

Trace element carriers in combined sewer during dry and wet weather: an electron microscope investigation

A.G. El Samrani^a, B.S. Lartiges^{a,*}, J. Ghanbaja^b, J. Yvon^a, A. Kohler^b

^a *Laboratoire Environnement et Minéralurgie (LEM-ENSG) Pôle de l'Eau, 15, Avenue du Charmois-BP 40-54 501 Vandœuvre, France*

^b *Université Henri Poincaré-Service Commun de Microscopie Electronique, BP 239. 54 500 Vandœuvre Cedex, France*

Received 15 April 2003; received in revised form 19 January 2004; accepted 28 January 2004

Abstract

The nature of trace element carriers contained in sewage and combined sewer overflow (CSO) was investigated by TEM-EDX-Electron diffraction and SEM-EDX. During dry weather, chalcophile elements were found to accumulate in sewer sediments as early diagenetic sulfide phases. The sulfuration of some metal alloys was also evidenced. Other heavy metal carriers detected in sewage include metal alloys, some iron oxihydroxide phases and neoformed phosphate minerals such as anapaite. During rain events, the detailed characterization of individual mineral species allowed to differentiate the contributions from various specific sources. Metal plating particles, barite from automobile brake, or rare earth oxides from catalytic exhaust pipes, originate from road runoff, whereas PbSn alloys and lead carbonates are attributed to zinc-works from roofs and paint from building siding. Soil contribution can be traced by the presence of clay minerals, iron oxihydroxides, zircons and rare earth phosphates. However, the most abundant heavy metal carriers in CSO samples were the sulfide particles eroded from sewer sediments. The evolution of relative abundances of trace element carriers during a single storm event, suggests that the pollution due to the “first flush” effect principally results from the sewer stock of sulfides and previously deposited metal alloys, rather than from urban surface runoff.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Heavy metal; Speciation; Storm water; Combined sewer overflow; SEM; TEM; EDX

1. Introduction

The impact of combined sewer overflows (CSO) upon quality of receiving aquatic systems is a major concern in environmental protection. In most cases, the pollution issued from CSO exceeds annual discharges from factories and sewage plants [1,2]. Contaminants in CSO are derived from a number of sources. Thus, materials from wet and dry atmospheric deposition, traffic-related activities (tire wear, vehicle brake emissions, fluid leakages), or released from roofs and building siding, may be flushed by rainfall and collected

in the municipal sewer system [3,4]. In addition, sewage and sewer-deposited material can also represent a significant contribution to CSO pollutant load [5].

Early work has focused on estimating the relative contributions of specific sources to CSO pollutant load in terms of total amount of heavy metals, hydrocarbons, nutrients. [6,7]. Such an approach only provides a rough assessment of contaminant mobility and bioavailability in receiving waters, since pollutant behavior is mainly governed by its speciation [8–10]. Indeed, heavy metals may be present under numerous physicochemical forms such as soluble, adsorbed on mineral surfaces, complexed with organic matter, precipitated or entrapped in mineral phases. Exchangeable forms are usually considered as immediately bioavailable species [8]. The partitioning of metal contaminants between specific forms is classically determined using sequential

*Corresponding author. Tel.: +33-383-596294; fax: +33-383-596255.

E-mail address: bruno.lartiges@ensg.inpl-nancy.fr (B.S. Lartiges).

extraction methods [11–13]. Thus, sorbed metal ions, metals associated with carbonates, iron and manganese oxihydroxides, sulfides, can be distinguished by adding appropriate reagents to the sample. Such procedures have been applied to separate CSO contributors such as street deposits [8,14], gully pot solids [15,16] and combined sewer suspended solids of dry and wet weather [5].

However, it is now recognized that metal fractions obtained by selective chemical extraction procedures are only operationally defined, as incomplete dissolution of the target phase, dissolution of nontarget species, incomplete removal of dissolved species due to re-adsorption or precipitation, may occur [17,18]. Furthermore, such speciation does not identify with certainty the various phases that may contain heavy metals. An alternative approach is to use microscopy techniques such as Transmission (TEM) and Scanning (SEM) electron microscopies combined with energy-dispersive X-ray spectrometry (EDX). TEM-EDX-Electron diffraction and SEM-EDX observations in Backscattered Electron Imaging (BEI) mode allow direct determination of heavy metal occurrences and provide combined data on both mineralogy and texture of heavy metal carriers [19–21]. Such information is essential for the description of trace element cycles in urban environment [20]. Knowledge of heavy metal-bearing species can also be useful to improve the management of sludges retained in detention basins or generated during physicochemical treatment of CSO. The aim of the present study was then to evaluate the use of TEM-EDX and SEM-EDX for determining the nature of heavy metal carriers contained in sewage and CSO.

2. Experimental section

2.1. Study site

Samples (sewage and CSO) were taken from the sewer pipe “Libération”, up-stream Boudonville detention basin (Fig. 1). Boudonville watershed lies in the North West part of the city of Nancy (France) on the left bank of Meurthe River. The catchment area receives runoff from 246 ha of urban surfaces, both residential and commercial areas ($\sim 20,000$ inhabitants), and is essentially drained with a combined sewer system [22].

The average slope of the watershed is 0.034 m/m with about 40% of impervious surface. To prevent flooding at the lower part of the watershed during storm events, three detention tanks have been built. In consequence, Boudonville watershed is equipped with eight rain-gauges and 20 limnimeters, and has been used as an experimental catchment area for hydraulic and pollution transport studies for the past two decades [22,23]. In this study, data of “libération” limnimeter and of two rain-

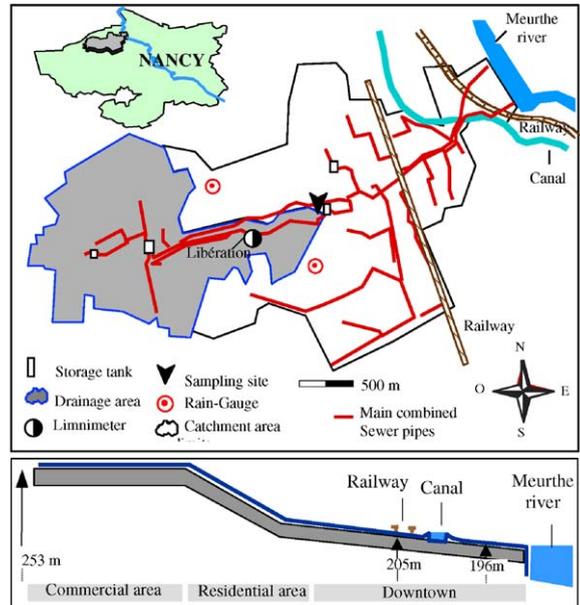


Fig. 1. Study site location and map of Boudonville catchment area.

gauge stations close to the sampling site, were graciously provided by Service Hydraulique urbaine of Nancy Urban Community.

2.2. Sample collection and preparation

Dry and wet weather flows (weak intensity rain events of long duration and storm events), were collected between June 2001 and April 2002. Sampling dates and simple characterization of effluents are given in Table 1. Samples, taken from the sewer using either a 1 L chemo-sampler (Fisher Scientific) or a peristaltic pump (Delasco “Z”—flow rate ~ 5 l/min) (Fig. 2a), were collected in 10 L polyethylene jerrycans, transported to the laboratory and processed within one hour after sampling.

The preparation procedure is schematized in Fig. 2b. After gentle over-end agitation of jerrycans, 1 L samples of raw water were taken and allowed to settle in Imhoff cones for two hours. This sedimentation time was selected to mimic large particle removal in conventional depollution tanks [24]. It allows to separate a “settleable fraction” from a “suspended fraction”. The “settleable fraction” was centrifuged at 12000 rpm ($\sim 15,000g$) for 20 min (Beckman-L8-55 M), and the sediment thus obtained was recovered and freeze dried (Virtic-Sentry). The “suspended fraction” was filtered without stirring through a 0.45 μ m pore size polycarbonate membrane (Nucleopore—diameter 60 mm), and the filter was air dried at room temperature.

Table 1
Sampling dates and corresponding physicochemical characteristics of sewage and CSO during storm and weak rain events

	Date (Month/ Day/Year)	Suspended solids (mg/L)	Volatile solids at 550°C (mg/L)	pH	Alkalinity (meq/L)
Sewage (Dry weather)	06-03-2001	785	523	7.63	1.51
	10-30-2001	980	590	7.58	1.70
	02-28-2002	835	562	7.35	1.61
	04-18-2002	910	540	7.84	1.68
CSO (weak rain event)	03-08-2001	165	98	6.10	0.12
	09-19-2001	147	89	6.15	0.14
	10-23-2001	255	155	6.40	0.18
	02-25-2002	185	103	6.10	0.16
CSO (storm event)	05-14-2001	595	434	6.92	0.34
	07-06-2001				
	<i>Local time</i>				
	19h30 min	750	410	7.32	1.44
	19h37 min	820	600	7.39	1.18
	19h42 min	840	470	7.44	0.54
	19h45 min	910	560	6.75	0.46
	20h07 min	650	380	7.02	0.54
	20h15 min	540	320	5.95	0.34
	20h21 min	720	420	6.00	0.24
	08-30-2001	1275	1055	6.32	0.32

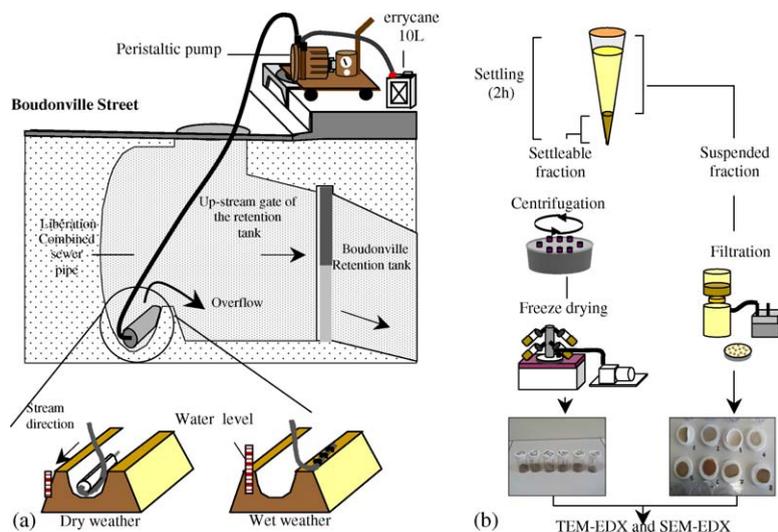


Fig. 2. Schematics of (a) sampling procedure and (b) sample preparation.

2.3. Trace element speciation by electron microscopy

Electron microscopy observations were performed with a Philips CM20 TEM (200 kV) coupled with an EDAX energy dispersive X-ray spectrometer (EDX), and with a S-2500 Hitachi SEM equipped with a

Kevex 4850-S EDX. Trace element carriers were identified from elemental analysis of individual particles. Stoichiometric ratios were first calculated from atomic percentages given by EDX spectra, and then compared with known mineralogical compositions. Electron diffraction patterns provided by

TEM were also used to specify the crystal structure of particles.

About 1250 mineral particles from samples of sewage, weak rain events, and storm events, were examined over the period of study (800 SEM-EDX spectra and 450 TEM-EDX spectra). For TEM imaging and microanalysis, the sample was re-suspended in ethanol under ultrasonication, and a drop of suspension was evaporated on a carbon-coated copper grid (EuroMED-EX, Mesh200-Car#CF200CU). A spot size of about 70 nm was used to record EDX spectra with a counting time of 40 s. EDX calibration standards were run to obtain quantitative analyses of major and trace elements with a detection limit of about 100 ppm.

Samples for SEM-EDX examination were sprinkled onto 2 cm² plates and carbon coated. BEI was used to locate the particles of interest. In that mode, brightness is related to the average atomic number of materials, and the mineral particles appear as bright spots within the organic matrix of sediment. The relative abundance of a given trace element carrier can then be assessed by conducting systematic microanalysis of bright spots. It should nevertheless be noted that this procedure largely overlooks mineral phases with low-atomic-number elements such as clays and carbonates. Statistics were conducted on about 100 trace element carriers identified per event. In order to increase the emission of back-scattered electrons, the SEM microscope was generally operated with a beam current of 3 pA and an accelerating voltage of 20 kV (analysed microvolume of about 6 μm³). However, to improve the quantification of low atomic number elements, EDX analysis was sometimes carried out at an accelerating voltage of 10 kV (sampling volume of 3 μm³).

3. Results and discussion

3.1. Trace element speciation in sewage

Typical electron micrographs and corresponding EDX spectra of trace element carriers found in sewage are illustrated in Fig. 3. Particles of anthropic origin such as metallic alloys were easily recognized (Figs. 3a and b). The ternary alloy of chemical composition (Fe 70 ± 0.7%, Ni 14.4 ± 1.5%, and Cr 15.5 ± 1%) identifies stainless steel which is used in a variety of outdoor and indoor materials such as kitchen utensils or wall claddings [25,26]. The flake morphology of the particle in Fig. 3a suggests removal under corrosive conditions [26]. Particles containing Ni (61%), Fe (18%), and Cr (21%), associated with uses such as electrical resistances or thermocouple materials [27], were also observed. Pb–Sn alloys (Fig. 3b), generally used for soldering in zinc-works, pyrophyllite particles carrying Zn (2–3%),

probably originating from cosmetic products, provide other examples of heavy metal carriers directly related to human activity. Titanium oxides of various stoichiometry (TiO₂ rutile and anatase, TiO, and Ti₂O₃) used as pigments, and zeolites present in washing powders, were also frequently found in sewage samples but always devoid of trace elements.

In contrast, mineral particles such as anapaite (Ca_{2-x}Fe_x)(PO₄)₂ · 4H₂O, readily identified in TEM (Fig. 3c), are likely formed within the sewer system. Indeed, this phosphate mineral is characteristic of slightly alkaline/reducing conditions, and is frequently detected in brackish and freshwater sediments [28]. Anapaite particles were found to entrap zinc traces in their structure. Other phosphate species identified in sewage samples, include whitlockite (Ca,Mg)₃(PO₄)₂, and apatite (Ca_{5-x/2}Y_{x/2})(PO₄)_{3-x}(CO₃)_x. Even though apatite has been reported to regulate heavy metal concentration in natural environments [29], neither phases carried trace elements. In addition, fluoride or chloride substitutions were never detected in the apatite structure.

Sulfide particles found in sewage should also correspond to neoformed species. For instance, Fig. 3d shows an electron micrograph of a binary sulfide of silver and mercury. The EDX spectrum reveals a non-stoichiometric relationship between Ag, Hg, and S, characterized by a pronounced deficit in S. Some sulfur release under the electron beam may occur during analysis, and could account for such a deficit. However, the agglomerate aspect of the particle and the Ag/Hg association are reminiscent of dental amalgam [30,31]. As Ag and Hg are known to present a strong affinity for sulfur [32], the observed particle could correspond to the transformation of a piece of dental amalgam with fixation of reduced sulfur under anaerobic conditions within the sewer. Another sulfide particle found in sewage contained Hg, Ag, Cu, Sn, and S, could similarly be derived from the sulfurization of a dental amalgam. However, the most common metal sulfide minerals in sewage were monosulfides of Fe, Zn, and Pb, with some binary sulfides of Zn–Fe and Cu–Fe. In natural sediments, sulfide formation is usually associated with bacterial sulfate reduction, H₂S thus produced subsequently reacting with Fe²⁺ and trace metals [33–35]. As anoxic conditions are often encountered in stagnant portions of the sewer system [16,36], precipitation of sulfide species can then be expected.

Iron oxides and oxihydroxide particles such as goethite, hematite, and maghemite, were frequently identified in dry weather. Although such minerals are generally considered as potential sinks for heavy metals [37,38], EDX spectra revealed that less than one third of iron oxides found in sewage were carriers of trace elements such as Cr, Cu, and Zn.

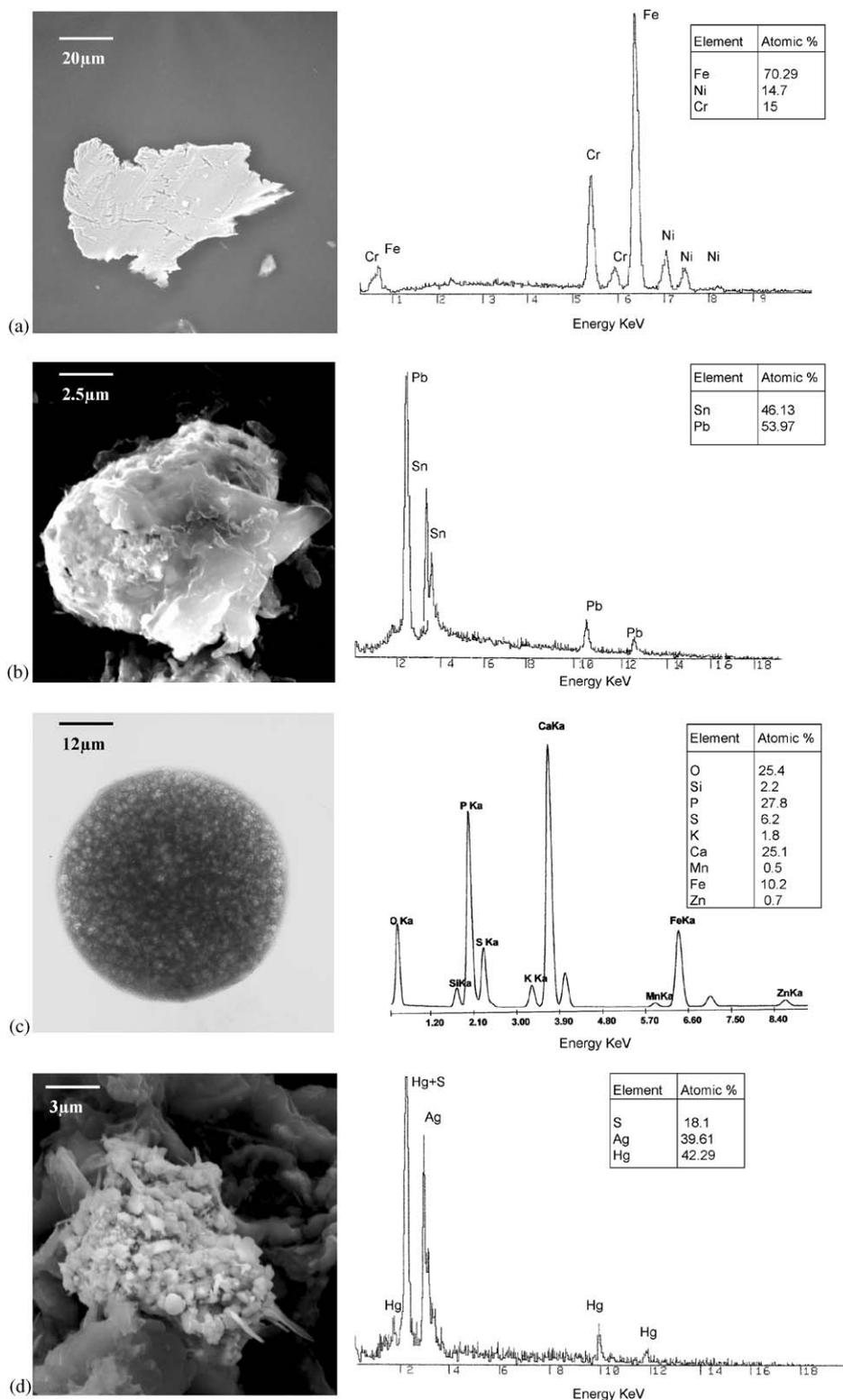


Fig. 3. Electron micrographs and corresponding EDX spectra of heavy metal carriers found in sewage: (a) BEI of stainless-steel particle; (b) BEI of a Pb-Sn alloy; (c) TEM image of anapaite and (d) SEI of a sulfurized amalgam particle.

3.2. Trace element speciation in CSO (wet weather)

Both sewage and surface runoff contribute to CSO. Runoff sources of trace elements include wet and dry atmospheric deposition, and specific release from urban surfaces such as roads (tires, automobile brakes), roofs and building siding, and from soil surfaces (garden, outcrops) [3,4]. Resuspension of sewer sediment has also been demonstrated to represent a significant contaminant input [5,39]. As shown in Figs. 4–6, mineral particles from these various sources can be identified in CSO.

3.2.1. Contribution from urban surfaces

Particles of barium sulfate, 10–20 μm in size, were frequently observed in wet weather samples (Fig. 4a). The electron diffraction pattern revealed crystallization in an orthorhombic lattice, thus identifying barium sulfate particles as barite. Among the potential sources of barite in urban environment, automobile brake (inset of Fig. 4a) and road paint are the most likely in wet weather. Barite particles would then originate from road runoff.

Micron size W–Cr–Co carbide granules (Fig. 4b) are also probably flushed from the road surface. Indeed, these carbide particles are especially used as metal coating in vehicles to prevent wear and corrosion [40]. The coating is applied to steel surface by air plasma spraying in presence of oxygen in order to promote the nucleation of oxycarbide [41]. This may explain the relatively high percentages of oxygen and Fe in the EDX spectrum. Rare earth oxides such as the La–Ce particle shown in Fig. 4c, were exclusively found in CSO. These particles present excellent catalytic properties and they are generally used for gaz depollution in vehicle exhaust-pipes [42,43]. Small aggregates of micron-sized carbon particles were also detected by TEM; such agglomerates are reminiscent of bitumen droplets and would provide further evidence of road runoff.

Numerous particles of lead carbonates were observed by SEM-EDX in wet weather samples. Such lead carriers have been reported to be released from weathered paints [64,65], although lead compounds such as cerussite are now forbidden in most paints. Cuprite particles (Cu_2O), likely originating from the corrosion of copper roofing materials [66], may also be considered as a contribution from drained urban surfaces. Franklinite ($\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$) (Fig. 4d), a face-centered cubic structure in which Zn is substituted for Mn, was identified in CSO by TEM-EDX. Although franklinite presents some applications as inductor in transformers and in loud-speakers [44], this high temperature spinel is mainly known to be emitted during Zn-ore smelting operations [45] and household waste incineration [46]; it is then likely to result from atmospheric deposition.

3.2.2. Contribution from sewer sediments

CSO samples were found to be substantially enriched in sulfide particles. EDX analyses and microscopic observations revealed that the sulfide species occurred in a wide range of composition and textural forms. Thus, iron sulfides were encountered both as framboid-like and well-crystallized particles (Fig. 5a), with Fe/S ratios close to 1:1, 1:2 and 3:4. Such iron-to-sulfur ratios identify mackinawite (FeS), pyrite (FeS_2), and greigite (Fe_3S_4), respectively. Coexistence of iron sulfides of variable composition has already been reported in freshwater canal sediments and anoxic marine sediments (e.g. [47–49]). Mackinawite is a known precursor to pyrite formation [34,50], whereas greigite has been shown to be easily formed by oxidation of mackinawite [50], and is usually present in environments which show a seasonal oxic/anoxic cyclicality [51].

Similarly, EDX microanalyses revealed that Zn-monosulfides occurred as two main forms with Zn/S elemental ratios of approximate 1:1 and 2:3. The 1:1 ZnS mineral phase corresponds to sphalerite which is commonly found in anaerobic sediments [52,53,47]. On the other hand, the 2:3 stoichiometry has only been evidenced as nanoclusters that are intermediates in ZnS mineral formation [54]. Pb-monosulfide minerals were also found in CSO samples, but the overlap of S $K\alpha$ and Pb $L\alpha$ radiations make the EDX assessment of lead-to-sulfur ratios inaccurate.

Zinc, lead, and iron monosulfides represented respectively, 48.6%, 22.4%, and 9.3% of all sulfide species observed in CSO samples. Other chalcophile elements occurred as binary sulfides with stoichiometries close to that of chalcostibite (CuSbS_2) (Fig. 5b) or chalcopyrite (CuFeS_2), and as traces associated with iron sulfide phases. All these sulfides certainly precipitate as a consequence of the reaction between dissolved heavy metals and reduced sulfur species derived from microbially mediated sulfate reduction [55]. They accumulate in sewer sediments during dry weather and are resuspended in CSO during rain events. Such interpretation is consistent with Gromaire's observation that dissolved zinc, cadmium, copper, and lead concentrations are drastically reduced between the inlet and the outlet of the combined sewer [5]. These authors attributed this decrease to a change in metal speciation within the sewer system.

In situ formation of sulfides is also evidenced by the observation of sulfide coating on minerals allochthonous to the sewer. Thus, Fig. 5c shows SEI and BEI (inset) of Zn-sulfide grains grown on a barite surface. Even though numerous sources of sulfur such as detergent surfactants or organic matter may be recognized in sewage [36,56], the association barite–Zn sulfide suggests that SO_4 from barite may be mobilized as sulfide by sulfate-reducing bacteria. The solid-phase transformation of some mineral particles in presence of H_2S ,

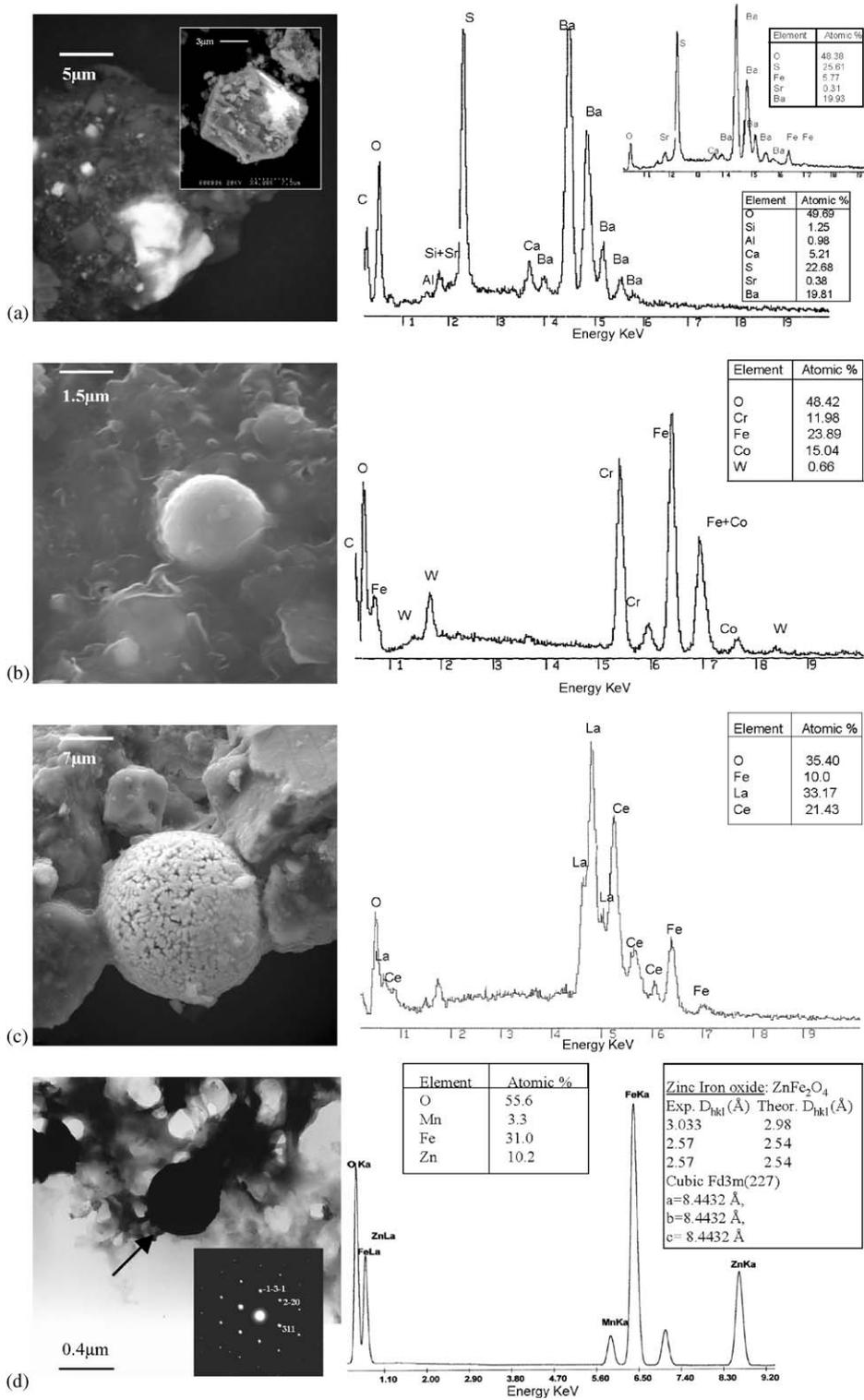


Fig. 4. Electron micrographs and corresponding EDX spectra of particles from urban surfaces: (a) BEI of barite in CSO and barite of automobile brake (inset); (b) BEI of W-Cr-Co carbide; (c) SEI of rare earth oxide particle and (d) TEM image of a franklinite particle and corresponding electron diffraction pattern (inset).

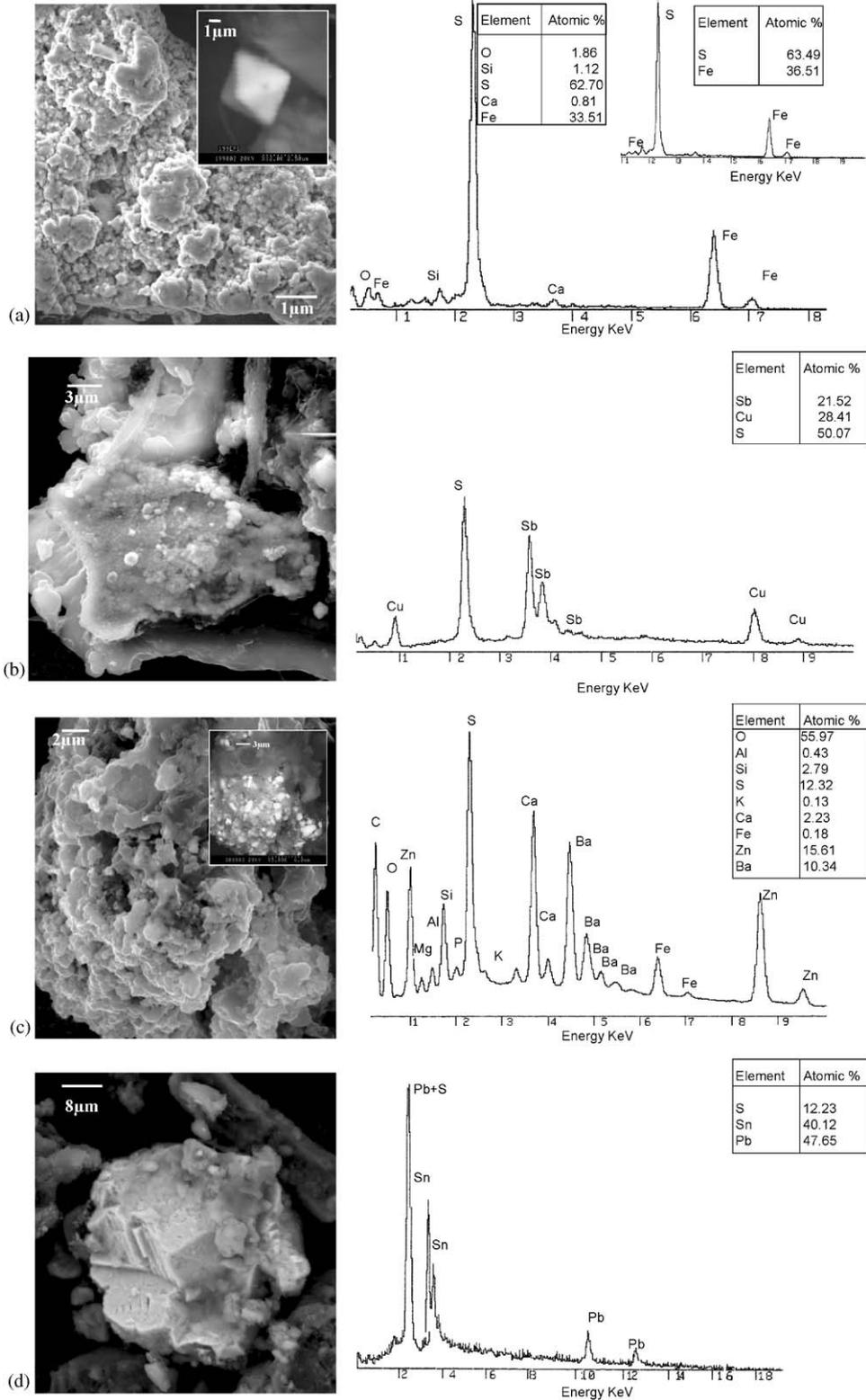


Fig. 5. Electron micrographs and corresponding EDX spectra of particles found in CSO and likely originating from sewer sediments: (a) BEI of framboidal and well-crystallized pyrite (inset); (b) SEI of Chalcocitibite; (c) SEI and BEI (inset) of Zn-sulfide grains and barite particle and (d) SEI of transformed Pb-Sn alloy.

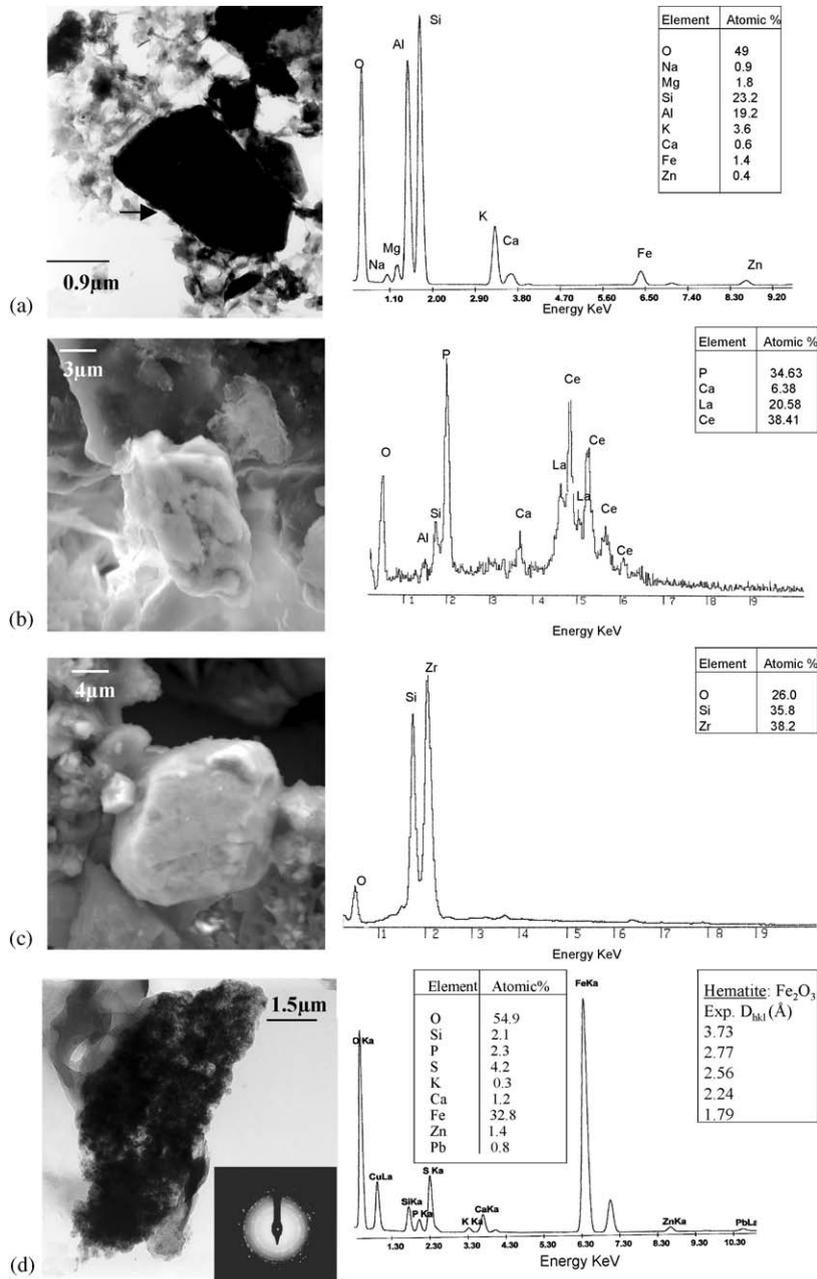


Fig. 6. Electron micrographs and corresponding EDX spectra of particles found in CSO and likely originating from soil surfaces: (a) TEM image of kaolinite; (b) SEI of monazite. (c) SEI of zircon particles and (d) TEM image of hematite and corresponding electron diffraction pattern (inset).

already suggested by “dental amalgam-sulfides” found in dry weather samples, is further substantiated by the observation of particles such as the Pb–Sn–S phase presented in Fig. 5d. This particle displays obvious cleavage planes which were absent in the original alloy (Fig. 3b), and EDX microanalysis revealed a small non-stoichiometric percentage of associated sulfur. This

indicates that the Pb–Sn alloy is unstable in anoxic sewer sediments and evolves towards a sulfide phase.

3.2.3. Contribution from soil surfaces

Illite and kaolinite particles were frequently observed in wet weather samples by TEM-EDX (Fig. 6a). The increased abundance of kaolinite was further confirmed

Table 2

Percentage of contaminated iron oxyhydroxides species in settled and suspended fractions of sewage and CSO of storms and weak rain events (n = number of particles)

Particle fraction	Contaminated iron oxyhydroxide species		
	Sewage (dry weather)	CSO (weak rain)	CSO (storm)
Settleable	29%	32%	40%
Suspended	33%	54%	49%

by the presence of characteristic bands at 3698 and 3620 cm^{-1} (respectively, anti-symmetric stretching of external and internal OH in kaolinite) in infrared spectra of freeze-dried CSO settleable fraction [57]. Illite and kaolinite are known to be dominant minerals in terra fusca soils formed on the Bajocian calcareous parent rocks of the catchment area [58]. As a consequence, the presence of illite and kaolinite in wet weather samples should indicate a contribution from soil surface runoff. Fig. 5a shows an illite particle with a minor amount of Zn. Clay minerals have been shown to be potential trace element carriers [59]. However, most clay particles identified in CSO samples were free of heavy metals.

Phosphate phases found in dry weather samples such as anapaite or apatite, were not detected in CSO presumably because of sewage dilution by runoff. On the other hand, a variety of rare earth phosphate minerals such as La–Ce (monazite Fig. 6b), La–Y, Eu–Th and La–Eu phosphates were identified in CSO. These phosphate minerals, originally formed in igneous rocks, are known to be stable phases in the sedimentation cycle [60], and probably come from the sedimentary rocks of the catchment area. Also commonly observed in CSO samples are slightly rounded zircon particles (Fig. 6c). Zircon, considered as the most resistant mineral to weathering and dissolution [61], should also reflect outcrop erosion during rain events.

Iron oxyhydroxide minerals such as ferrihydrite, goethite, and hematite (Fig. 6d), were present in wet weather samples. However, unlike iron oxide phases observed in sewage, EDX microanalyses indicated that about half of iron particles in CSO entrapped heavy metal contaminants (Zn, Cu, Cr), thus suggesting a different origin (Table 2). The likely source of iron oxide particles during rain events is the terra fusca soil where goethite and hematite have been previously described [58].

Such contribution from soil runoff can be further evidenced by plotting the relative abundance of particles identified by SEM-EDX as a function of time for a given storm event (6 July 2001). Indeed, Fig. 7a reveals that the highest proportion of iron oxyhydroxides is shifted with regard to the peak of flow rate. This can be explained by the time needed to mobilize and transport

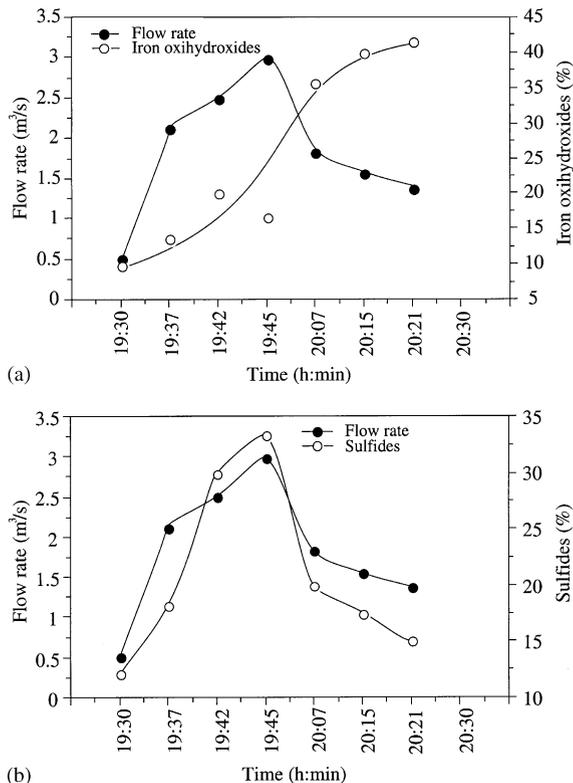


Fig. 7. Flow rate and relative abundances of (a) iron oxyhydroxides and (b) heavy element sulfide particles during a storm event.

particles from soil surfaces to the combined sewer. Such an interpretation is further supported by the fact that rare earth phosphates and most zircon particles observed in this storm event, were found in the three samples collected after 20h00 min.

On the other hand, the evolution of sulfide abundance closely follows the flow rate dynamics (Fig. 7b). This agrees with a pattern of sediment resuspension and redeposition as flow rate changes in the combined sewer during the rain event. In parallel of EDX microanalyses, a sequential extraction for heavy metals (Zn, Pb, Cu, Cd, Cr) was conducted on CSO samples. It revealed that the oxidizable fraction represents the dominant

contribution for Zn (30–46%), Cu (31–55%), and Cd (35–56%), while the exchangeable fraction was relatively insignificant for the same metals [57]. As a consequence, the “first flush” effect, characterized by similar trends in flow rate and in heavy metal concentrations [62], can be explained not only by urban surfaces runoff, but also by the mobilization of sulfide minerals formed in sewer sediments. In that case, the first flush would remain related to the length of the dry period preceding the rain [63], as the stock in sulfide phases should principally increase during dry weather. Copper was also reported as mainly originating from the sewer sediment by Gromaire et al. [5].

3.3. Abundance of heavy metal carriers

The averaged distributions of trace element carrier abundances for sewage and CSO samples are illustrated in Fig. 8. Interestingly, sewage and CSO samples from storm events display relatively similar patterns for settleable and suspended fractions, whereas the proportions of iron oxides and sulfide phases drastically differ in fractions of CSO samples generated by weak rain events. Many factors such as size distribution, grain shape, and density, influence the settling velocity of particles. It is then unlikely that, after 2 h of settling, the

relative abundances of various trace element carriers can be similar in settleable and suspended fractions. As the amount of volatile solids is particularly high in sewage and storm event samples (Table 1), one possible explanation is that heavy metal carriers become enmeshed in organic matter during transport, the deposition being controlled by the hetero-aggregates thus formed. In contrast, heavy metal carriers transported in CSO resulting from weak rain events should settle as individual particles.

It must be pointed out that the proportions of trace element carriers such as carbonates, clays, and organic matter, are largely underestimated by electron microscope examination if not completely overlooked. Thus, sequential extractions indicated that, in CSO samples, the dominant fraction of Pb was associated with carbonates and phosphates (36–51%), while Cr showed a relatively high exchangeable fraction (9–16%) [57].

Barite particles (96% of sulfates) have been described in CSO as originating from paint and brake wear. However, their relatively high abundance (16%) in sewage suggests that other sources of barite such as medical application, may also contribute to their presence in sewage. Finally, it was noticed that tungsten carbide and Pb–Sn alloys became much more frequent than stainless-steel particles in wet weather samples.

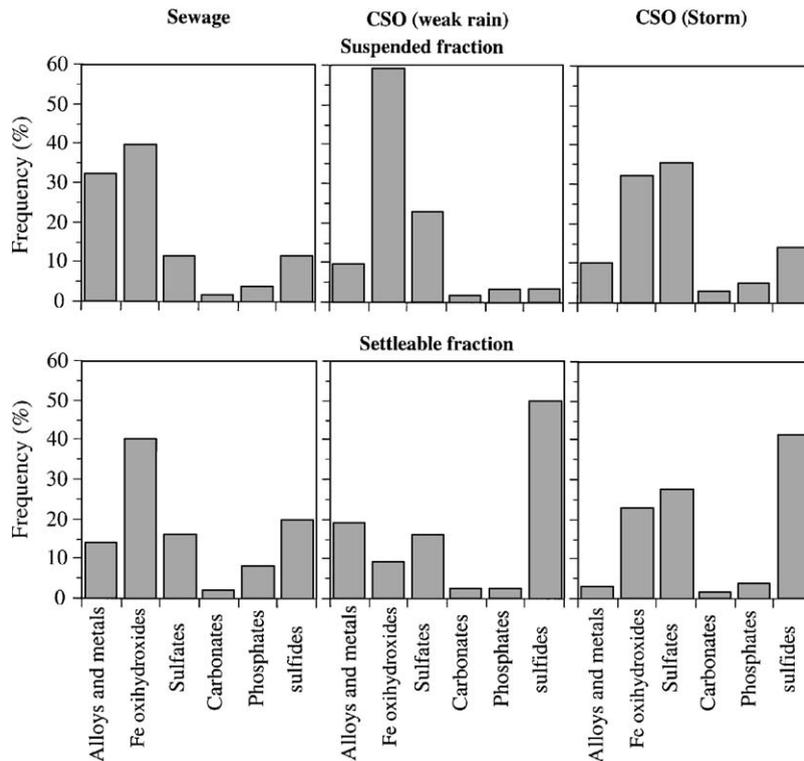


Fig. 8. Distribution of trace element carriers abundances identified by SEM-EDX within suspended and settleable fractions of sewage and CSO during storms and weak rain events.

Table 3
Nature of trace element carriers in sewage and CSO

Sewage dry weather	Alloys and metals	(Pb) (Ag) (Fe, Cr) (Fe, Ni, Cr)
	Iron oxihydroxides	(Pb), (Cu), (Cr), (Mn), (Cr, Mn), (Zn, Cu)
	Carbonates	(Fe, Pb)
	Phosphates	(Fe), (Zn)
	Sulfides	(Zn) (Pb) (Fe) (Ag) (Cu) (Cu, Cr, Fe) (Cu, Sn, Fe) (Cu, Fe, Sb, Zn) (Ag, Hg)
	Sulfates	(Ba) (Ba, Sr)
	Clays	(Zn)
Combined sewer overflow	Alloys and metals	(Pb) (Ag) (W) (Ni, Sn) (Fe, Cu) (Fe, Ni, Cr) (Fe, Ni, Mn, Cr) (W, Fe, Cr, Co)
	Iron oxyhydroxides	(Fe, Zn) (Fe, Zn, Mn) (Fe, Zn, Cr) (Fe, Pb, Cu)
	Carbonates	(Pb)
	Phosphates	(La, Ce) (Zn, Fe) (Zn, Pb) (Y, Er, Yb)
	Sulfides	(Zn) (Pb) (Fe) (Ag) (Cu) (Zn, Pb) (Zn, Fe) (Fe, Cu) (Fe, Mn) (Cu, Zn, Fe) (Ag, Hg, Sn, Cu)
	Sulfates	(Ba) (Ba, Sr)
	Clays	(Zn)

Such behavior is consistent with a re-suspension of high density alloys from sewer sediment during CSO events.

4. Concluding remarks

The main trace element carriers identified by TEM-EDX and SEM-EDX in sewage and CSO, are summarized in Table 3. Most metal contaminants are present under various mineral forms. Thus, in CSO samples, Zn was found associated with iron oxihydroxides, phosphates, clays, and occurred predominantly as sulfide species. The chemical extraction also indicated that Zn was present to a lesser extent as exchangeable ions. Such a variety of physicochemical species suggests that sludge retained in detention basins or generated by CSO treatment can only be disposed off in controlled landfills. In particular, such sludge can not be applied to land as heavy metals contained in sulfides will be released under oxidizing conditions.

This study provides a preliminary inventory of various particle types that can be encountered in sewage and combined sewer overflows (CSOs). Electron microscope investigations always raise the problem of results representativity. Clearly, the number of heavy metal carriers examined here remains infinitesimally small compared to the total amount of particles actually transported in the sewer system during either dry or wet weather. Extreme caution should then be exerted as to the conclusions inferred from microscopical observations. Still, our results strongly suggest that (i) in the sewer system, chalcophile elements accumulate in anaerobic portions as early diagenetic sulfide phases, which are resuspended during rain events. (ii) The various sources (urban surfaces, soils, or sewer sedi-

ments) contributing to the load transported in combined sewer can be recognized from a detailed analysis of individual particles. (iii) As some types of particles can be considered as markers, the changes in their relative abundance during the course of a rain event can provide useful insights about the pollution sequence occurring in CSOs.

Acknowledgements

The financial support provided by Grand Nancy Urban Community is gratefully acknowledged. The authors wish to express their sincere thanks to Patrice Robaine and his staff for technical support. Thanks also go to Guillaume Defontaine and Vincent Chanudet for their help in the field, and to Didier Perret for insightful comments about the manuscript.

References

- [1] Bedient P, Harned DA, Characklis WG. Storm water analysis and prediction in Houston. *J Environ Eng Div ASCE* 1978;104:1087–100.
- [2] Ellis JB, Hvitved-Jacobsen T. Urban drainage impacts on receiving waters. *J Hydraul Res* 1996;34(6):771–83.
- [3] Mason Y, Ammann A, Ulrich A, Sigg L. Behavior of heavy metals, nutrients, and major components during roof runoff infiltration. *Environ Sci Technol* 1999;33:1588–97.
- [4] Davis A, Shokouhian M, Ni S. Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources. *Chemosphere* 2001;44:997–1009.
- [5] Gromaire MC, Garnaud S, Saad M, Chebbo G. Contribution of different sources to the pollution of wet

- weather flows in combined sewers. *Water Res* 2001;35(2):521–33.
- [6] Chebbo G, Mouchel JM, Saget A, Gousailles M. La pollution due aux rejets urbains par temps de pluie: flux, nature et impacts. *TSM* 1995;90:796–806.
- [7] Lee J, Bang W. Characterization of urban stormwater runoff. *Water Res* 2000;34(6):1773–80.
- [8] Morrison GMP, Revitt DM. Assessment of metal species bioavailability and geochemical mobility in polluted waters. *Environ Technol Lett* 1987;8:361–72.
- [9] Florence TM, Morrison GM, Stauber JL. Determination of trace element speciation and the role of speciation in aquatic toxicity. *Sci Total Environ* 1992;125:1–13.
- [10] Perin G, Fabris R, Manente S, Rebello Wagener A, Hamacher C, Scotto S. A five-year study on the heavy metal pollution of Guanabara Bay sediments (Rio De Janeiro, Brazil) and evaluation of the metal bioavailability by means of geochemical speciation. *Water Res* 1997;31(12):3017–28.
- [11] Tessier A, Campbell PGC, Bisson M. Sequential extraction procedure for the speciation of particulate trace metals. *Anal Chem* 1979;51(7):844–51.
- [12] Lake DL, Kirk PWW, Lester JN. Fractionation, characterization, and speciation of heavy metals in sewage sludge and sludge—Amended Soils: a review. *J Environ Qual* 1984;13(2):175–83.
- [13] Serne RJ. Geochemical distribution of selected trace metals in San Francisco bay sediments. Water and Waste Management Section, Bahelle, Pacific North West Laboratories, Richland Washington, 1975
- [14] Förster J. Patterns of roof runoff contamination and their potential implications on practice and regulation of treatment and local infiltration. *Water Sci Technol* 1996;33(6):39–48.
- [15] Morrison GM, Revitt DM, Ellis JB. Sources of storm loading variations of metal species in a gullypot catchment. *Sci Total Environ* 1989;80:267–78.
- [16] Butler D, Xiao Y, Karunaratne S, Thedchanamoorthy S. The gully pot as a physical, chemical and biological reactor. *Water Sci Technol* 1995;31:219–28.
- [17] Ostergren JD, Brown Jr. GE, Parks GA, Tingle TN. Quantitative speciation of lead in selected mine tailings from leadville, Co. *Environ Sci Technol* 1999;33:1627–36.
- [18] La Force MJ, Fendorf S. Solid-Phase iron characterization during common selective sequential extractions. *Soil Sci Soc Am J* 2000;64:1608–15.
- [19] De Boer D, Crosby G. Evaluating the potential of SEM/EDS analysis for fingerprinting suspended sediment derived from two contrasting topsoils. *Catena* 1995;24:243–58.
- [20] Zaggia L, Zonta R. Metal-Sulphide formation in the contaminated anoxic sludge of the Venice canals. *Appl Geochem* 1997;12:527–36.
- [21] Buatier M, Sobanska S, Elsass F. TEM-EDX investigation on Zn and Pb-contaminated soils. *Appl Geochem* 2001;16:1165–77.
- [22] Marchand A, Badot R, De Belly B, Romain M. Les bassins de retention des eaux pluviales-Mode d'emploi. NANCIE 1993, 222pp.
- [23] Laurennot F. Caractérisation de la charges métallique des eaux de temps de pluie, Contribution des différents réservoirs à la pollution des eaux de temps de pluie. R-apport final, LHRSP, Nancy-France 1998, 45pp.
- [24] Michelbach S, Weib G. Settleable sewer solids at storm-water tanks with clarifier for combined sewage. *Water Sci Technol* 1996;33:261–7.
- [25] Kumar R, Srivastava K, Srivastava P. Leaching of heavy metals (Cr, Fe, and Ni) from stainless steel utensils in food simulants and food materials. *Bull Environ Contam Toxicol* 1994;53:259–66.
- [26] Wallinder I, Lu J, Bertling S, Leygraf C. Release rates of chromium and nickel from 304 and 316 stainless steel exposure—a combined field and laboratory study. *Corrosion Sci* 2002;44:2303–19.
- [27] Marucco A. Phase transformations during long term ageing of Ni–Fe–Cr alloys in the temperature range 450–600°C. *Mater Sci Eng A* 1995;194:225–33.
- [28] Stamatakis MG, Koukousas NK. The occurrence of phosphate minerals in lacustrine clayey diatomite deposits, Thessaly, Central Greece. *Sediment Geol* 2001;139:33–47.
- [29] Chen X, Wright J, Conca J, Peurrung L. Effects of pH on heavy metal sorption on mineral apatite. *Environ Sci Technol* 1997;31:624–31.
- [30] Chern Lin J, Chen K, Ju C. Transmission electron microscopic study of early stage $\gamma 1$ (Ag_2Hg_3) and $\beta 1$ (Ag–Hg) phases, Technical note. *Dent Mater* 2002;18:422–4.
- [31] Acciari H, Guastaldi A, Brett C. Corrosion of dental amalgams: electrochemical study of Ag–Hg, Ag–Sn and Sn–Hg phases. *Electrochem Acta* 2001;46:3887–93.
- [32] Hesterberg D, Chou J, Hutchison K, Sayers D. Bonding of Hg(II) to reduced organic sulfur in humic acid as affected by S/Hg ratio. *Environ Sci Technol* 2001;35:2741–5.
- [33] Morse J, Millero J, Cornwell J, Rickard D. The chemistry of the hydrogen sulfide and iron sulfide systems in natural waters. *Earth-Sci Rev* 1987;24:1–42.
- [34] Herbert Jr. R, Benner S, Pratt A, Blowes D. Surface chemistry and morphology of poorly crystalline iron sulfides precipitated in media containing sulfate—reducing bacteria. *Chem Geol* 1998;144:87–97.
- [35] Taillefert M, Lienemann C-P, Gaillard J-F, Perret D. Speciation, reactivity, and cycling of Fe and Pb in a meromictic lake. *Geochem Cosmochim Acta* 2000;64:169–83.
- [36] Hvitved-Jacobsen T, Raunkjaer K, Nielsen P. Volatile fatty acids and sulfide in pressure mains. *Water Sci Technol* 1995;31:169–79.
- [37] Bellanca A, Hauser S, Neri R, Palumbo B. Mineralogy and geochemistry of Terra Rossa soils, western Sicily: insights into heavy metal fractionation and mobility. *Sci Total Environ* 1996;193:57–67.
- [38] Fanfani L, Zuddas P, Chessa A. Heavy metals speciation analysis as a tool for studying mine tailings weathering. *J Geochem Explor* 1997;58:241–8.
- [39] Gromaire MC, Chebbo G, Saad M. Origins and characteristics of urban wet weather pollution in combined sewer systems: the experimental urban catchment “le marais” in paris. *Water Sci Technol* 1998;37:35–43.
- [40] Kusoffsky A, Jansson B. A thermodynamic evaluation of the Co–Cr and the C–Co–Cr systems. *Calphad* 1997;21:321–33.
- [41] Murthy J, Rao D, Venkataraman B. Effect of grinding on the erosion behaviour of a WC–Co–Cr coating deposited

- by HVOF and detonation gun spray processes. *Wear* 2001;249:592–600.
- [42] Pestryakov A, Davydov A. The influence of modifying additions of La and Ce oxides on electronic state of surface atoms and ions of supported copper. *Appl Surf Sci* 1996;103:479–83.
- [43] Kili K, Normand F. Modification of the catalytic properties of palladium by rare earth (La, Ce) addition, Catalytic activity and selectivity in hydrocarbon conversion. *J Mol Catal A* 1999;140:267–85.
- [44] Guaita F, Beltran H, Cordoncillo E, Carda J, Escribano P. Influence of the precursors on the formation and the properties of $ZnFe_2O_4$. *J Eur Soc* 1999;19:363–72.
- [45] Roberts D, Scheinost A, Sparks D. Zinc speciation in a smelter-contaminated soil profile using bulk and micro-spectroscopic technique. *Environ Sci Technol* 2002;36:1742–50.
- [46] Jdid E, Yvon J, Barrès O, Lhote F. Evaluation du comportement à long terme des résidus fins d'incinération des ordures ménagères (REFIOM) syabilisés aux liants hydrauliques. Laboratoire Environnement et Minéralurgie. Rapport de la convention LIFE 99. Env/B-000638-2000, 45pp.
- [47] Large D, Fortey N, Milodowski A, Christy A, Jodd J. Petrographic observation of iron, copper, and Zinc sulfides in freshwater canal sediment. *J Sediment Res* 2001;71: 61–9.
- [48] Cutter G, Kluckholn R. The cycling of particulate carbon, nitrogen, sulfur, and sulfur species (iron monosulfides, greigite, pyrite, and organic sulfur) in the water columns of Framvaren Flord and the Black Sea. *Mar Chem* 1999;67:149–60.
- [49] Schippers A, Jorgensen B. Biogeochemistry of pyrite and iron sulfide oxidation in marine sediments. *Geochem Cosmochem Acta* 2002;66:85–92.
- [50] Lennie A, Redfern S, Champness P, Stoddart C, Schofield P, Vaughan D. Transformation of mackinawite to greigite: an in situ X-ray powder diffraction and transmission electron microscopy study. *Am Mineral* 1997;82:302–9.
- [51] Hilton J. Greigite and the magnetic properties of sediments. *Limnol Oceanogr* 1990;35:509–20.
- [52] Labrenz M, Druschel G, Thomsen-Ebert T, Gilbert B, Welch S, Kemmer K, Logan G, Summons R, De Stadio G, Bond P, Lai B, Kelly S, Banfield J. Formation of sphalerite (ZnS) deposits in natural biofilms of sulfate-reducing bacteria. *Science* 2000;290:1744–7.
- [53] O'Day P, Carrol S, Randall S, Martinelli R, Anderson S, Jelinski J, Knezovich J. Metal speciation and bioavailability in contaminated estuary sediments, Almenda Naval air station, California. *Environ Sci Technol* 2000;34: 3665–73.
- [54] Luther III G, Theberge S, Rickard DT. Evidence for aqueous clusters as intermediates during Zinc sulfide formation. *Geochem Cosmochem Acta* 1999;63:3159–69.
- [55] Norsker N, Nielsen P, Hvitved-Jacobsen T. Influence of oxygen on biofilm growth and potential sulfate reduction in gravity sewer biofilm. *Water Sci Technol* 1995;31: 159–67.
- [56] Matthijs E, Debaere G, Itrich N, Masscheleyn P, Rottiers A, Stalmans M, Federle T. The fate of detergent surfactants in sewer systems. *Water Sci Technol* 1995;31:321–8.
- [57] El samrani AG. Dépollution des eaux pluviales: Spéciation des éléments traces et optimisation du traitement de coagulation-floculation. Thèse, INPL-Nancy-France 2003, 270pp.
- [58] Guillet B, Burtin G, Delcroix P, Gury M. Le fer des calcaires et des terra fusca des plateaux lorrains (France). *Pedologie*. 1984;XXXIV3:301–18.
- [59] Du Q, Sun Z, Forsling W, Tang H. Adsorption of copper at aqueous illite surfaces. *J Colloid Interface Sci* 1997;187:232–42.
- [60] Cliff RA, Drewery SA, Leeder MR. Sourcelands for the carboniferous Pennine river system: constraints from sedimentary evidence and U–Pb geochronology using zircon and monazite. In: Morton AC, Todd SP, Haughton PDW. editors. *Developments in sedimentary provenance studies*, vol. 57. Geol. Soc. London, Bath, Spec. Publ; 1991. p. 137–59.
- [61] Velbel MA. Bond strength and the relative weathering rates of simple orthosilicates. *Am J Sci* 1999;299:679–96.
- [62] Morrison GM, Revitt DM, Ellis JB, Svensson G, Balmer P. Variations of dissolved and suspended solid heavy metals through an urban hydrograph. *Environ Technol Lett* 1984;7:313–8.
- [63] Sonzogni WC, Chesters G, Coote DR, Jeffs DN, Konrad JC, Ostry RC, Robinson JB. Pollution from land runoff. *Environ Sci Technol* 1980;14:148–53.
- [64] Barnes G, Davis A. Dissolution of lead paint in aqueous solutions. *J Environ Eng* 1996;122:663–6.
- [65] Davis A, Burns M. Evaluation of lead concentration in runoff from painted structures. *Water Res* 1999;33: 2949–58.
- [66] Krätschmer A, Odnevall Wallinder I, Leygraf C. The evolution of outdoor copper patina. *Corrosion Sci* 2002;44:425–50.