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URBAN RUNOFF IMPACTS ON PARTICULATE METAL CONCENTRATIONS IN RIVER SEINE

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Abstract. Metallic contents (Cd, Cu, Pb, Zn) of suspended solids (SS) were measured in two sites (Suresnes and Chatou) in the river Seine, downstream Paris, during three summer periods. These two sites, which are respectively located downstream and upstream two of the most important combined sewer overflows (CSO's) of the Parisian sewer system (Clichy and La Briche), allow us to assess these CSO immediate impacts. Samples were collected using sediment traps, weekly during dry weather and daily during the week following the major CSO's events. The heavy metal concentrations, relatively large but stable during summer periods, were shown to further increase downstream Paris after main rain discharges occurred. Metal concentrations measured within the Seine SS during rain events, allowed us to establish that the observable immediate impact of Clichy overflows is only 5% of what it could be. The general principle demonstrated through this work is that most SS originating from CSO's rapidly settle once they reach the river. These polluted particles greatly contribute to the SS chronic pollution downstream Paris during dry weather, through a slow resuspension mechanism of the deposited sediments.

Key words: CSO, heavy metal, river, suspended solids, urban runoff

1. Introduction

Anthropic activities have strongly increased trace metals inputs to the atmosphere and the hydrosphere. In river basins supporting highly devloped human activities, these densified sources may significantly alter aquatic ecosystems quality. Trace metal exports from urban areas mostly consist of land disposal of solid wastes and sewage sludges, emissions to the atmosphere (industrial, domestic heating or automative exhausts) and direct waste discharges in the receiving aquatic ecosystems. On a world wide basis, Nriagu and Pacyna (1988) presented a synthetic evaluation of the inputs of metals due to anthropic activities to the world aquatic ecosystem. Very different patterns of inputs are demonstrated depending on the metal: cadmium inputs are mainly of industrial (including mining) origin, lead inputs are most dominated by atmospheric inputs while the situation is more balanced between domestic inputs, atmospheric inputs and industrial inputs for copper and zinc.

However, the range of values proposed by Nriagu and Pacyna for each type of input is generally wide, which reflects the variability and uncertainties concerning various sources along the world. Backscaling to smaller hydrographic units is

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questionable and would hardly lead to relevant conclusions in terms of local pollution management. In particular, Nriagu and Pacyna data on atmospheric inputs are dominated by direct transfer from the atmosphere to the ocean. The transfer of atmospheric trace metal inputs through river catchments is very poorly known, impervious areas inside a catchment could be major pathways.

Back to the Seine basin (80,000 km^2), and looking at the particular case of zinc, we have raw estimates of atmospheric fallout issued from data by Granier (1991), and Garnaud (in prep.) mostly in the central urbanised fraction of the basin, which lead to an annual estimate of c.a. 2000 tons of zinc, only a fraction of which is expected to be drained to the aquatic ecosystem. A survey based on sampling of representative urban and industrial point discharges and extrapolated to the whole basin lead to an estimate of 2520 t y^{-1} of zinc (Merlet, 1990), 2/3 of which being due to discharges from urban sewerage with or without treatment but containing significant amount of metals from industries connected to the sewer networks. Direct disposal to land (wastes and sludges) are much less known: we would expert that they strongly overpass direct inputs to the aquatic system while their rate of transfer from soils to water is unknown. These raw evaluations suggest that, inside river basins, direct discharges remain a major input to the aquatic ecosystems. A similar conclusion can be drawn for other metals concerned by this study (Pb, Cu and Cd).

In addition to point discharges, urban runoff has been identified as an additional important diffuse source of trace metals to aquatic ecosystems (Torno *et al*., 1985) in urban areas. Numerous studies have been conducted in order to evaluate trace metal concentrations in urban runoff or road runoff in most industrialised countries (Hogland *et al*., 1984; Tasker and Driver, 1988; Aalderlink *et al*., 1990; Murakami and Nakamura, 1990; Saget *et al*., 1995). Ranges of concentrations have been derived, fluxes have also been sometimes computed in small representative urban catchments and extrapolated to wider areas (Songzoni *et al*., 1980, Marsalek, 1991), but measured concentrations can be highly variable and it is always very difficult to get and verify global estimates of urban runoff compared to continuous point source urban or industrial discharges in a conurbation.

The study we developed is based on a receiving medium point of view and on the characterisation of hardly measurable sources (urban runoff in Paris conurbation) by a signature derived from trace metals concentration ratios. This survey allowed to derive fluxes of metals due to urban runoff, to compare them to point sources and to fluxes transported in the river Seine, but also to illustrate some of the transport patterns and the residence time of metals in the receiving aquatic ecosystem, the river Seine. Because trace metals in urban runoff are mostly in a particulate form (Chebbo, 1992; Balades *et al*., 1991), most of our study is focussed onto suspended solids (SS).

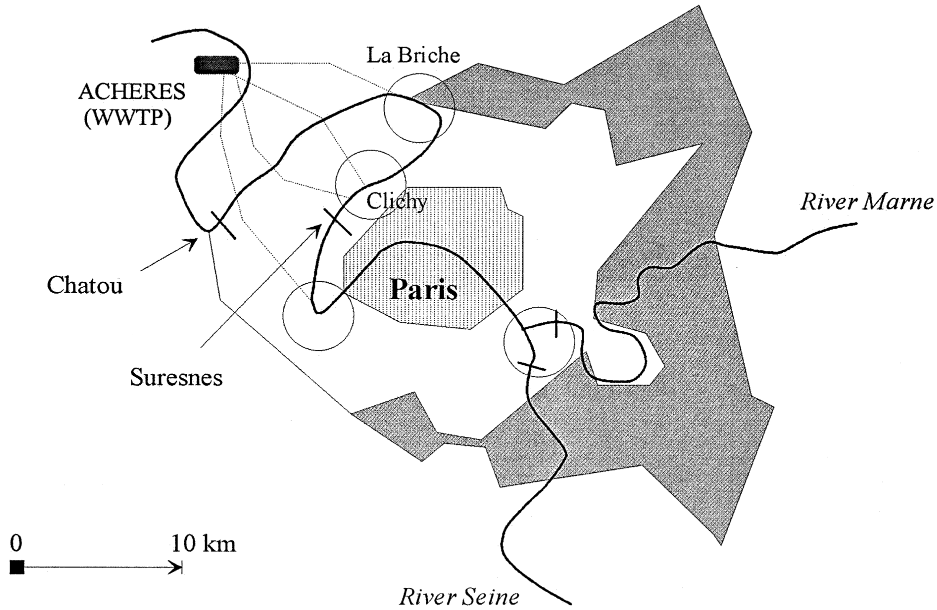

Figure 1. Map of Paris conurbation. The grayed area is drained by a separate sewer system while the centrale white area is drained by a combined system. Circles figure the areas where major combined sewer overflow occur. Small perpendicular bars figure the navigation dams where traps were deployed.

2. Methods

2.1. Study area

Paris urban area has a total population of about 10 million inhabitants. Most of this population is connected to the sewer system, and about 80% of the total amount of wastewaters produced by Paris and its suburbs are conducted downstream Paris to the Achères treatment plant. During strong rain events waste water of poor quality is discharged into the river through combined sewer overflows from the central unitary sewer system which construction started during the nineteenth century and at the outlet of catchments with separate sewer systems in the newer outer part of the conurbation. Large combined sewer overflows (CSO's) occur at the inlet of the larger sewer trunks during rainy events as soon as the sewer trunks are saturated. Areas with the larger CSO's are circled on Figure 1, the most important CSO's of the Parisian sewers system occur at Clichy and La Briche. In 1991, the SIAAP, in charge of the main sewers system of Paris conurbation, implemented a continuous velocity and water level measurement system which enables the evaluation of the flow rates transmitted to the Achères plant or discharged as overflows at Clichy and La Briche. Unfortunately, more than 200 other wet weather outlets have been identified in Paris and suburbs, their discharges are not yet monitored. The unitary catchment of Clichy covers some 12,000 ha, and includes most of Paris city plus souhern and eastern suburbs. During dry weather, an average of 12 m^3 s^{-1} waste water flows through Clichy to Achères treatment plant. At La Briche the unitary catchment is about 5200 ha mostly inside the Seine Saint Denis district, northern from Paris city, the mean dry weather waste water flow is 4 m^3 s^{-1}. Outlet from separate catchments also contribute to wet weather pollution at La Briche. Of course, the present hierarchy between overflows is modified in response to new major equipments constantly being designed by SIAAP and local partners to overcome the negative effects of CSO's. In particular, the new Colombes waste water treatment plant to be achieved within two years will significantly reduce over flows at Clichy.

The base flow of the river Seine is controlled, in summer, by water release from large reservoirs, situated in the upper part of the catchment, on the Seine and its major tributaries. A consequence is that during the whole dry weather period the Seine flow through Paris is rather constant compared to non-impounded rivers.

The studied area includes several reaches, separated by navigation dams. Navigation dams strongly decrease water velocity in summer, down to 0.1 to 0.2 m s^{-1}. The upper station where traps have been deployed was at Suresnes, 17 km downstream Paris center (Figure 1). This site was selected in order to observe the impact of Paris city on river Seine SS heavy metal concentrations, but it also reflects the impacts of two CSO outlets, Ivry-Meudon and St Cloud, located on the left river bank, immediately downstream Paris city. The Chatou station, 45 km downstream Paris center, gathers the impact of wet weather discharges from the whole Parisian conurbation, and particularly those of Clichy and La Briche CSO's except excess water by-passed at the Achères treatment plant during wet weather. Because of the short distance between Clichy and La Briche outlets, the complete transverse mixing of polluted waters issued from Clichy is far from being reached at La Briche. Consequently, it was not possible to install a monitoring station in between both CSO's in order to better evaluate their respective contributions to the global impact observed in the river Seine. A compilation of several tracer experiments and transverse diffusivities assessments (Bujon, 1983; Simon, 1995) allowed us to estimate that Chatou situated in the right arm of Chatou island overestimated the impact of Clichy and La Briche CSO's (also on the right bank) by about 15% during the summer period. This small correction has been further applied when analysing source/impact relationships.

2.2. Sampling and Analytical Procedures

River sediment traps have been derived from devices already functioning in lacustrine and marine environments (Blomqvist and Håkanson, 1981; Gardner, 1980a,b), The turbulence breaking systems have been oversized in order to limitate kinetics energy transport to the bottom of traps and to avoid resuspension of deposited suspended solids. The 70 L plastic body is filled with a honeycomb-like structure made of parallel hexagonal tubes of 50 cm height and 2 cm diameter (Figure 2). Traps are made of polypropylene and polyethylene. The sampler collects the

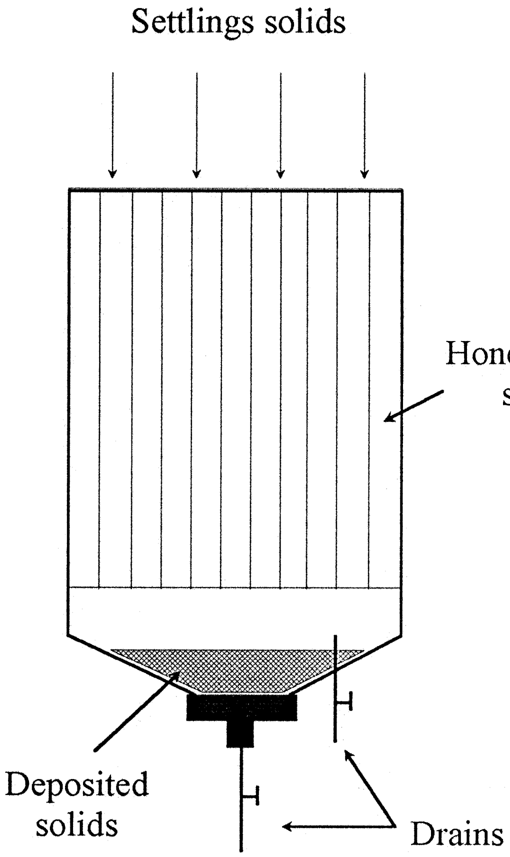

Figure 2. Suspended solid trap.

settleable fraction of suspended solids, 40 cm below the water surface. A conical end allows the recovery of about 3 litres of mud after draining out the overlying water. Several grams (dry weight) of mud are daily concentrated inside the traps, while SS content in the Seine river water is only 10 to 15 mg L^{-1} during summer period. At Clichy, suspended solid samples have been recovered after settling of a 2 m^3 water sample collected by pumping in sewer at constant rate during the overflows. For convenience, the pump was installed some 50 m away from the overflow downstream a grid system eliminating gross solids.

The collected samples were concentrated by centrifugation and dried (110 °C). Organic matter content was estimated by weight loss after a 550 °C calcination. One gram of dried and ground sample was digested by a warm concentrated nitric:perchloric acid mixture (18:2 v:v, 110 °C in a sand bath until dryness) and further diluted with 10% HNO_3 and centrifugated (Merck ultrapure reagents). Only the supernatant was analysed. Particulate heavy metal analyses were performed by flame atomic absorption spectrometry (Perkin Elmer 1100 B) for cadmium,

Table I
Trace metals obtained on the standard Buffalo river sediment from NIST (mg/kg d.w.), mean ± sd

Metal	NIST certified value	Our results (n = 7)
Cd	3.45 ± 0.22	3.05 ± 0.53
Cu	98.6 ± 5	84 ± 3.5
Pb	161 ± 17	162 + 14
Zn	438 ± 12	429 ± 56
Fe	41 100 ± 100	29 121 ± 1954

copper, lead and zinc. Certified material (US NIST 2704, Buffalo River Sediment) has been digested following the same procedure than our samples. This standard has been chosen because its metallic concentrations are in the same range than our samples. Results obtained (Table I) in the case of iron confirm that our digestion is not total, the missing iron (20–30%) is most likely contained in the brownish residue remaining after the last centrifugation. Slightly lower values have also been obtained for cadmium and copper (10–15%) while all zinc and lead seem to have been extracted. It is expected that most of the residual non-recovered fraction of metals is firmly bound to the crystalline minerals and therefore not anthropogenic.

All digestions and analysis have been duplicated providing two completely independent metal concentration results for each sample. We computed the mean and deviation to the mean of both analysis. The mean and maximum observed deviations where 2.3 and 21.5% for cadmium (n = 167), 3.3 and 18% for copper (n = 167), 2.5 and 21% for lead (n = 166), 3.4 and 15% for zinc (n = 169) respectively. We consider that these results (exceptional disagreements between replicates reached 20%, while the mean deviation was only about 3%) are highly acceptable.

The representativity of traps as suspended solids samplers for trace metal analysis has been evaluated by comparing heavy metal levels in suspended solids, after collection by traps, by filtration (Cd, Cu, Pb and Zn) and by continuous centrifugation (Cu and Zn). The comparison with solids recovered by filtration has been realised on several samples collected at Chatou on the 4th and 5th of August 1993, during a dry weather period. One liter water samples were filtrated on acid-washed 0.2 μm porosity polycarbonate filters. Filters were totally digested in a mixture of high purity HNO_3 and HF and analysed by furnace AAS (Huang *et al*., in prep.). Results have been compared with those obtained for two traps simultaneously deployed at Chatou between July 29th and August 8th. Table II displays the results of this experimentation. A continuous centrifuge (Westfalia Separator KA) was deployed at Nogent sur Seine (150 km upstream Paris) in November 1993, and March and June 1995, simultaneously with the traps. Results for copper and zinc are presented on Figure 3. No significant difference has been noted with filtered SS for cadmium concentrations and with the filtered or centrifugated samples for zinc.

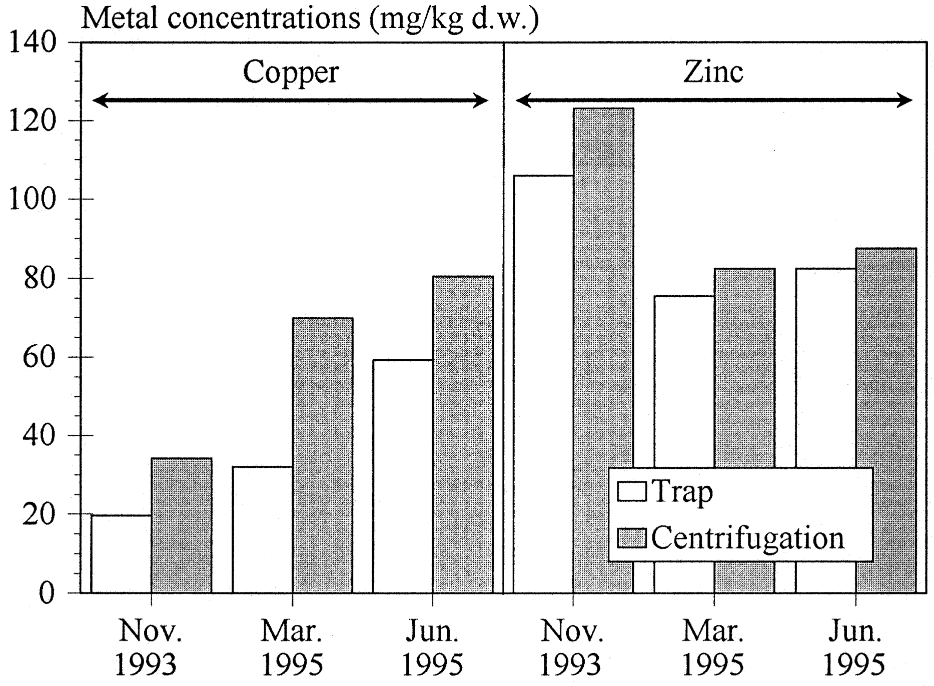

Figure 3. Comparison of Cu and Zn concentration of SS collected by our traps and by continuous centrifugation at Nogent sur Seine.

Lower copper concentrations have been measured in suspended solids collected in the traps compared with centrifugated samples.

This is most likely due to a poor recovery of organic matter, in particular of phytoplankton, in traps because of its lower fall velocity compared with the high fall velocities of aggregates usually observed in this slowly flowing river (Maldiney and Mouchel, 1995). In particular, differences between sampling systems decreases during periods of lower phytoplanctonic activity (November and March) despite higher velocities which could be expected to favour the settling of solids with the higher fall velocities. The higher values of lead we obtained in august 1993 compared to filtrated suspended solids are not explained, this difference may be due to the natural variability of lead concentrations in suspended solids in the river Seine. Table II demonstrates a lower variability of heavy metal concentrations measured in sediment trap samples compared to filtered water samples. Not as expensive as the continuous centrifugation and requiring only very limited support (no electrical power, light weight devices...), traps also allows a time integration hereby reducing the measurements variability. Despite the bias due to the poor recovery of organic (probably planctonic matter), comparisons remain valid between sites because traps deployment was very similar everywhere, in slowly flowing areas

Table II
Metal concentration range of SS collected by our traps, and filtration (Huang *et al.*, in prep) at Chatou site (mg kg^{-1} dry weight)

	Cd	Cu	Pb	Zn
trap (n = 2)	4.5 – 4.9	234 – 242	275 – 277	609 – 620
filtration (n = 5)	2.0 – 7.2	119 – 217	127 – 212	433 – 797

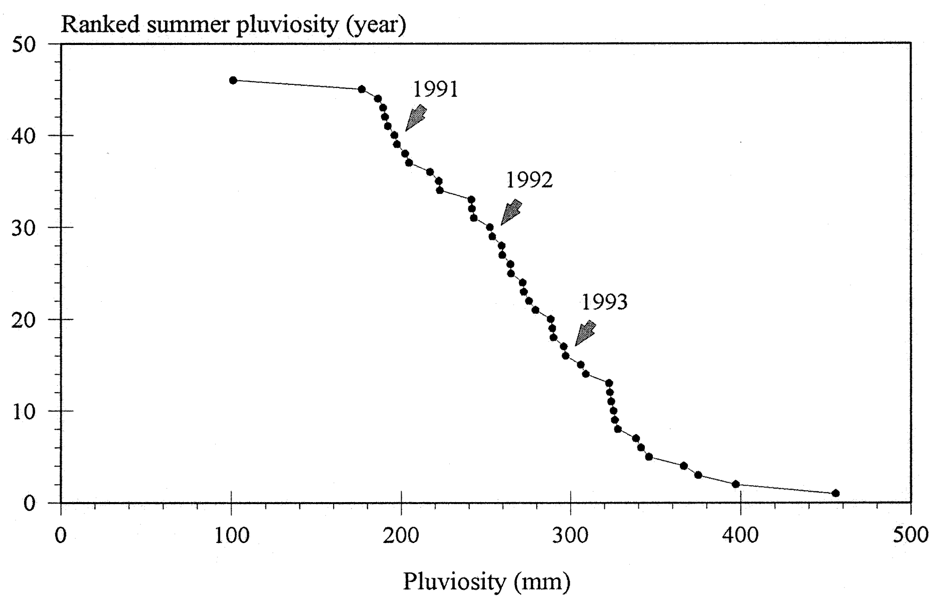

Figure 4. Ranked summer (June to October) pluviosity at Montsouris Paris meteorological station from 1950 to 1995.

few tens of meters upstream navigation dams. Mass balances of particulate metal fluxes may be biaised, and comparison with filtered or centrifugated solids gives an assessment of these errors.

3. Results and Discussion

3.1. Hydrology

The data presented in this paper have been collected in the river Seine during summers of 1991, 1992 and 1993, which have been increasingly wet as shown in Figure 4. Although controlled by upstream reservoirs, the river mean summer flow is also influenced by summer rains. More than 50 yr of river flow allow to estimate the mean summer (June to October) river flow observed in 1993 (170 m^3 s^{-1}) has a return period of 4 yr, while the mean river flows observed in

Table III
Volume, duration and flow rate of Clichy overflows from 1991 to 1993

	Volume (m^3)	Duration (h:mn)	Flow rate ($m^3\ s^{-1}$)	
			average	maximum
average	240 000	6 : 30	8.3	21.6
min.-max.	5 400 – 1 400 000	0 : 40 – 18:00	1.2 – 27.2	2.7 – 93
n	79	79	69	52

Table IV
Main characteristics of the three Clichy CSO's which have been monitored in the river Seine at Suresnes and Chatou (Figures 5 and 6)

Data	Volume (m^3)	Duration (h:min)	Flow ($m^3\ s^{-1}$)		River flow ($m^3\ s^{-1}$)	Return Period (month)
			average	maximum		
06/30/92	500 000	10:00	14.5	41	90	2
08/31/92	600 000	10:30	17.3	35	106	3
09/22/93	1 000 000	16:30	18	35	145	7.5

1991 and 1992 have been commonly overstepped, forty times during the last 52 yr. Naturally, the total volume of wet weather urban discharge is correlated to pluviosity. Total volumes discharged at Clichy from June to October in 1991, 1992 and 1993 were respectively of 1,395,000, 2,982,000 and 9,205,000 m^3. The last figure overestimates wet weather overflows at Clichy because of the occurrence of dry weather overflows due to the management of the sewer system which sometimes requires the closure of trunks for control and repair and consequently overloads other sewer trunks. From the 9,205,000 m^3 discharged in 1993, we estimate that 23% (2,100,000 m^3) are due to dry weather discharges, which have been authorised in October, while the river flow was high enough to dilute waste waters and avoid dramatic consequences such as fish kills.

Duration and volume of CSO's at Clichy and La Briche fluctuate with storm event characteristics. At Clichy, where the more complete database is available from SIAAP, they can last from less than one hour to nearly one day. The discharged volumes vary from few thousands to more than one million cubic meters (Table III). Return periods have been approximately evaluated using periods from June to October only, to avoid interferences with provoked dry weather discharges. The return period of an event of 400,000 m^3 is about 2 months, whereas the largest event we could notice during the 15 months period we studied was as large as 1,800,000 m^3. These return periods are only indicative because (i) the data base is still limited and (ii) dry weather overflows can still interfere with the time series of wet weather overflows. The characteristics of the 3 major CSO's which have been studied are given in Table IV. Both 1992 events are usual, with low volumes

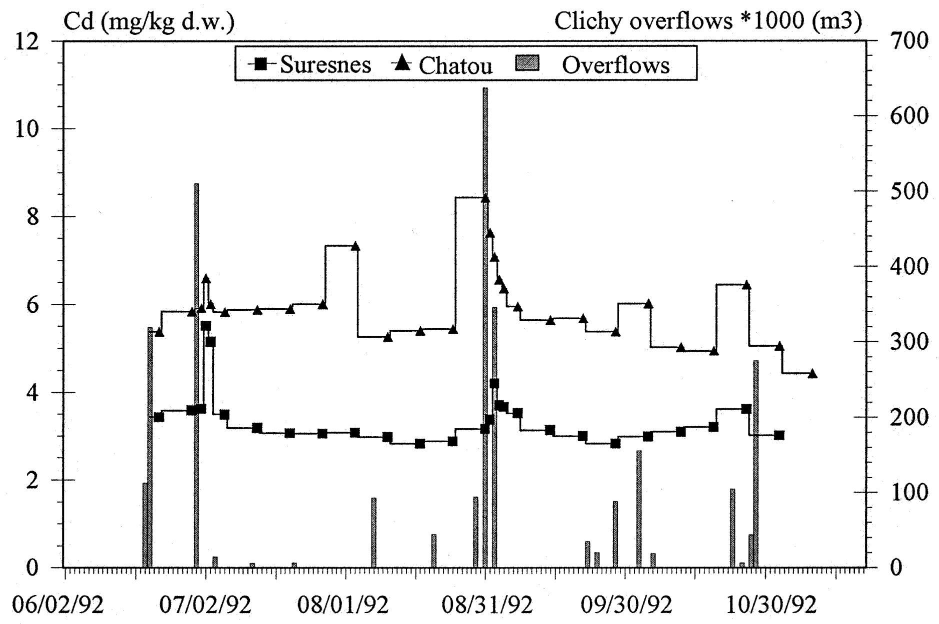

Figure 5. Cadmium level evolution in SS sampled at Suresnes and Chatou sites from June to October 1992.

and short return periods. The third event, in September 1993, is more important. However, it happened simultaneously with high river flow conditions. Thus, its impact may not be as significant as it could have been with river flow conditions similar to 1991 or 1992 ones.

3.2. Heavy metals content of suspended solids

Samples have been collected during summer 1991 to 1993 (i.e. from June to October), weekly during dry weather, and daily during the week following major CSO's. On the following Figures (5 and 6), heavy metal particulate level evolution is represented versus time. Patterns show the measured heavy metal levels, whereas lines figure the sampling periods, i.e. the integrated time corresponding to each sample. Histograms display the Clichy CSO volumes. They have to be considered as indicators of the strength of the rain event which occurred over the city, but it should not be concluded that Clichy is the only discharge inside Paris conurbation. Figure 5 presents the results which were obtained during a complete summer period (1992) for cadmium is suspended solids at Suresnes and Chatou. Cadmium levels are always higher at Chatou; they keep a stable value during dry weather and they increase after rain events large enough to generate a strong CSO. Observations are similar for lead and zinc, but not for copper. The evolution of particulate metals daily concentration is described for each major storm event on Figure 6.

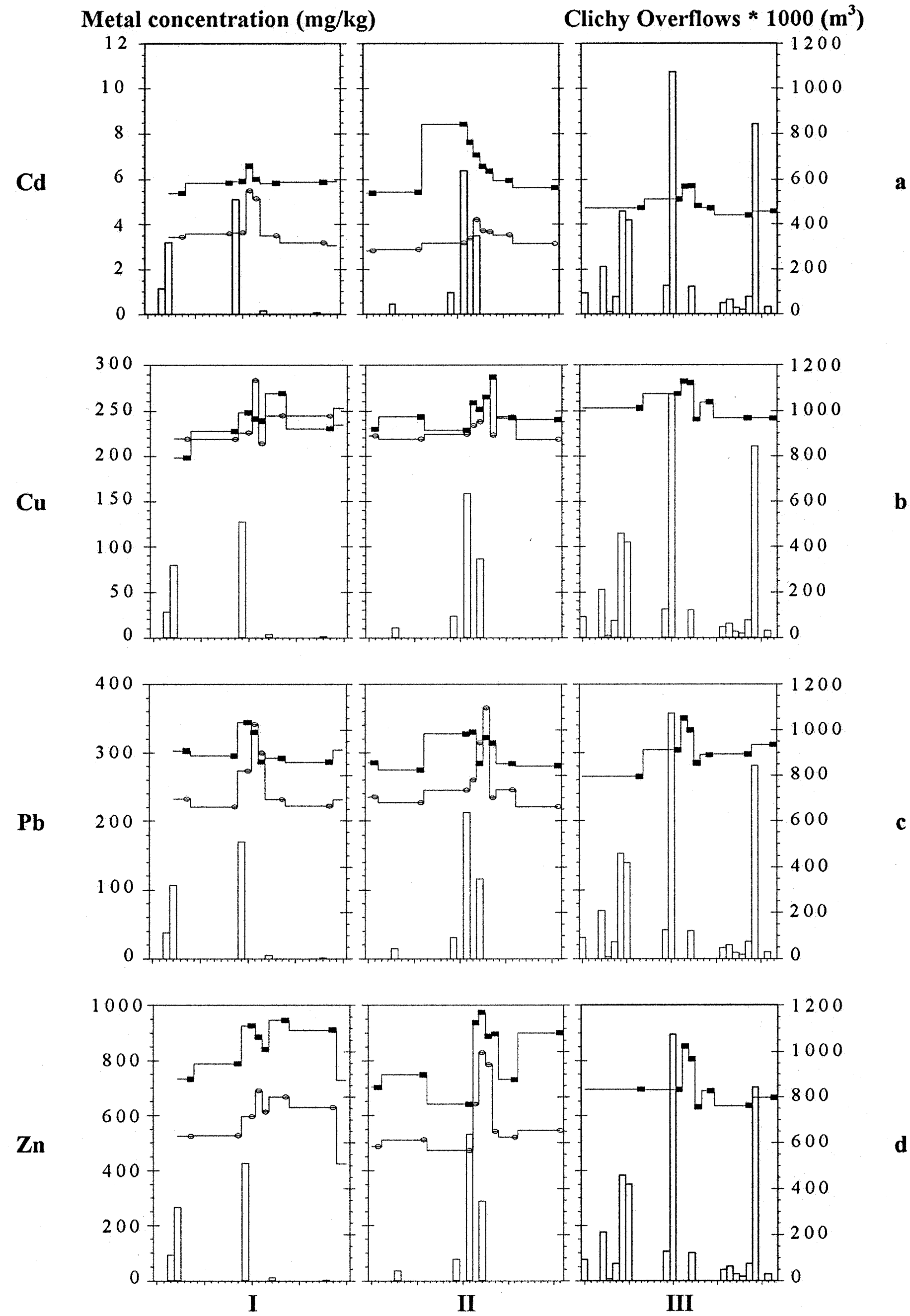

Figure 6. Metals concentration variations in SS sampled at Suresnes (⦰) and Chatou (■) from 17/6/92 to 15/7/92 (I), from 16/8/92 to 13/9/92 (II) and from 8/9/93 to 6/10/93 (III), and volume of Clichy overflows (□): (a) Cd, (b) Cu, (c) Pd and (d) Zn.

Copper concentrations are very close at both sampling sites and they do not seem much modified by CSO's (Figure 6b). On the contrary, in the case of essentially urban-born metals as cadmium, lead and zinc, metal concentrations increase from Suresnes to Chatou (Figures 6a, c, and d). Wet weather discharges from overflows and separate catchments outlets could contribute to the observed increase during dry weather periods, but other unknown (non-authorised) urban sources cannot be excluded. After major overflows, concentration increases are noticeable for all three metals. Concentrations at Suresnes reach the higher values observed at Chatou during dry weather. They remain constant during dry weather, and increase significantly just after a storm event. Thus a chronical urban pollution, as well as a chock effect of wet weather periods are observed on river Seine SS metal concentrations.

The observations resulting from the previous graph examination can be confirmed by a statistical analysis of Suresnes and Chatou data. We separated the set of sample into 'after overflow' samples and 'dry weather' samples. 'After overflow' samples are somehow arbitrarily defined as samples collected in traps less than 2 days after a rain event which lead to an overflow larger than 100,000 m^3 at Clichy. Results are presented in Table V. Student T-test have been used to compute the statistical significance of the difference between means for each metal and each station. For copper, the difference between the average concentrations for dry and wet periods is not significant, but in the case of cadmium, lead and zinc, the tests indicates that the differences between average concentrations for dry and wet periods are significant at 99, 99.9, and 95% respectively. Very similar statistical significance levels are obtained for both stations.

It is noticeable that the metal which concentration do not appear to increase from Suresnes to Chatou is also the metal which does not show any increase after sewer overflows. This suggests a non urban or very particular non-diffuse major source of copper. This would also suggest that urban runoff very strongly contributes to metal (lead, zinc and cadmium) fluxes from the Parisian urbanized areas to such an extent that the chronical pollution demonstrated by dry weather particulate metal concentrations is influenced by wet weather discharges.

3.3. Fate of Suspended Solids Issued from CSO's

Although the immediate influence of urban runoff onto metal concentrations is statistically established, mass balances still have to be assessed. Suspended solids fluxes in the river Seine inside Paris can be estimated from river flow rates monitored by the Service de Navigation de la Seine and from suspended solid concentrations that we regularly measured during periods of sediment trap deployment. Fluxes at Clichy outlet can also be estimated from discharged volumes monitored by SIAAP and from the mean suspended solids event mean concentration measured by Paffoni (1994) who carefully analysed a series of 23 overflows at Clichy in 1990 and 1991 (254 ± 128 mg L^{-1}). Finally, oxygen concentration records at Chatou (Mouchel

Table V
Mean metal concentration values within Clichy and La Briche CSO's as well as in river Seine SS during summer 1992 and 1993 (June to October) during dry (dw) and wet weather periods (ww)

		Cd	Cu	Pb	Zn
SEINE					
Suresnes	(n = 39)	3.4 ± 0.7	237 ± 22	251 ± 39	566 ± 98
Chatou	(n = 39)	5.6 ± 0.9	242 ± 21	293 ± 21	782 ± 110
Suresnes	dw (n = 39)	3.1 ± 0.24	234 ± 20	231 ± 13	529 ± 63
	ww (n = 10)	3.9 ± 0.89	240 ± 25	281 ± 47	622 ± 117
	t-test	0.995	–	0.999	0.95
Chatou	dw (n = 24)	5.3 ± 0.7	241 ± 20	283 ± 13	749 ± 109
	ww (n = 15)	6.2 ± 1.0	243 ± 23	309 ± 20	835 ± 93
	t-test	0.99	–	0.999	0.95
CSO's					
La Briche	our results (n = 3)	15	502	543	2591
Clichy	our results (n = 14)	7 ± 2.5	638 ± 160	773 ± 313	6661 ± 2065

et al., 1994) show most important sags when polluted waters pass at Chatou, and allow to precisely define the trap samples which have been under the influence of water masses issued from Clichy overflow, as well as the fraction of the water which readily contributed to suspended solids collected in a given trap sample.

The combination of all previous informations allows to compute the theoretical dilution of Clichy suspended solids into Seine river ones for any trap sample. α_{dil} is defined as:

$$\alpha_{\text{dil}} = 100^{*} \frac{(SS_{\text{Clichy}})}{(SS_{\text{Seine}}) + (SS_{\text{Clichy}})}$$

where SS_{Seine} is the amount of suspended solids originating from the Seine river which transited at Chatou during the period of deployment of the trap and SS_{Clichy} is the amount of suspended solids which is expected to transit at Chatou during the same period if no deposition occurs during their 20 km transit from Clichy to Chatou.

The fraction of suspended solids issued from Clichy may also be computed from trace metal concentrations, by comparing concentrations characterising the preceding dry weather period, in the trap concerned by the waste waters issued from the overflow and by metals concentrations in the overflow. The fraction is given by:

$$\alpha_{\text{metal}} = 100^{*} \frac{C_{\text{ww}} - C_{\text{dw}}}{C_{\text{cso}} - C_{\text{dw}}}$$

where C_{ww}, C_{dw} and C_{CSO} are particulate metal concentrations in the Chatou trap sample after a CSO event, in the Chatou trap sample before the event and in the Clichy overflow respectively. Such computations are only relevant for the three major events we chose to monitor with a daily trap sampling frequency. For other smaller events, we kept the weekly frequency and suspended solids from the overflows have been too much diluted to expect any significant impact.

The use of metals as tracers of suspended solids is only valid in as the influence sorption/desorption processes is minimal. We have no direct evidence from sorption experiments performed in the real conditions encountered in the river Seine during wet weather. However, sequential extractions revealed that while metals in street dusts were highly exchangeable (Harrison *et al.*, 1981; Lebreton and Thévenot, 1992) only a very small fraction of metals contained in sewers suspended solids was exchangeable (Harison and Wilson, 1985b; Flores-Rodriguez *et al.*, 1994; Lebreton and Thévenot, 1992), except under some circumstances for cadmium. Experimental desorption experiments have also been performed in batch or flow through experiments (Lebreton *et al.*, 1993) with higher suspended solids concentrations than those observed in the river Seine confirmed the strong binding of metals to suspended solids showing that not more than 2% of the total metal content is suspended solids could be released within 5 days.

The computed α_{metal} values have to be considered with care since the variations of metallic concentrations in trap samples before and after the overflow are in the same order of magnitude as the experimental reproducibility or as the standard deviation of dry weather concentrations. The reproducibility of all trace metal analysis on river suspended solid samples gathered in Table VI is better than 3%. The larger source of uncertainties is the choice of the dry weather reference value and of the Clichy reference value for the event of September 1993 since no direct data have been obtained in this overflow. While the 'optimum' α_{metal} is computed using the last concentration obtained immediately before the rain event, the range of values ([] in Table VI) is obtained by choosing the mean dry weather concentration more or less one sigma (Table V) or mean Clichy concentration more or less one sigma. In the case of cadmium in particular, the variability of α_{metal} estimates is too large to be significant, mostly because observed concentrations in Clichy suspended solids are in the range of observed river values. Estimates for this metal will not be considered in the next paragraph.

The other metals give a more coherent picture of the behaviour of suspended solids issued from Clichy overflows. α_{metal} values are much lower than α_{dil} values demonstrates a highly non conservative behavior of suspended solids issued from Clichy. Zinc data would lead to an estimate of 95% loss between Clichy and Chatou, lead or copper data give lower loss estimates (80% only). The losses should be considered as minimal, since other overflows and discharges from separate urban catchments occurred simultaneously and also contributed to the increase of metal concentration on the trap samples where suspended solids issued from Clichy were expected. Since Clichy overflow suspended solids are particularly highly loaded

Table VI

Comparison of (α_{dil}) SS fraction and (α_{metal}) SS metal fraction from Clichy CSO's which have been monitored at Chatou on 06/30/92, 08/31/92 and 09/22/93

	C_{CSO} (mg kg^{-1} d.w.)	C_{dw}	C_{ww}	α_{metal} (%)
06/30/92 overflow, $57 \leq \alpha_{dil} \leq 84\%$				
Cd	6.3	5.4	5.9	55.6 [0 – 76.5]
Cu	723	198	248	9.5 [0 – 5.4]
Pb	982	303	345	6.2 [7.1 – 10.5]
Zn	8,366	733	926	2.5 [0.9 – 3.7]
08/31/92 overflow, $47 \leq \alpha_{dil} \leq 74\%$				
Cd	5.1	5.4	7.6	–
Cu	598	243	259	4.5 [0 – 10.1]
Pb	803	275	330	10.4 [6.7 – 11.3]
Zn	7,538	748	937	2.8 [1.2 – 4.3]
09/22/93 overflow, $60 \leq \alpha_{dil} \leq 87\%$				
Cd	7	4.7	5.7	43.5 [0 – 45.8]
Cu	638	253	282	7.5 [6.6 – 14.6]
Pb	773	265	350	16.7 [11.3 – 15.9
Zn	6,661	695	853	2.6 [0 – 3.5]
				[2 – 4.1]

with zinc compared to other metals (Table VI), the influence of other discharges being lessened for this metal and α_{zinc} data have to be considered as the best loss estimate.

It is most likely that the observed losses are due to a very strong deposition of most of the discharged solids. Such an in-stream settling behaviour of suspended solids issued from wet weather discharges had already be mentioned (Harremoës, 1982; Lavallée *et al*., 1984): it is likely enhanced in a slowly flowing river such as the river Seine. More recent studies have confirmed the high settling velocities of sewer suspended solids (Chebbo and Bachoc, 1992; Michelbach and Wöhrle, 1994). Since it appears that the observable immediate impact of Clichy overflows in terms of metal concentrations is only 5% of what it could be, it is now necessary to assess what is the contribution of the remaining 95% to the chronical trace metal pollution observed, in summer, in river Seine suspended solids.

3.4. EVALUATION OF FLUXES OF PARTICULATE METALS IN PARIS CONURBATION

The importance of wet weather discharges during a whole summer, i.e. June to October, can be evaluated by comparing urban wet weather metal fluxes with river Seine metal fluxes or with trace metal fluxes coming in and out of Achères waste water treatment plant (WWTP), the major plant inside Paris conurbation. Clichy CSO's metal fluxes were estimated from known volumes discharged and from mean suspended solids concentrations (Paffoni, 1994) and mean metal concentrations (Table V). For an homogeneous rain of 10 yr return period, Dégardin (1991) estimated that the volume discharged at Clichy was 9% of the total volume discharged in Paris conurbation. More recent studies based on careful hydraulic simulations of the global sewer network (Mazaudou, personal communication) confirmed this evaluation and indicated that, for more frequent rainfall, the relative importance of Clichy reaches 15% for 6 month return period rainfalls. The total wet weather discharges, in the Suresnes-Chatou river reach, appear as high as 50% of the wet weather water discharges of the total conurbation. To estimate global particulate metal fluxes, we just expanded the fluxes estimated at Clichy using the above ratio. Of course, this procedure is quite rough, and we have no evidence that the quality of water discharged in other outlets of greater Paris is really comparable with the quality observed at Clichy, since no existing data set allows such a precise evaluation.

Particulate metal fluxes in the river Seine have been calculated from daily river flow rates, from suspended solids loads in Seine river water measured after each trap sampling, and trace metals concentrations measured in trap samples. When the sampling period was lower than five months (i.e. in 1991), fluxes evaluation have been simply extrapolated to a five months. Achères total metal in- and outfluxes have been calculated using daily water discharges in major trunks feeding the Achères WWTP and average daily concentrations of trace metals in waters coming in and out of the plant (Rougemaille, 1994, 1996).

Table VII demonstrates that metal fluxes discharged during rain events are much lower than metal fluxes reaching the WWTP. Only during the rather wet summer of 1993, does the estimated wet weather zinc flux represent more than 40% of the total flux reaching Achères. But it should be reminded that the total wet weather outflux has been extrapolated from data at Clichy which is particularly highly loaded with zinc. It is very difficult to determine the fraction of metals arriving at Achères which are issued from urban runoff. Indeed, metal concentrations have been determined on average daily samples which may include both wet and dry periods, and a significant amount of solids issued from runoff may settle in sewers (Laplace *et al*., 1992) and contribute later to dry weather fluxes. However, lead and zinc wet weather fluxes can be equal to or higher than fluxes discharged by Achères after treatment, depending on total summer rainfall. For example, wet weather discharges are more important than fluxes after treatment at Achères during year 1993, which had the highest pluviosity (Figure 4).

Increase of particulate trace metals fluxes from Suresnes to Chatou are not always well explained by the estimated wet weather discharges (about 50% of the total wet weather fluxes are expected to occur between Suresnes and Chatou). For cadmium, wet weather discharges cannot explain the observed increases in this river

Table VII

Metals loadings (tons) during June to October periods for years 1991, 1992, and 1993. Wet Weather Discharge (WWD) and fluxes in the river Seine at Suresnes and Chatou are particulate fluxes. Fluxes at Achères (in and out) are total metal fluxes. WWD have been extrapolated from water quality at Clichy CSO, fluxes at Suresnes, Chatou and Achères have been measured (Estèbe, 1996, Rougemaille, 1996)

	Cd			Cu			Pb			Zn		
	1991	1992	1993	1991	1992	1993	1991	1992	1993	1991	1992	1993
WWD	0.01	0.03	0.07	1.2	2.9	6.5	1.5	3.6	7.9	13	31	68
Suresnes	0.05	0.05	–	2.7	3.4	–	2.9	3.5	–	7.3	7.8	–
Chatou	0.11	0.09	0.06	3.1	3.9	3!	3.9	4.5	3.7	9.5	12.3	9.3
Achères (in)	1.34	1.62	1.88	73	74	69	32	35	34	194	171	162
Achères (out)	0.35	0.2	0.5	19	8.3	21	5.3	3.9	4.6	38	31	37

reach. For copper and lead, wet weather discharges are in good agreement with the observe increases in river. For zinc, wet weather discharges seem much too high, which may again be an artefact due the extrapolation from Clichy data. We conclude that, except for cadmium, the observed concentration increases through Paris may be entirely due to wet weather discharges. Other probably local sources have to be invoked for cadmium. In particular, Cd/Zn ratios are much higher in waters entering Achères WWTP that in wet weather discharges: this would indicate the occurrence of dry weather cadmium discharges (probably from industries), which could be strongly diluted by cadmium poor, but zinc rich, suspended solids during rain events. It likely that such unauthorised discharges occur between Suresnes and Chatou.

3.5. Fluxes validation using tracer ratios

Given the uncertainties entailing our preceding global wet weather discharges estimates, a validation is still necessary. Table VIII gathers Zn/Pb ratio issued from our own measurements in the river Seine and sewer solids but also issued from studies for Paris conurbation and from international urban runoff water quality programs. To get representative means, we selected sampling programs with a large number of sites and/or events. Concentrations in suspended solids are scare and we often had to compute Zn/Pb ratio for total samples. Nevertheless, ratio for total samples and ratio for particulate matter can be compared because the dissolved plus colloidal fraction of metals in sewer water in usually low (Astruc *et al*., 1979; Harrison and Wilson, 1985; Chebbo and Bachoc, 1992; Hewitt and Rashed, 1992). To get a comprehensive image of Zn/Pb ratio in Paris conurbation, we sometimes had to use data from sewer deposits. Although total concentrations in deposits are probably lower than concentrations in suspended solids because of a grain-size effect, metal concentration ratios should be comparable. Moreover, sewer deposits are integrated samples, they are more representative than data collected from few suspended solid samples randomly collected. Table VIII demonstrates that higher Zn/Pb ratio can be measured in the lower part of the sewer system (inputs to Achères or Clichy overflows) while much lower rations are observed in the upper part of the sewer network, mostly equipped with separate sewers. The reasons for this evolution are not well understood.

We observe that the Zn/Pb ratio in suspended solids from the river Seine increases from the upstream reference (Samois) to Alfortville (just entering Paris city), is constant from Alfortville to Suresnes and strongly increases again from Suresnes to Chatou. The progressive evolution is the consequence of a regular loading with an unknown urban source of suspended solids having a high Zn/Pb ratio, which seems to be a tracer of urban pollution in Paris conurbation. As shown by Table VIII, several elements argue in favour of urban runoff as an interesting candidate: (i) Zn/Pb ratio is particularly high in Paris conurbation compared to other urban

Table VIII

Zn/Pb representative ratios in urban runoff, combined sewers during wet weather and in the river Seine summer (° suspended solids, * total concentrations, ** sewer deposits)

International References			
Urban runoff	U.S.A.	1.5 [0.3 – 7]*	Tasker and Driver, 1988
Urban runoff	Lelystad (Netherlands)	6.3*	Aalderink *et al*., 1990
Combined	Sweden	3.5*	Hogland *et al*., 1984
Combined	Munich	3.2*	Schulz *et al*., 1994
Upstream Paris			
Urban runoff	Sediment from several ponds	0.6 – 1.7 °	Flores-Rodrigues *et al*., 1994
Combined	Montreuil	2.9**	IRH 1983
Combined	33 sewer trunks	1.2 – 1.6*	Val de Marne district 1995
Downstream Paris			
Combined	Gagny city	3**	IRH, 1983
Combined	5 sewer trunks	1.8 – 5*	Seine St Denis district, 1991
Combined	Clichy	6.7*	Paffoni, 1994
Combined	Clichy	9.9 °	Estèbe, 1996
Combined	La Briche	4.8 °	Estèbe, 1996
Collectors arriving at Achères WWTP (wet and dry weather)			
Combined	St Denis	10.3*	Rougemaille, 1996
Combined	Clichy Argenteuil	10.1*	Rougemaille, 1996
Combined	Clichy Bezons	12.6*	Rougemaille, 1996
Combined	Sèvres	7.6*	Rougemaille, 1996
River Seine			
	Bois le Roi	1.9 °	Estèbe, 1996
	Alfortville	2.2 °	Estèbe, 1996
	Suresnes	2.2 °	Estèbe, 1996
	Chatou	2.7 °	Estèbe, 1996

areas in the world and (ii) the Zn/Pb ratio is higher in sewers downstream Paris where the higher increase of the ratio in the river Seine is observed.

Knowledge of trace metal ratio is enough to determine the composition of a binary mixture. Assuming that suspended solids observed at Chatou result from the perfect mixture of suspended solids coming from upstream and suspended solids from an additional source, expected to be wet weather discharges, we can determine the origin of metals observed at Chatou as a function of β_{up}, β_{down} and β_{AS}, respectively Zn/Pb ratios in suspended solids at the upstream station, at Chatou (downstream) and in the additional source. Simple arithmetics allow to verify that

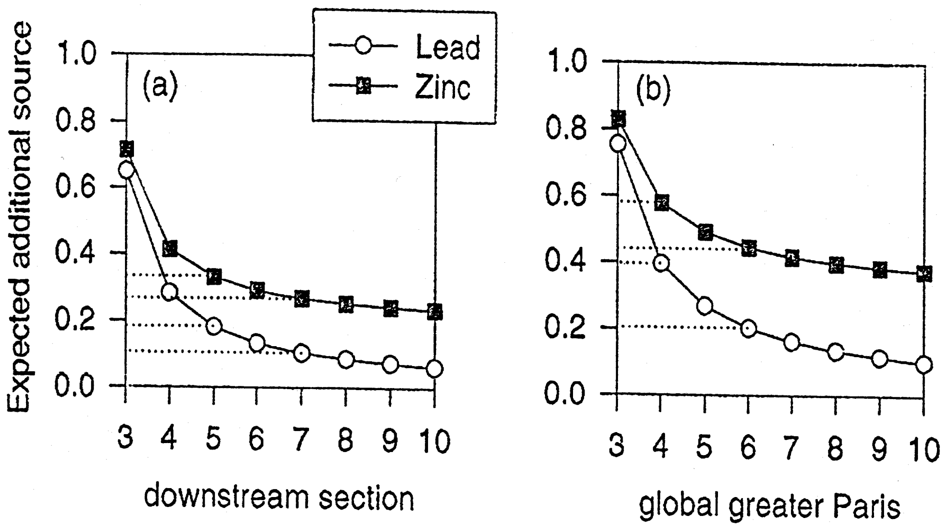

Figure 7. Fraction of metals issued from an additional source as a function of its Zn/Pb ratio; (a) for the Suresnes-Chatou river reach and (b) for the whole conurbation.

the ratio between lead issued from the additional input and upstream river inputs is given by:

$$\frac{\alpha.\mathrm{Pb}_{\mathrm{AS}}}{1-\alpha)\mathrm{Pb}_{\mathrm{up}}} = \frac{\beta_{\mathrm{down}} - \beta_{\mathrm{up}}}{\beta_{\mathrm{AS}} - \beta_{\mathrm{down}}}$$

where α is the fraction of suspended solids issued from wet weather discharges at Chatou. For zinc, the ratio is given by:

$$\frac{\alpha.\mathrm{Zn}_{\mathrm{AS}}}{(1-\alpha)\mathrm{Zn}_{\mathrm{up}}} = \frac{\beta_{\mathrm{AS}}}{\beta_{\mathrm{up}}} * \frac{\beta_{\mathrm{down}} - \beta_{\mathrm{up}}}{\beta_{\mathrm{AS}} - \beta_{\mathrm{down}}}.$$

While β_{up} and β_{down} have been well characterised in summer 1992 (2.23 at Suresnes and 2.73 at Chatou), β_{AS} can only be evaluated at some particular places in the greater Paris sewer system and is only partly known (Table VIII). With regards to the Suresnes-Chatou river reach, its value should be in the range 5 (La Briche) to 7 (Clichy), and we have no information about the composition of other less important wet weather discharges occurring between Suresnes and Chatou. A lower ratio should be considered to evaluate the potential importance of the global conurbation since lower ratios have been observed upstream Paris in catchments with separate sewers and in sewer deposits in Val-de-Marne district.

The contribution of the additional source in Chatou suspended solids as computed from Zn/Pb ratios is demonstrated in Figure 7. 30% of zinc in suspended solids at Chatou should come from wet weather discharges occurring between Suresnes and Chatou and 15% of lead. About 50% of zinc carried by particles at Chatou would come from wet weather discharges from the whole conurbation and 20 to

40% lead. These estimates are only in poor agreement with direct flux evaluation reported in Table VII. In summer 1992, lead inputs from wet weather discharges are similar to upstream inputs in the Suresnes-Chatou reach, and zinc inputs are much higher. In addition to wet weather discharges a supplementary source with a very low Zn/Pp ratio could explain the observed ratio at Chatou. However, since total inputs (upstream plus wet weather) are in strong excess compared to the outputs at Chatou, an supplementary source is unlikely. A more acceptable explanation would be that the pool of suspended plus freshly deposited solids in the Suresnes-Chatou reach is indeed not well mixed. A significant fraction of the wet weather inputs would remain firmly bound to the bottom after settling, and would not participate to the exports at Chatou, thus enabling a rather low Zn/Pb ratio compared to the ratio we could observe in the case of the mixing hypothesis.

4. Conclusion

This study, based on the example of Paris conurbation, demonstrates the importance of wet weather diffuse sources of trace metals in urban areas. On a long term basis, while fluxes of cadmium and copper are much higher in effluents from the major waste water treatment plant, zinc and lead fluxes due to diffuse wet weather discharges dominate fluxes from the WWTP after treatment during wet years. Clearly, different origins of trace metal in anthropic activities in urban areas reflect into different loading patterns to the receiving hydrosystem.

After an important rain event, suspended solids, which carry most of the trace metals transported in sewers, very rapidly settle down to the bottom of the river. Only few percents of the instantaneous inputs remain in the water column after one day. Polluted solids deposited at the bottom after events are progressively mobilised during dry weather, even when the river flow is very low, and significantly contribute to the total export of zinc and lead by the river Seine out of Paris conurbation. However, given the very high inputs of particulate metals by wet weather dicharges during summer compared to upstream inputs by the river Seine, the concentration increase observed throughout the conurbation only requires a fraction of the total load by wet weather discharges, a fraction of which is only exported during the first high water period following summer. It becomes obvious that the metallic contamination of the river Seine will not decrease as long as urban wet weather discharges will be directly evacuated to the river.

This work illustrates the major interest of better understanding the fate of suspended and freshly deposited solids in rivers. They may completely modify the pattern of impacts of pollutions, even during low flow periods where the transport of suspended solids is often regarded as a secondary problem compared to suspended solid transportation during flood events.

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