

## Characterization and transfer of heavy metals in two different urban stormwater infiltration work sediments : an experimental approach

Caractérisation et dynamique des métaux lourds dans les sédiments de deux ouvrages d'infiltration des eaux pluviales : approche expérimentale

Delolme C.\*, Béchet B.\*\*, Fevrier L.\*\*\*, Floriani M.\*\*\*, Faure P.\*\*\*\*, Gérémia R.\*\*\*\*\*

\*Laboratoire des Sciences de l'Environnement, Ecole Nationale des travaux Publics de l'Etat, Rue M. Audin, 69518 Vaulx-en-Velin, France  
[Cecile.delolme@entpe.fr](mailto:Cecile.delolme@entpe.fr)

\*\*Division eau et Environnement, LCPC, Centre de Nantes, Route de Bouaye - BP 4129 44341 Bouguenais Cedex, France, [bechet@lcpc.fr](mailto:bechet@lcpc.fr)

\*\*\*Laboratoire de Radioécologie et d'Ecotoxicologie, IRSN/DEI/SECRE, BP 1, 13108 Saint Paul Lez Durance Cedex, France, [Magali.floriani@irsn.fr](mailto:Magali.floriani@irsn.fr)

\*\*\*\*UMR G2R 7566, Université Henri Poincaré, BP 239 , 54506 Vandoeuvre Les Nancy Cedex, France, [pierre.faure@g2r.uhp-nancy.fr](mailto:pierre.faure@g2r.uhp-nancy.fr)

\*\*\*\*\*Laboratoire d'Ecologie Alpine, BP 53, 2233 Rue de la Piscine , 38041 Grenoble Cedex 9, France, [roberto.geremia@ujf-grenoble.fr](mailto:roberto.geremia@ujf-grenoble.fr)

### RESUME

Ce travail a pour objectif d'étudier la mobilisation du Cadmium, du Cuivre et du Zinc accumulés à la surface des bassins d'infiltration d'eaux pluviales dans le cas de phase d'infiltration/drainage ou lors d'un front de salinité. Des sédiments de surface sont échantillonnés dans deux sites différents. Malgré la diversité des constituants solides, leurs caractéristiques physico-chimiques globales (teneur totale en éléments chimiques et analyse moléculaire de la matière organique) sont proches. Les études macroscopiques en colonnes de laboratoire montrent que les métaux sont peu mobilisables (moins de 1% de la teneur totale) et bien corrélés à la solubilisation du COT. Les phases de drainage favorisent l'éluion du Zinc sous forme soluble, alors que le front de salinité favorise l'éluion du Cuivre sous forme soluble et colloïdale.

### ABSTRACT

This work aims at studying the release of Cadmium, Copper and Zinc that accumulate at the surface of rainwater infiltration ponds in the case of infiltration/drainage phases or during a salinity front. Sediments were sampled at two different sites. Despite the heterogeneity of the particles present in the sediments, their physico-chemical characteristics (total element content and molecular analysis of organic matter) were close. The results of laboratory columns experiments show that heavy metals are strongly sorbed on the sediment (less than 1% released in both conditions) and their elution is correlated to the one of TOC. The infiltration/drainage phases enhance the release of soluble Zinc whereas the salinity front leads to a strong solubilization of soluble and colloidal Copper.

### KEYWORDS

Heavy metals, urban soils, organic pollutants, transfer, colloids, microorganisms.

## 1 CONTEXT AND OBJECTIVES

The stormwater produced by urban areas contain heavy metals and organic pollutants mostly in the suspended matter. In the case of infiltration works, the suspended matter accumulate at the surface of the receiving soil and threaten the quality of the subsoil and the receiving aquifer (Winiarski et al, 2006).

Among all the toxic metals that are present in this type of sediment, the most concentrated ones are Zinc, Lead and Copper (Lee et al 2005 ; Clozel et al, 2006). Sequential extraction on different urban sediments have led to the conclusion that Cd is highly exchangeable such as Zn and Pb and Cu mostly sorb on organic matter and oxides and could become mobile with changing physico-chemical conditions (Clozel et al 2006, Lee et al 2005, Kirpichtchikova et al, 2006). As far as the organic matter is concerned, previous works have shown the high hydrocarbon content in these materials (Durand et al., 2004). Urban atmospheric deposition and road runoff imply important organic pollutant to be accumulated in sediments. These organic pollutants are mostly inherited from petrogenic (used engine oils, road asphalts, fuel) and pyrogenic sources (incomplete fuel combustion).

Few informations are available on the main mechanisms controlling the retention and/or mobility of heavy metals at the surface of these specific works. The extraction protocols described before are usually used to study the potential mobility of contaminants in soils. But as they are performed with strong reagents and in static conditions, this approach has to be completed with column experiments in dynamic conditions to study the coupled effect of reactivity and flowrate on trace metals mobility. Moreover, a better description of the microbial role on the mobility of metals has to be done.

The purpose of this work is to study the main physico-chemical conditions that can enhance the mobility of heavy metals from the polluted surface in a soluble or colloidal form. This research work focuses on the effect of two different changing environmental conditions on the mobility of the metals initially concentrated in the surface sediments of two different infiltration works: infiltration/drainage events, modification of the salinity of the leaching water. We will only deal with the mobility of Zn, Cd and Cu as they are the most mobile metals and their reactivity towards organic matter is known to be different. After a macro and micro characterization of both materials, the mobility was mainly macroscopically evaluated through laboratory column experiments. This paper outlines some results obtained within a two years multidisciplinary research program funded by the ANR ECCO (France).

## 2 MATERIALS AND METHODS

### 2.1 Sampling sites

The 10 to 20 first cms of the surface soil basins were collected and were constituted mainly from the accumulation of the suspended matter of the entering water and was called "sediment". The distinction between the polluted and non polluted zone was appreciated during the sampling.

#### 2.1.1 Cheviré

The sediment was sampled in a retention-infiltration pond receiving highway runoff waters of the main bridge of Nantes, France (drainage surface of 19000 m<sup>2</sup>). Opened in 1991, the Cheviré bridge supports nowadays an average daily traffic of 90 000 vehicles. The surface of the basin is 780 m<sup>2</sup>. The material was taken in December 2004 in the zone near the overflow of waters to the Loire. The 25-cm thick layer was sampled from 4 positions to constitute a mean sample.

### **2.1.2 Chassieu**

The second site is situated near Lyon (OTHU experimental Site) and collects the runoff water from a peri urban and industrial zone (185 ha). It is composed of a settling compartment and an infiltration one (1 ha). The sediments were sampled at the surface soil of the infiltration basin in november 2004. 5 differents samples of 1 kg each were randomly chosen on the site and homogenised.

## **2.2 Characterization of the sediments**

### **2.2.1 Sediment preparation**

For microbial and physico-chemical characterization, sediments were homogenised and kept refrigerated at 4°C ;coarser particles were removed. For total element analyses, the mean sample was air-dried during fews days and dry sieved under 2 mm to get a homogeneous sample.

### **2.2.2 Physico-chemical analysis and microbial enumerations**

The physico-chemical parameters (pH, conductivity, total organic carbon, volatile matter) were measured on the homogeneous sample. The sediment chemical analysis consisted in the measurement of the content of both total major elements and trace metals. These analyses were undertaken after calcinations of the samples at 550°C and an acid digestion (NF X 31-147). Determinations of chemical elements content were performed either by Inductively-Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) or by atomic absorption spectrometry (Cd, As).

The organic extract was isolated from sediments with dichloromethane using an accelerated solvent extractor (ASE 200 Dionex). The organic extract was fractionated into aliphatic hydrocarbons, aromatic hydrocarbons and polar compounds by liquid chromatography on alumina and silica micro-column and then analysed separately by GC/MS in fullscan mode (Faure et al, 2000). The quantification of the 16 polycyclic aromatic hydrocarbons (PAH) was quantified by GC-MS Jeanneau et al (2006). The polar compounds were characterized by Fourier transformed infrared microspectroscopy.

Total bacterial counts were carried out using epifluorescent microscopy (samples stained with DAPI) within 5 days maximum after the sampling date.

### **2.2.3 TEM observation of particles of the runoff waters**

Three parallel procedures were used for TEM sample preparation. In the first procedure, 100 ml of the water samples were held in a refrigerator for 7 h and the pellets were fixed with 2.5% glutaraldehyde in 0.1 M sodium cacodylate buffer (pH 7.4) for 48 h at 4°C. After washing, the samples were postfixed with 1% osmium tetroxide in cacodylate buffer for 1 h, dehydrated in ethanol and embedded in Epon 812. In the other two procedures, 200 ml of the water samples were filtered at 5 µm and 0.45 µm and ultracentrifugated at 100 000 g for 2 h. The supernatants and the pellets were saved for TEM analysis and prepared as described above. Ultrathin sections of 90 and 200 nm mounted on copper grids were studied by TEM (100 kV) coupled with EDX analysis.

## **2.3 Column leaching experiments**

### **2.3.1 Salinity decrease experiment**

The 200-µm sieved sediment was retained for use in column experiments. The packed columns had a 2.6-cm inner diameter and 11 cm length with a 10 µm size ring net at each end extremity of the porous bed. The leaching columns experiments were carried out in water saturated conditions to follow the elution of heavy metals and

TOC after a stepwise decrease of the inlet solution salinity ( $8 \cdot 10^{-2}$  M to  $10^{-4}$  M NaCl) with a constant inlet flow rate of 1 ml/min. Total major and trace elements concentrations and TOC were measured during the elution. [Total elution solution (5 pore volumes) was also fractionated by filtration and ultrafiltration ( $8 \mu\text{m}$  to 5000 Daltons) to investigate the carrier role of colloids for trace metals). This type of scenario is used to simulate the de-icing salts spreading followed by rainwater encountered in a road environment during winter periods.

### 2.3.2 Infiltration drainage transitory phase

The columns used were 10 cm in diameter and 10 cm high. The elution of heavy metals and TOC was measured after two infiltration/drainage events at an infiltration rate of 2 ml/min with a NaBr  $10^{-3}$  M solution in non saturated conditions. A two day period of drainage was used before the second experiment. Total and soluble (0.45  $\mu\text{m}$  filtration) heavy metal, and TOC contents were measured. The total number of eluted bacteria was also monitored with the DAPI method. A peristaltic pump was used to both introduce the leaching solution and to drain the effluent at the bottom of the column at the same flow rate. This experiment aims at enhancing the leaching of pollutant through solubilization and moistening phenomenon.

## 3 RESULTS AND DISCUSSION

### 3.1 Characteristics of the polluted sediments

These surface layers are very similar on both sites on a physico-chemical point of view (Table 1). Chemical measurement variability was less than 5%.

Main chemical characteristics	Chevire	Chassieu	Traces metals in mg/kg	Chevire	Chassieu
pH	7.9	6.5	Cd	1.36	5.6
Org. Matter %	21.0	15.5	As	31.45	11.06
TOC g/kg	162	94	Cr	107.0	181.0
Ntot g/kg	7.96	7.46	Cu	426	232
Ptot g/kg	2.34	1.57	Ni	39	116
Fe/Ca g/kg	42.3/8.9	27.0/104.5	Pb	379	165
Si g/kg	247.3	226.7	Zn	2115	2354

Table 1 : Physico-chemical characteristics of the surface sediments

The organic matter content varies from 15 to 20% with 10 to 20 % organic C. The nitrate and phosphate contents are high. The heavy metal contents are closed to those of other stormwater sediments. The calcareous property of the Chassieu catchment could explain the high content of Ca that could come from calcite particles and dissolved calcium adsorbed of clay or organic constituents. The microorganisms are very numerous and active ( $10^9$  to  $10^{10}$  bact/g of sediment).

The organic extracts are dominated by polar compounds whereas saturated and aromatic hydrocarbons are less abundant (Table 2). Organic constituent proportions are close for both sediments. The molecular characterization of the saturated hydrocarbons reveals in both sediment a predominance of pentacyclic triterpanes and steranes (figures 1a and 1b) already observed in this kind of sediment (Durand et al., 2004) typical of a thermal mature organic matter probably inherited from petrogenic sources (Bieger et al., 1996; Faure et al, 2000). Chromatograms are also marked by an intense unresolved complex mixture (UCM). Such UCM are encountered in heavy distillate petroleum by-products such as road asphalts. n-Alkanes are also observed but as minor compounds in the  $C_{14} - C_{41}$  carbon number range. The LMW/HMW ratio (corresponding to  $C_{15}-C_{20}/C_{21}-C_{41}$  abundance ratio) is equal to 0.07 and 0.15 for Chevire and Chassieu sediment respectively. Such heavy molecular mass n-alkanes

predominance confirms the major contribution of heavy distillate petroleum by-products. The 16 HAP distributions (not shown) are close for both sediments (Table 2).

	Cheviré sediment	Chassieu sediment
Organic extract (g/kg) dry)	22,22	31,56
Polar compounds (g/kg)	17,45	22,44
Saturated hydrocarbons (g/kg)	2,42	5,74
Aromatic hydrocarbons (g/kg)	2,36	3,38
$\Sigma$ 16 PAH (mg/kg)	29,02	28,29

Table 2 : Composition of the organic fraction of the sediments

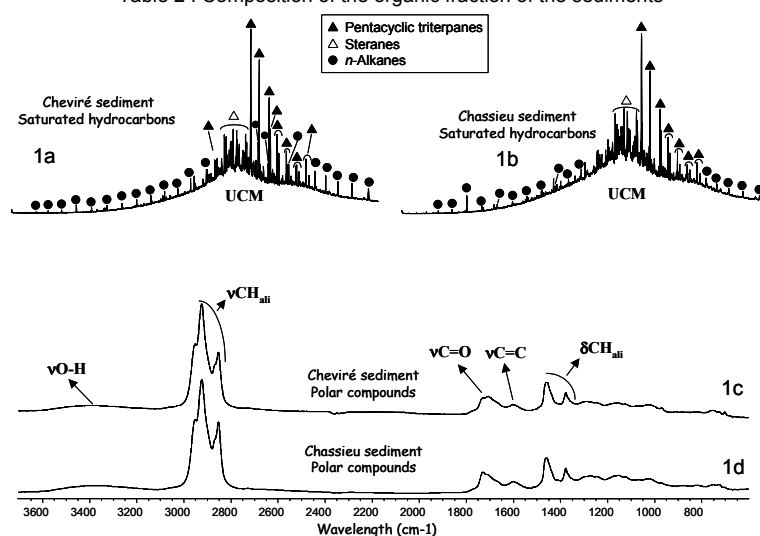


Figure 1 : Chromatogram of both sediments

Infrared spectra of polar compounds (figures 1c and 1d) are dominated by aliphatic bands ( $3000\text{--}2800\text{ cm}^{-1}$  and  $1470\text{--}1360\text{ cm}^{-1}$ ) whereas aromatic ( $1620\text{--}1590\text{ cm}^{-1}$ ) and oxygenated ( $3700\text{--}3100\text{ cm}^{-1}$  and  $1745\text{--}1705\text{ cm}^{-1}$ ) bands intensities are limited. Such spectra reveal a predominance of long length aliphatic chains.

Even if both sediments come from different locations, organic fraction amounts and characteristics are very close with a predominant signature inherited from heavy distillate petroleum by-products.

### 3.2 TEM observations

TEM observations show the high diversity of organic and mineral particles entering in the infiltration pond (Figure 2). EDX analysis of some of them show the predominance of mineral particles that could come from the soil surface catchment like quartz particles of 1 to 2  $\mu\text{m}$ , or others ones with Si, Ca, Fe and Mg. Very few particles contain heavy metals. Only mixture of Si, Fe, Pb and As particles were observed. This point underlines the fact that a great part of metals could be linked to organic matter that is not well analysed by this method.

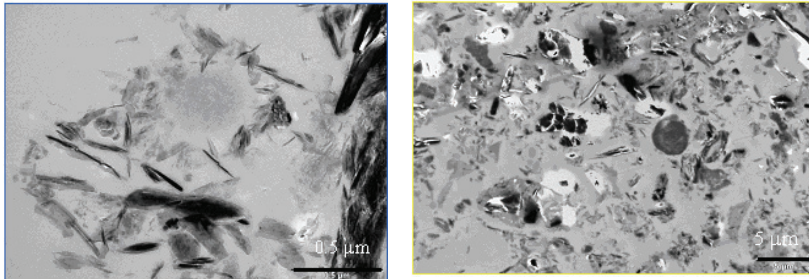


Figure 2 : TEM observation of particles entering in the infiltration pond of Cheviré

### 3.3 Specific mobility of Cu, Zn, Cd and TOC

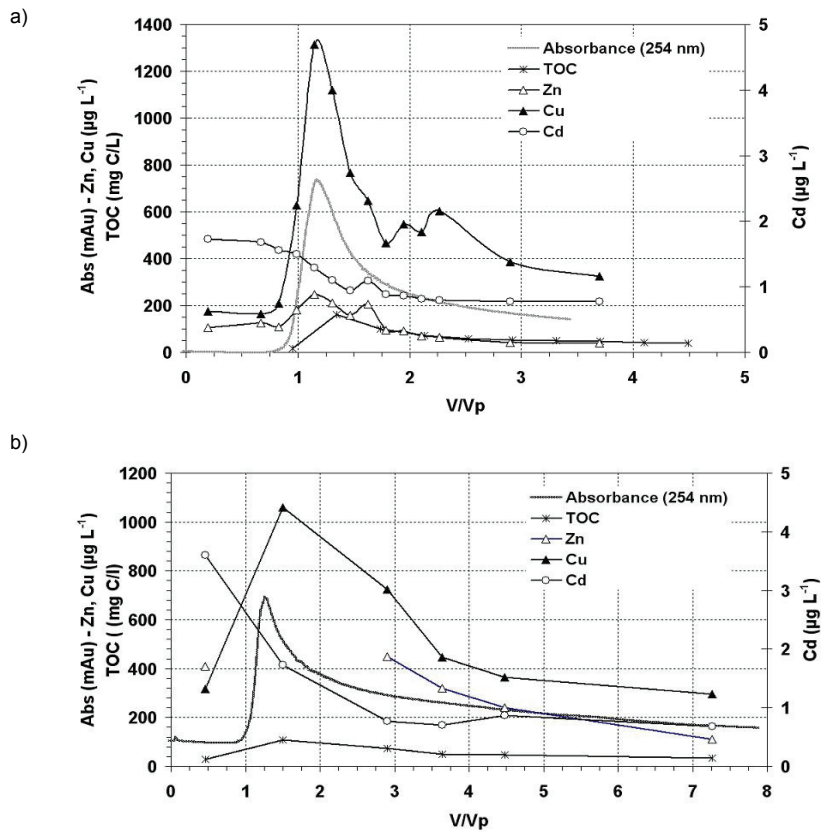


Figure 3 : Elution of Zn, Cu, Cd and TOC during a salinity decrease in column experiment – a) Cheviré sediment; b) Chassieu sediment

The decrease in salt concentration results in an increase of the absorbance signal, which is concomitant with the increase of TOC and heavy metals (Cu and Zn) in solution (Figure 3). The eluted concentrations of Cu and Zn are very high (up to 1 mg/L for Cu). Cu is the most reactive element to the change in salinity, whereas the

concentration of Cd decreases strongly with the salinity front. The lower formation of complexes with chlorides could explain the lower release of cadmium. In terms of mass balance less than 1.5% of the total content is leached. As constituents of colloidal oxyhydroxides, Fe and Al concentrations were also measured in eluate (not shown). Al is more reactive than Fe to the change in salinity, Fe being not affected or showing an increase later than the salinity front. An increase of one unit of pH was observed during the decrease of salinity. The fractionation showed that 40 to 80% of the trace metals was present in colloidal form in relationship with TOC and Fe.

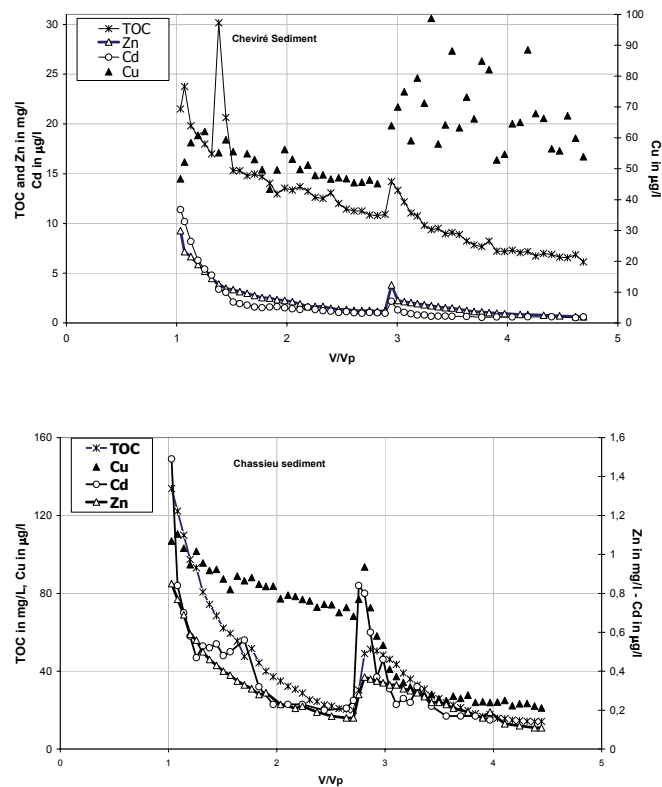


Figure 4 : Elution of Zn, Cu, Cd and COT during two consecutive infiltration/drainage phases (the second phase starts at  $V/V_p=2.8$ )

During the infiltration/drainage experiment, the first drop that appears at the bottom of the column is the most concentrated in metals and organic carbon (Figure 4). pH is stable during all the experiment. All the pollutant contents decrease exponentially with time except Cu that stays at a high concentration during the first infiltration event. COT and metals are in the  $0.45 \mu\text{m}$  filtered part. Zn reaches concentrations higher than  $1 \text{ mg/L}$ . Bacteria are also eluted simultaneously with TOC with an initial density of  $10^8 \text{ bact/ml}$  (not shown). As metals are present in the soluble part, bacteria do not seem to play a role in the pollutant release. The total quantity of eluted metal is less than 1% of the total content in the sediment. The second infiltration phase elutes less heavy metals and TOC. Indeed, the sediment water content has not changed during the two day drainage period. So, the enhancement of the microbiological activity due

## SESSION 4.1

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to the oxygene increase with drying has not been effective. The release of TOC and heavy metals are then lower.

When comparing both leaching experiments, it seems that the level of TOC released is in the same range of concentration. Polar organic molecules contribute to the soluble TOC. Heavy metals behave differently. The salinity front favor a higher release of Cu (10 to 20 times more than in the infiltration experiment) whereas the infiltration solubilize more Zn (2 to 5 times more than with the salinity front). Organic matter has a strong heavy metal complexing capacity, but this property can not explain the different elution curve shape of Zn and Cu. This difference could be explained by the presence of Cu in inner aggregated solids that are not rapidly reached by water in the case of infiltration tests. In the case of the salinity front, the destabilisation of Cu reach aggregated particles could explain the strong metal release. When comparing to its total content, Cd is not very mobile. Our results are quite different from those of specific extraction methods showing that 50% of the cadmium is mobile in different infiltration pond sediments.

## 4 CONCLUSION

Both sediments behave similarly. The total heavy metal content and the molecular composition of the organic matter can be attributed to the signature of the urban activity. The presence of hydrocarbons could explain the high bacterial density. During drainage periods, the microorganisms can mineralize easily degradable hydrocarbons in aerobic conditions and then favor the release of high content of soluble TOC during the following infiltration event. The release of metals is very low and sediments are very good chemical sorbers as less than 1% of the total Zn, Cd and Cu are eluted. The soluble TOC is one of the ligand that can solubilize metals. Cu seems to have a specific behaviour in both leaching conditions that is not correlated to the TOC elution and seems to be also eluted with minerals or aggregated particles. Chemical or hydrodynamical transient conditions lead to a high release of pollutant. These changing conditions should be avoided at the surface of infiltration ponds in order to prevent the aquifer from high carbon and heavy metals flow.

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