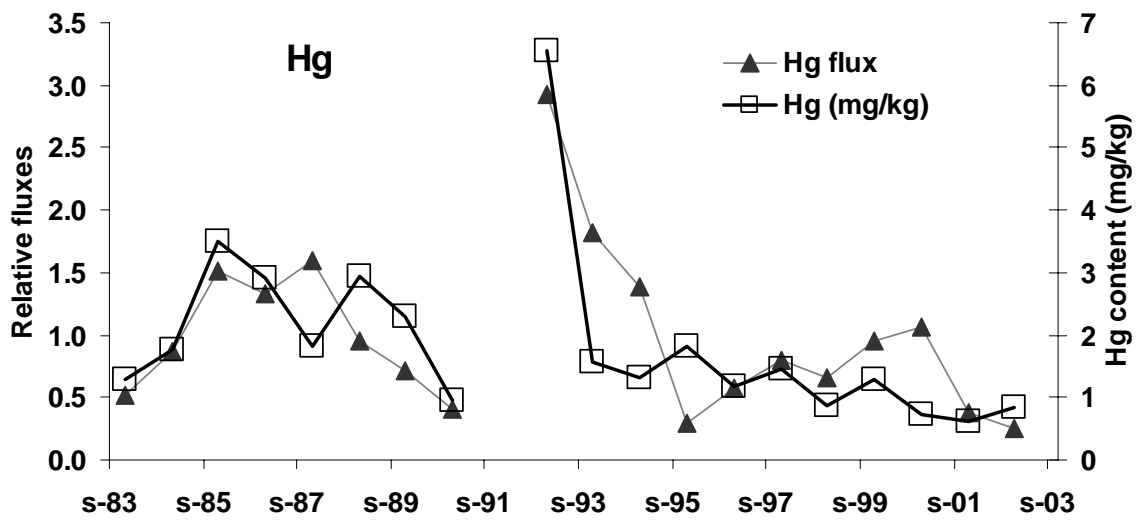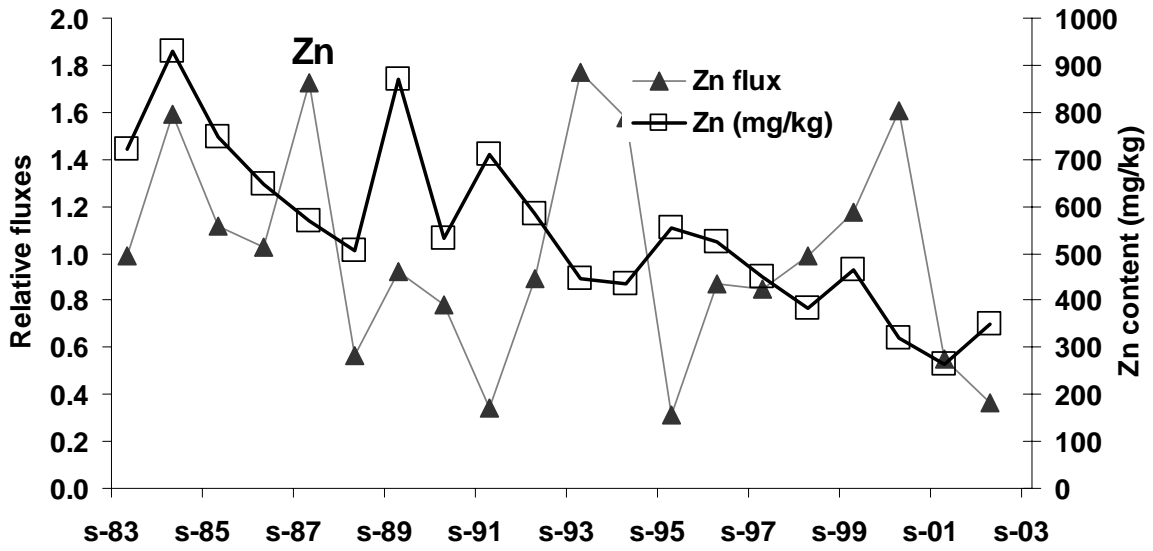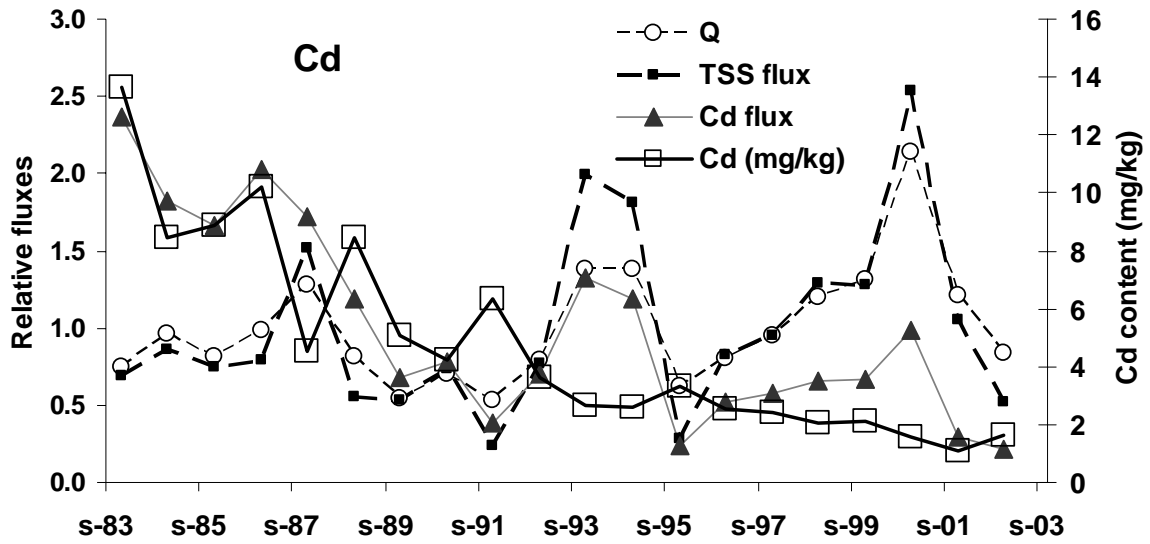
Figure 3: Annual fluxes and average contents of Cd (A), Zn (B) and Hg (C) in Lower Seine River suspended particulate matter (Sept. 1990-Aug. 2003). All flux values are normalized to average values for the period of record (see text).
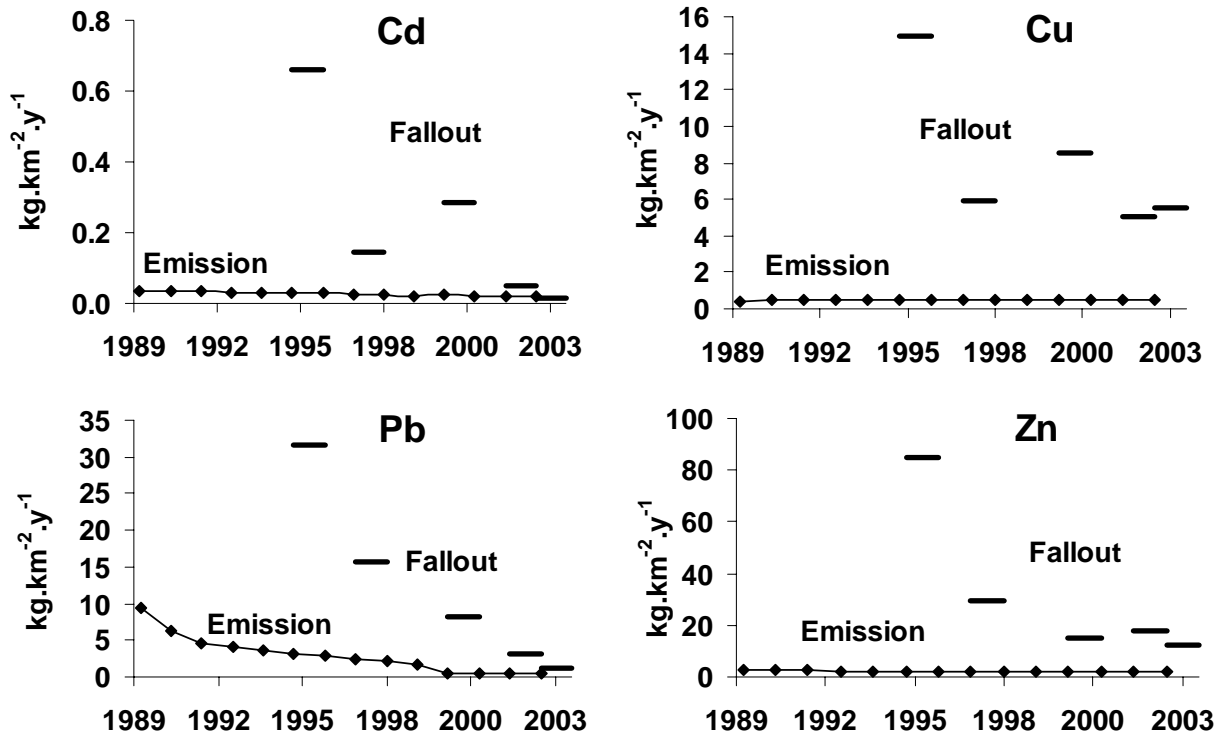
Figure 4: Average atmospheric emissions for the whole Seine river catchment (1990-2004) and weighted atmospheric fallout (kg metal.km^{-2}.y^{-1}) for Cd, Cu, Pb and Zn. Theoretical emissions from CITEPA (2004)
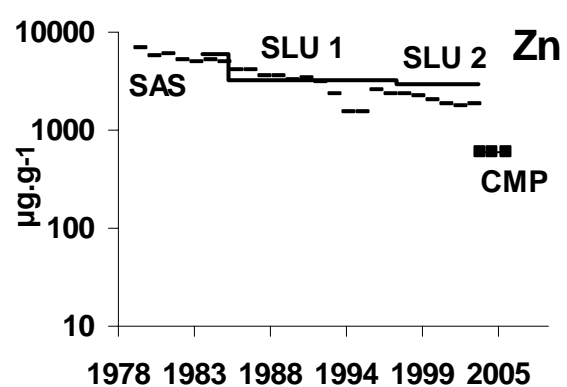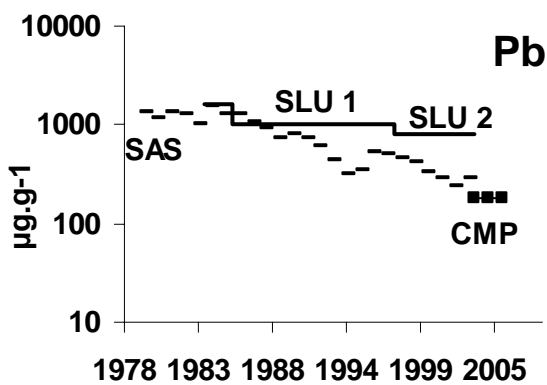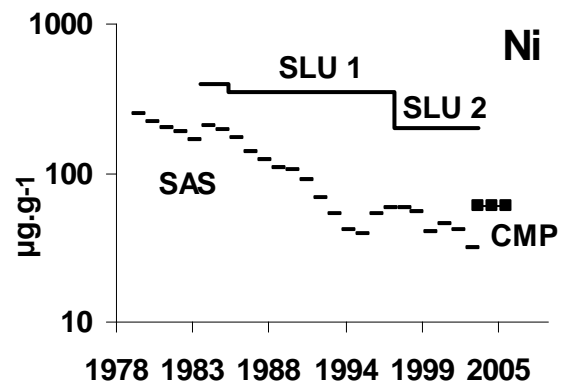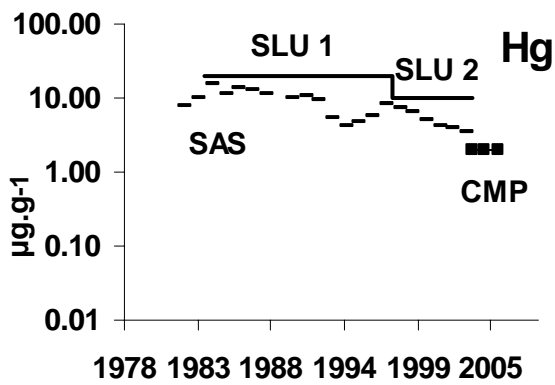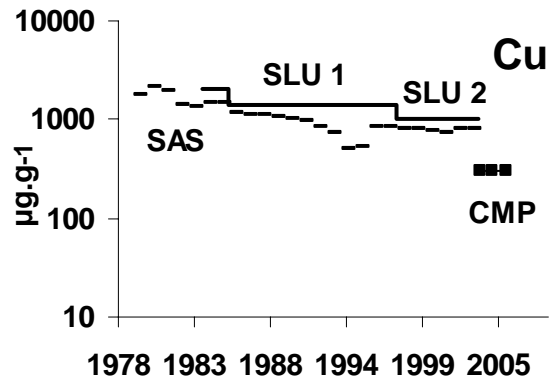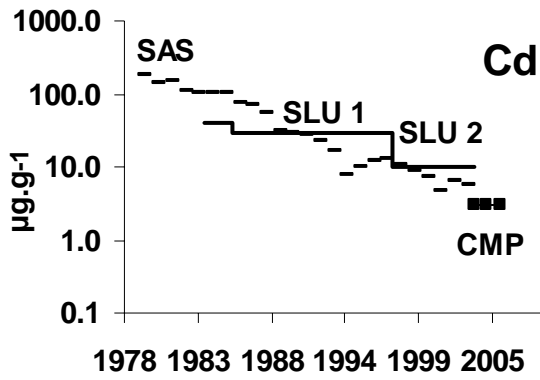
*Figure 5: Compared trends of metal contents (logscale in µg.g⁻¹) in Paris megacity sewage sludge.
SAS (--): Achères/Seine-Aval Sewage Sludge; SLU 1: reference criteria; SLU 2: regulatory standard
(▬) for agricultural sludge reuse; CMP: (•••) Standard for compost.*
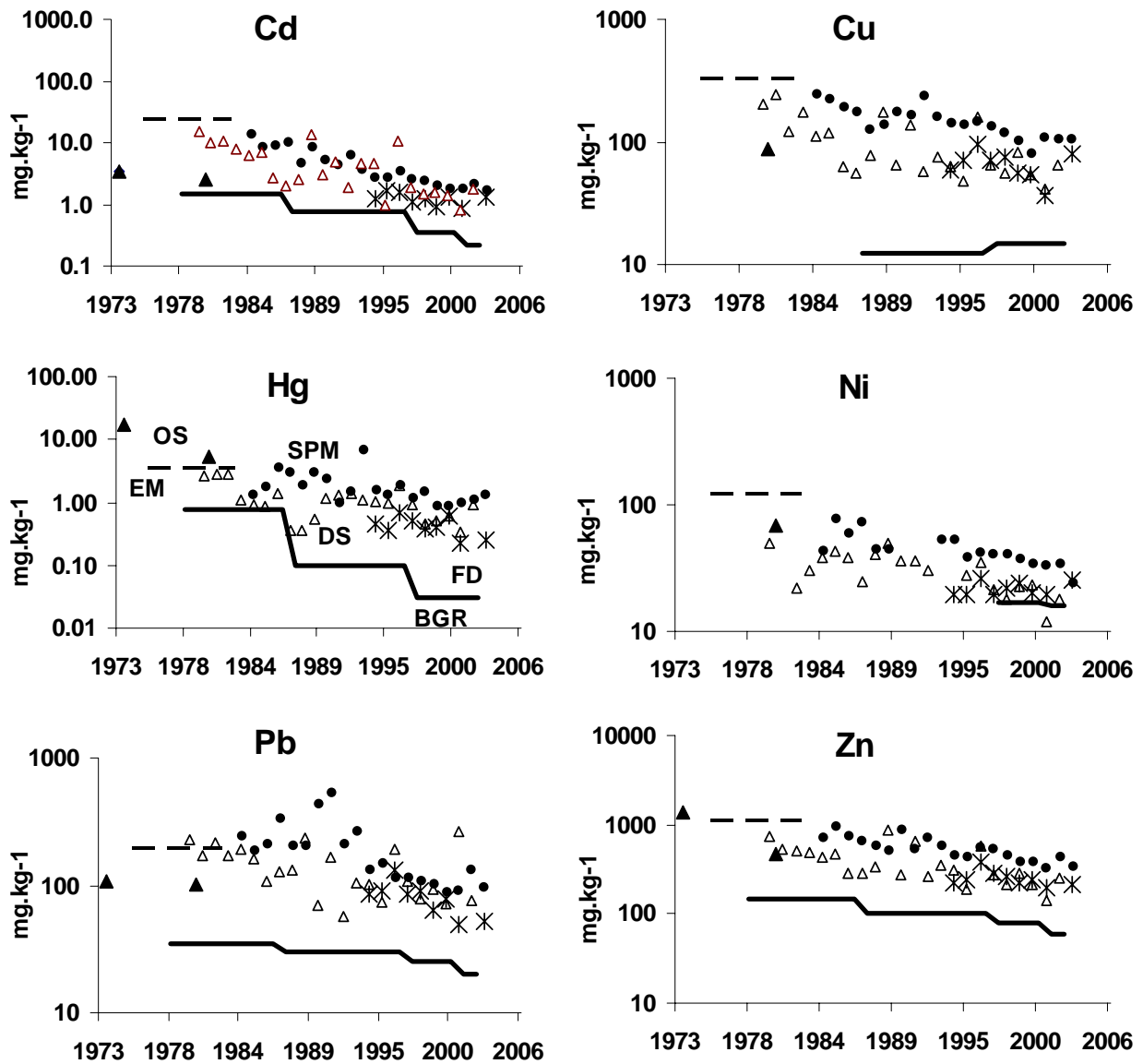
Figure 6: Compared trends of metal contents (logscale in mg.kg⁻¹ in the river particulates (Poses river mouth station for the period 1983-2003).

EM (- - -): estuarine sediments; BGR (--): estimated background; SPM (●): Suspended Particulate Matter ; FD (*): Flood Deposit (Horowitz et al., 1994; Grosbois et al, 2006); DS (Δ): Deposited sediment (RNB, 2003); OS (▲) Oise River sediments (Dessery, 1982).
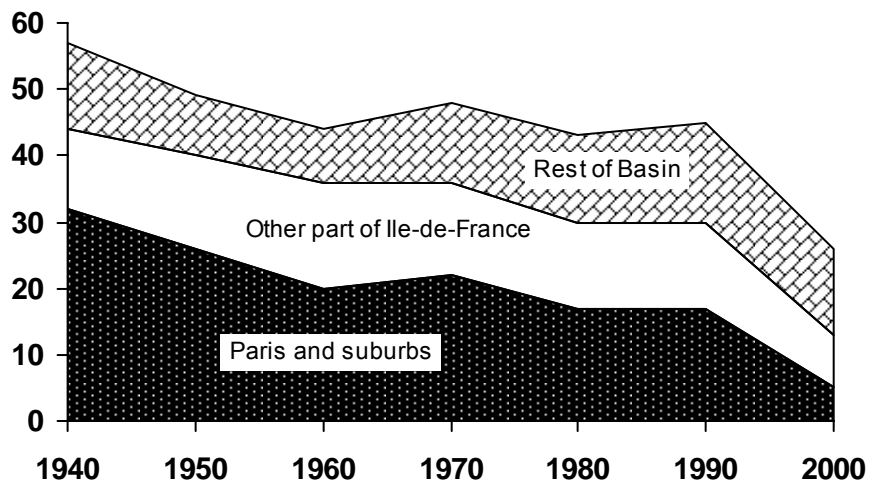
Figure 7: Decrease in the number of lead-related industries in the Seine basin (Lestel, in preparation)
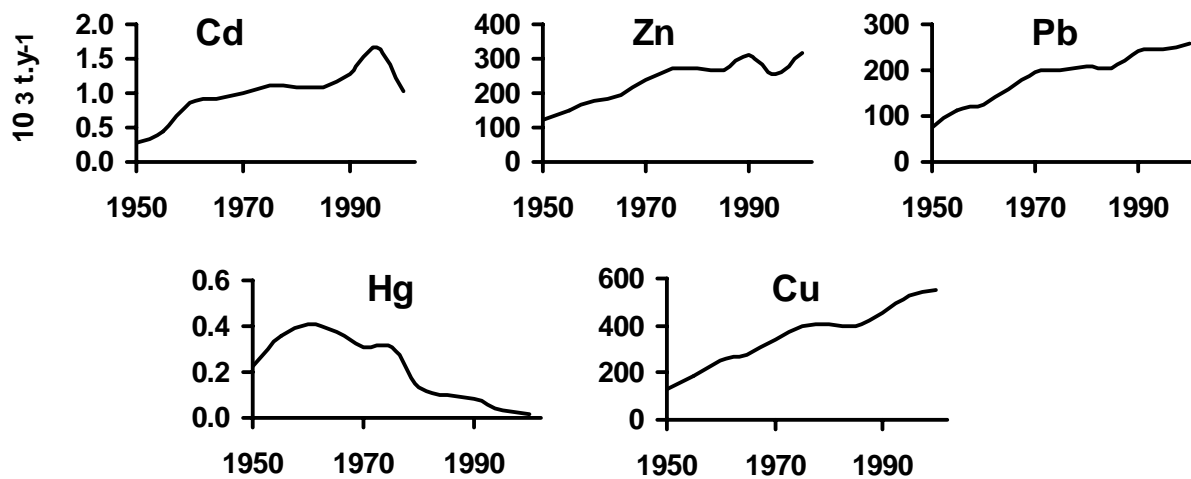
Figure 8: Total annual metal demand from industries in France (t.y^{-1}) (Lestel, in preparation)
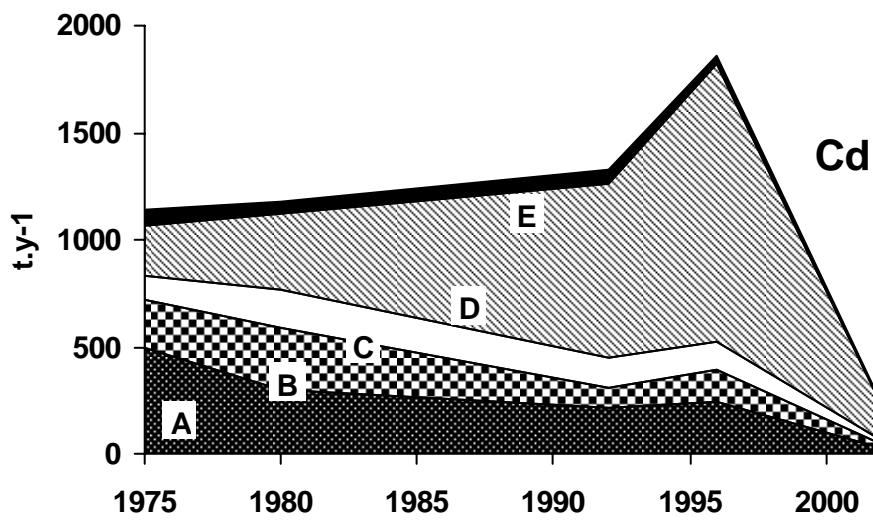
Figure 9: Annual cadmium demand from the industrial sector in France (1975-2000) (t.y^{-1}) (Imetal 1979, Vignes 1998, INSEE, International Cadmium Association). A: Pigments; B: Coating and plating; C: Stabilizers; D: Batteries; E: Non ferrous alloys and other.
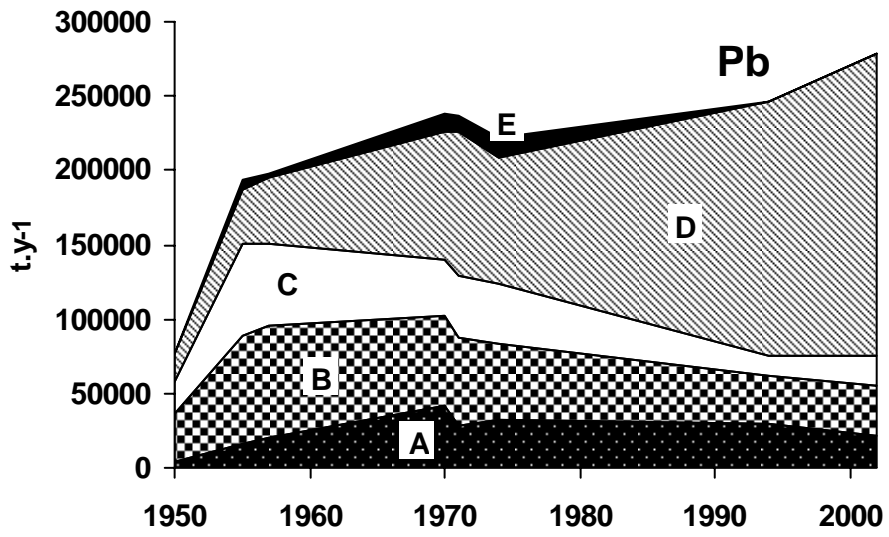
Figure 10: Annual lead demand from the industrial sector in France (1950-2000) (t.y⁻¹) (Gadeau 1959, Lhéraud 1974, Imetal 1979, Vignes 1998, INSEE). A: Chemicals including oxides; B: Other metal uses; C: Cables (metal); D: Accumulators (metal); E: Leaded gasoline.
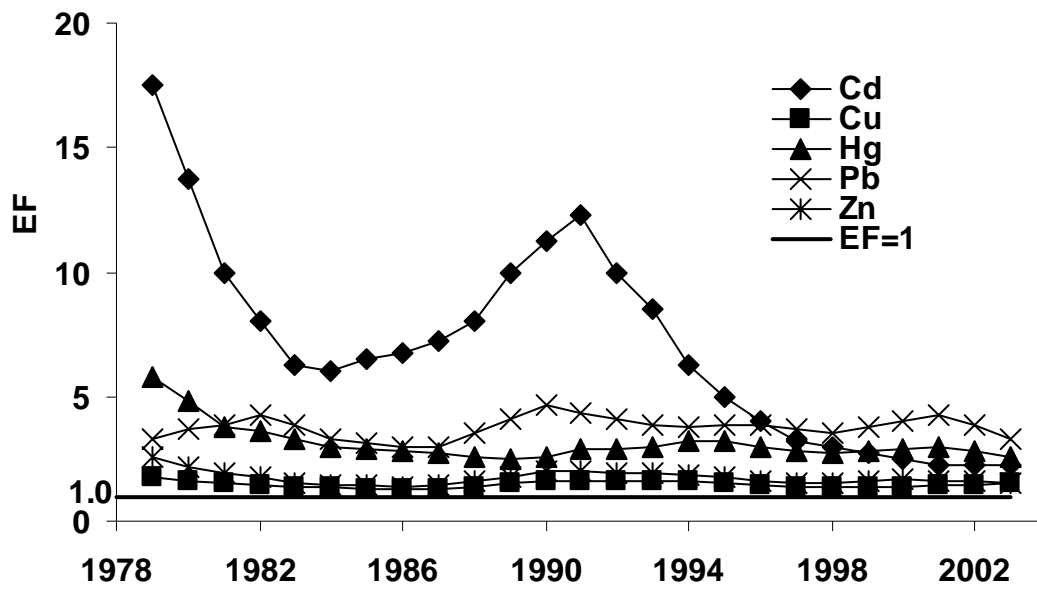
Figure 11: Metal enrichment factors (EF) in Seine estuary mussels at Villerville with regards to the Grandcamp reference site (analyses from RNO, 2005) (EF = 1.0 for background contents)
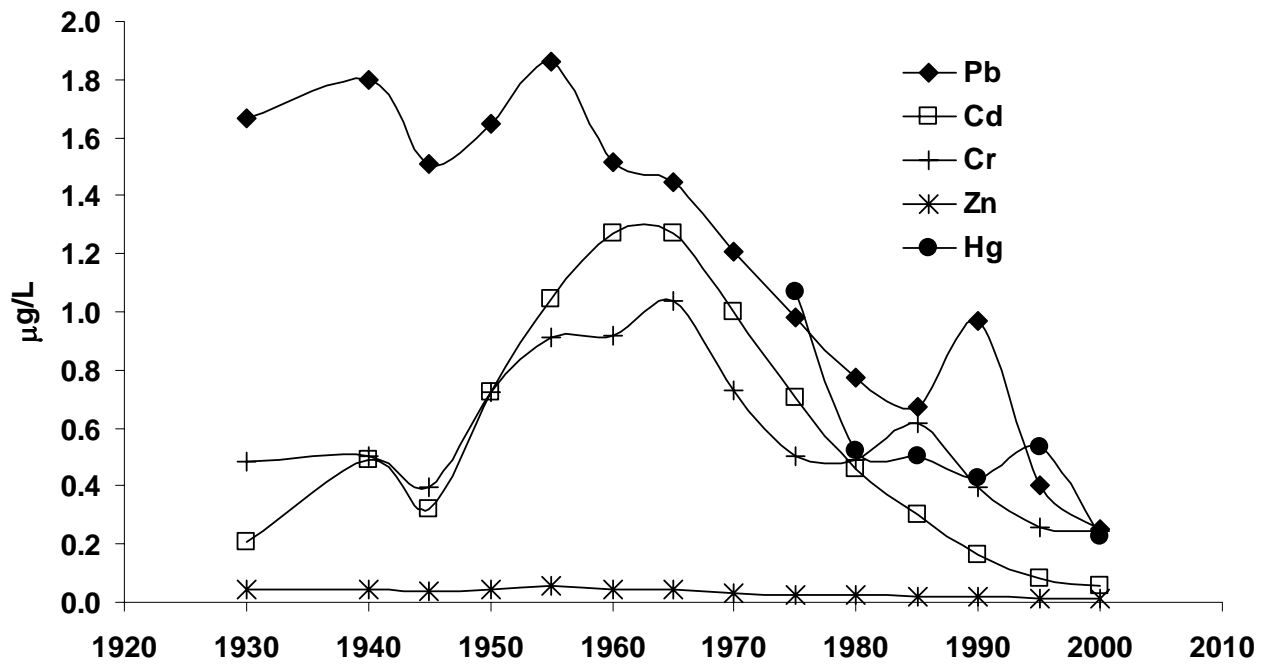
Figure 12A: Simulated concentrations of total metals in unfiltered waters at Seine river mouth during flood stage (µg/L, TSS = 150 mg/L)
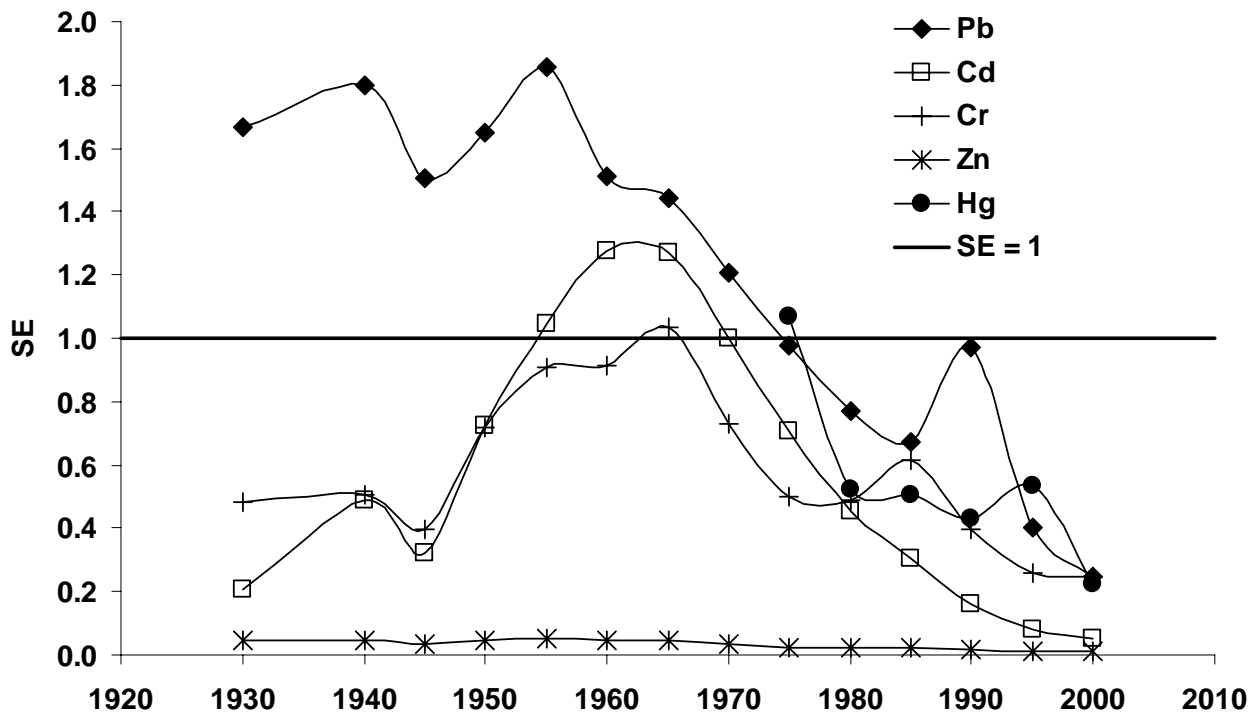
Figure 12 B: Simulated standard exceedance of total metals in unfiltered waters at Seine river mouth (for SPM = 150mg/L, water quality standard for 2005) (SE = total metal conc./standard)
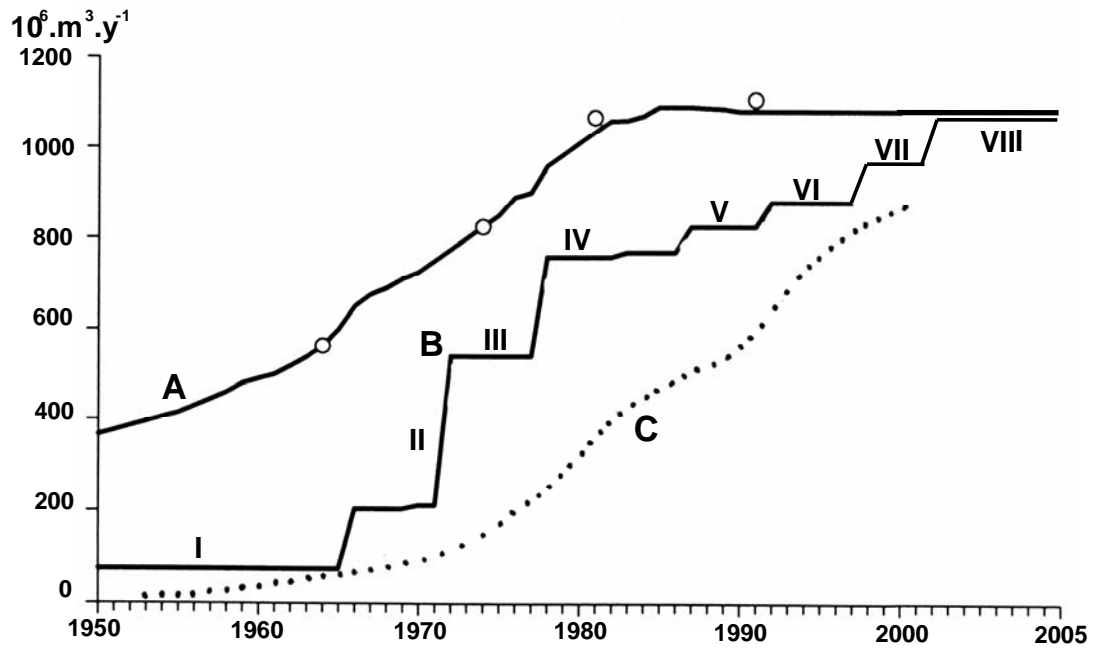
Figure 13: Societal responses concerning waste waters: A. Total volume of urban sewage waters collected within Paris megacity ($10^6.m^3.y^{-1}$). B Schematic urban wastewaters treatment capacity installed in Paris megacity (I, II, III, IV = Achères plants, V = Valenton IA, VI = Valenton IB, VII = Colombes, VIII = reduction of sewage overflow) ($10^6.m^{-3}.y^{-1}$). C. Trend of newly installed waste water equipments in a corpus of 160 lead-using industries in the catchment (relative units).
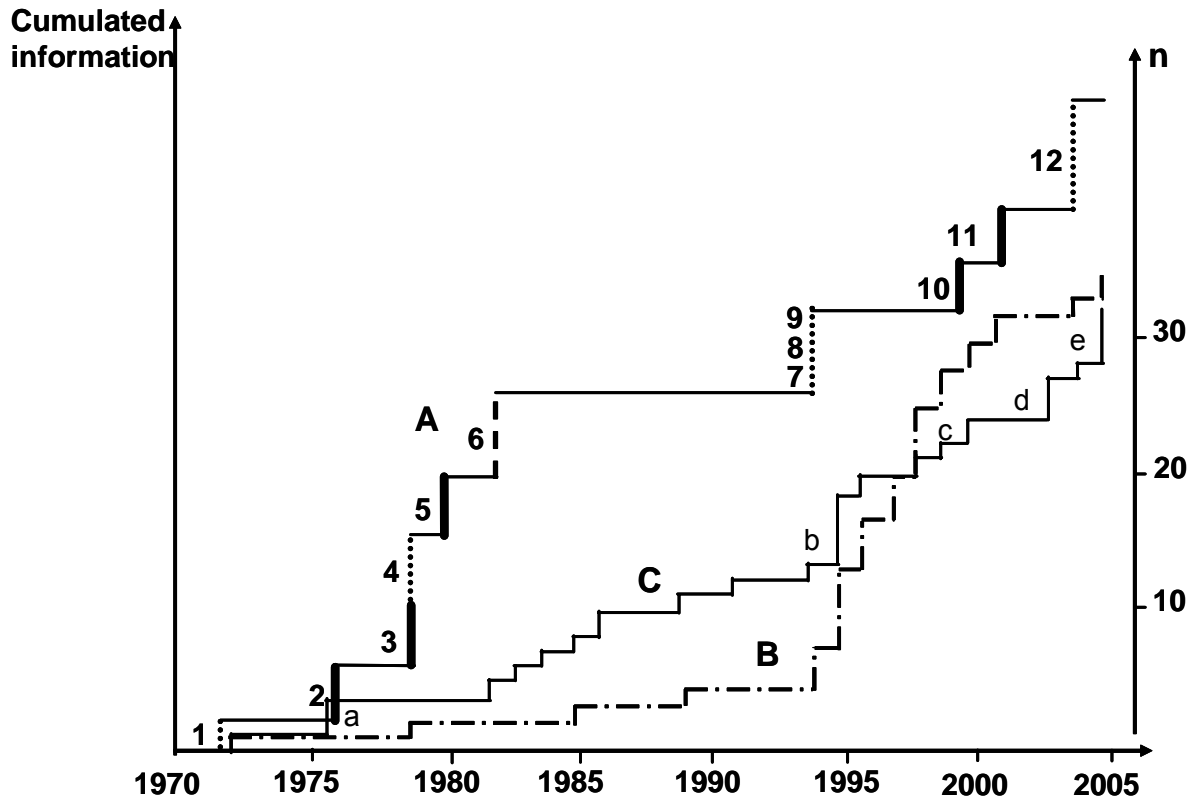
Figure 14: Responses to metal contamination in the Seine River catchment. A: number and importance of surveys as used in this paper (1 = total metals at drinking water intakes; 2 = total metal at key stations; 3 = mussel watch in estuary; 4 = Paris sewage sludge; 5 = river bed sediments; 6 = SPM at river mouth; 7 = flood deposits; 8 = atmospheric fallout; 9 = dredged sediments; 10 = terrestrial mosses; 11 = soils; 12 = floodplain cores. National network: #2,3,5,10,11; Seine network: #6; academic work and other studies: #4,7,8,9). B: cumulated number of scientific papers published on metal contamination (groundwater and estuary excepted). C: cumulated number of regulations and national assessment scales relative to metal contaminations in river systems used in this paper; benchmarks: a: ECE, 1976 Directive; b: SEQ-Eau Version 1; c: EU Directive 2000/60; d: SEQ-Eau Version 2; e: 2005 décrets d'application Directive 2000/60
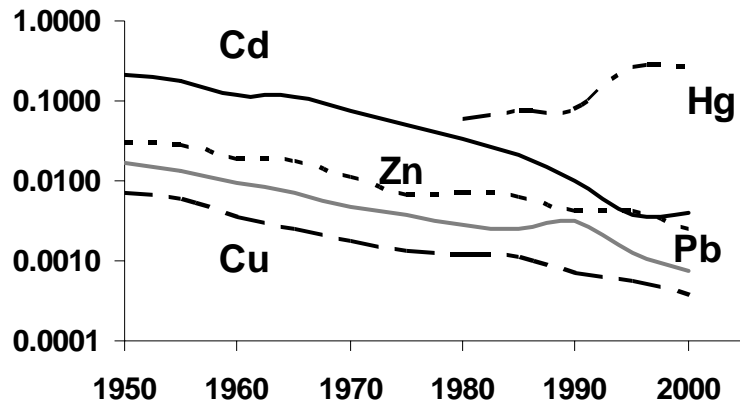
Figure 15: Compared evolution of leakage ratio (LR) from anthroposphere to hydrosphere for Cd, Cu, Hg, Pb and Zn. LR = excess Seine River flux/total metal demand within catchment
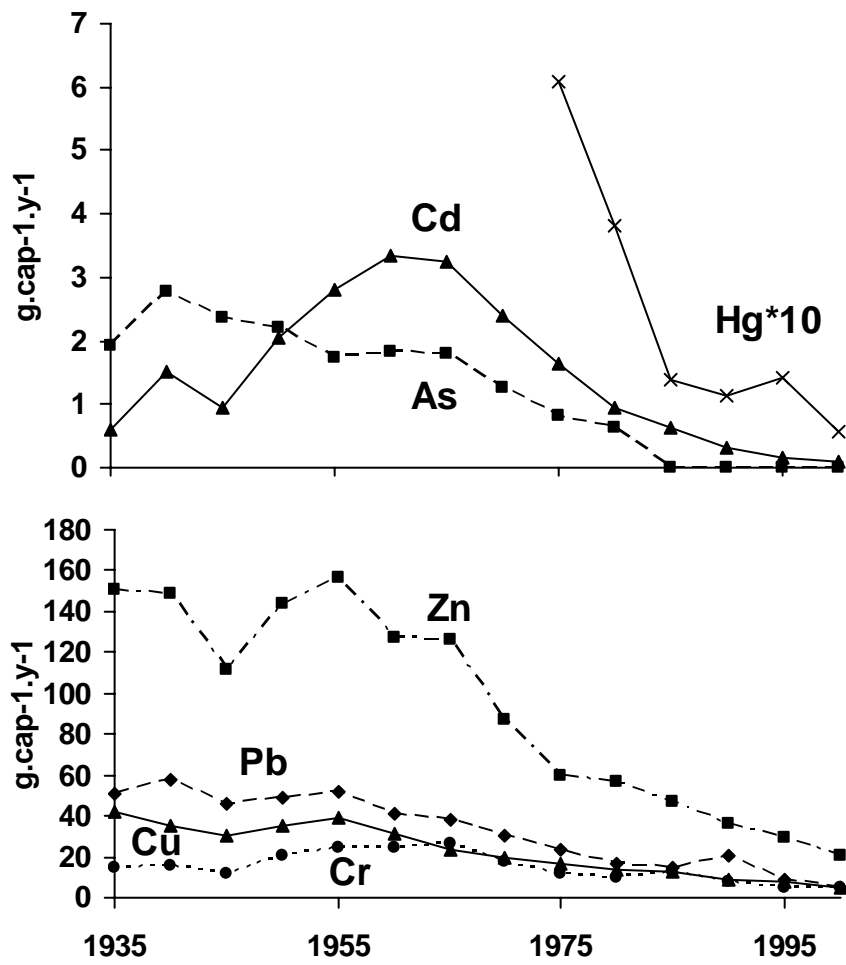
Figure 16: Evolution of per capita excess metal loads transported and stored in the Seine basin to the estuary (1930-2000) (g.cap⁻¹.y⁻¹).