

### Review on physical and chemical characterizations of contaminated sediments from urban stormwater infiltration basins within the framework of the French observatory for urban hydrology (SOERE URBIS)

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### Review on physical and chemical characterizations of contaminated sediments from urban stormwater infiltration basins within the framework of the French observatory for urban hydrology (SOERE URBIS)

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Abstract Urban stormwater infiltration basins are designed to hold runoff from impervious surfaces and allow the settling of sediments and associated pollutants. However concerns have been expressed about the environmental impacts that may be exerted by the trapped pollutants on groundwater, soils and ecosystems. In this context, sediment characterization represents a key issue for local authorities in terms of management strategies. During the last two decades, several

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Université de Lyon, LEHNA UMR5023 Ecologie des Hydrosystèmes Naturels et Anthropisés, Université Lyon 1, ENTPE, CNRS, INRA, Campus de Vaulx-en-Velin, 3 rue Maurice Audin, 69518 Vaulx-en-Velin, France studies were launched including either physical or chemical characterization of stormwater sediments but without real synthesis of data and methods used. Consequently, there is an important need for reviewing the current experimental techniques devoted to the physico-chemical characterization of sediment. The review is based on the outcomes of two experimental sites for which long term monitoring and data collection have been done: the Cheviré basin (near Nantes) and the Django Reinhardt basin (near Lyon). The authors summarize the studies dealing with bulk properties, pollutant contents, their potential mobility and speciation. This paper aims at promoting the significant progresses that were made through a multidisciplinary approach involving multi-scaled and combined experimental techniques.

Keywords Infiltration basins · Aggregation · Urban sediment · Technosol · PAHs · Trace metals · Multi-scaled methodology · Field observatory · SOERE URBIS

### Introduction

Retention and infiltration basins are widely used in urban stormwater management to provide protection from flooding, recharge of aquifers and improvement of downstream waters quality (Lawrence et al. 1996). These basins are actually supposed to accumulate large amount of sediment over time and trap pollutants such as trace metals, nutrients and polycyclic aromatic hydrocarbons (PAHs; Nightingale 1987; Yousef et al. 1990; Marsalek and Marsalek 1997; Barbosa and Hvitved-Jacobsen 1999). If the pollutant removal mainly associated with sediments seems a good way to improve the quality of downstream waters collected by networks and discharged to water courses, some drawbacks have to be taken into account such as environmental risks, including a risk to groundwater from pollutant transfer, degradation of infiltration capacity and sediment settling. As the maintenance strategy is commonly the cleaning out of the basins, it is also a charge for local municipalities that have to manage important quantity of sediments potentially highly polluted. Although various studies from both estimates and surveys differs in the assessment of amounts of sediment produced by road and motorway networks, a rough extrapolation for the entire French territory carried out by Pétavy et al. (2006) provides an estimation of about 5 million tons per year of sediments that have to be managed. As a comparison, the amount of sludge (in dry matter form) from French water treatment plants was estimated at 1.3 million tons/year in 2005 (IFEN 2006). In this context, sediment characterization represents a key issue for local authorities in terms of environmental issues, maintenance strategies for retention infiltration basins and treatment and valorization techniques of sediments.

Sediments from urban retention/infiltration basins are complex solid materials, composed of solid phases (mineral and organic phases) resulting mainly from the sedimentation of particles brought by runoff water. The term "sediment" used in this study describes the top soil easily distinguishable from the underlying soil by a significant difference of coloration and texture. Additionally, as suggested by Badin et al. (2009) these solid materials can be called "Technosol" according to their evolution characteristics (FAO 2006).

The first field studies on the characterization of these sediments were carried out in the seventies (Nightingale 1974) and they only concerned a few metals (Cu, Pb, Zn). In the eighties, other studies were also devoted to metals (Wigington et al. 1983; Nightingale 1987; Yousef et al. 1987), sometimes with few bulk parameters such as pH. Infiltration basins were still investigated in the nineties but the works continued to mainly address trace metals (Yousef et al. 1994; Legret et al. 1995; Lee et al. 1997), and sometimes hydrocarbons (Gautier 1998).

Researchers went on to assess the amount of sediments trapped, their biological, physical, chemical and even ecotoxicological characteristics, their location and evolution overtime in order to estimate their potential toxicity, treatability and to evaluate the mobility pollutants toward groundwater (e.g., Weinstein et al. 2010; Gallagher et al. 2011; Tixier et al. 2012). Therefore, studies were launched during the last decades including both metals and organic pollutants and taking into account the physical characteristics of the particles (e.g., in France: Durand et al. 2003; Dechesne et al. 2004; Clozel et al. 2006). The pollutant mobility was also taken into account through speciation studies, together with a few works on the correlation between particle size distribution and pollutant concentrations (Clozel et al. 2006; Badin et al. 2008; Pétavy et al. 2009; El-Mufleh Al Husseini et al. 2013). Finally, the diversity of microorganisms in sediment aggregates (Badin et al. 2009) and the role of plants on the characteristics of this type of technosol (Saulais et al. 2011) were studied.

Whereas results in terms of sediment characterization for environmental issues and management practices are of growing concern for practitioners it appears from this review that an increasing combination of methods was used to characterize sediments from stormwater basins with a real difficulty to compare or combine the results.

Among the most complete studies are those carried out by the French teams now involved in the national observatory for urban hydrology (SOERE URBIS) created in January 2007 and gathering the three national observatories: OPUR (Observatoire des Polluants Urbains) in Paris, OTHU (Observatoire de Terrain en Hydrologie Urbaine) in Lyon and ONEVU (Observatoire Nantais des Environnements Urbains) in Nantes. Many results on each different experimental site have already been published but the results with regards to characterization methods and potential complementarity have not been addressed.

This paper focuses on results obtained on two experimental sites of the SOERE URBIS for which long term monitoring and data collection have been done and significant progresses made through a multidisciplinary approach involving multiscaled and combined experimental techniques: the Cheviré (near Nantes) and Django Reinhardt (DjR) basin (near Lyon). The objective of this paper is more precisely to compare and discuss the complementarity of the experimental procedures illustrated by the main results obtained on the characterization of the sediments trapped by two different systems (one draining a small road catchment, and the other a large one).

Apart from the description of experimental sites and types of investigations, the paper consists of three parts. The first one is dedicated to the characterization of trace metal and organic pollutant concentrations in sediments. The second one summarizes the physical and chemical studies carried out to improve knowledge on the bulk properties of these particular sediments and relations with the pollutant loads. As the decision-making process of sediment management could not only rely on the estimation of pollutant total content, the third part of the paper focuses on the experimental methods aimed at the study of the speciation and potential mobility of pollutants, in particular in terms of bearing phases. To our knowledge, there is no such complete review devoted to the investigation methods for stormwater sediments.

# Two decades of works on two urban stormwater infiltration basins

Description of the experimental sites

The main characteristics of the Cheviré and DjR sites are summarized in Table 1.

Table 1         Main characteristics of the experimental s	ites
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	Cheviré	DjR
Type of catchment	Urban/road	Urban/industrial
Total drainage area (ha)	1.9	185
Impervious coefficient (%)	100	75
Volume (m <sup>3</sup> )	1,170	61,000
Basin area (m <sup>2</sup> )	780	8,000
Type of subsoil	Sandy alluvial deposits	Carbonated fluvio- glacial deposits
Vadose zone depth (m)	1.5-3.5	13
Observation period	1993–2011	1999–2011

### Cheviré infiltration basin

This infiltration basin receives highway runoff waters from the south part of the main bridge of Nantes crossing the Loire River. Opened in 1991 to close the ring road around Nantes, it supports a total average daily traffic of 90,000 vehicles. The Cheviré bridge is 1,562 m long, 24.6 m large and 40 m high. Carriageways consist of three lanes in each direction, separated by a central reservation. The drainage area for the southern basin is around 1.9 ha. Runoff waters are collected in gulleys, driven through an aluminum swallow and then through a concrete pipe to the basin. The surface of the basin is  $780 \text{ m}^2$  and its depth is about 1.5 m. The main pipe collecting stormwater in the basin is 0.8 m in diameter. Gravel settlement was observed in the collector, preventing a part of the coarser particles carried by runoff waters from settling in the basin. The runoff waters are infiltrated all along a single flowpath from the entrance to the overflow of the basin to the Loire River. No sediment removal of the basin (except in the inlet area CH1; Fig. 1a) since 1991 has led to a sedimentary accumulation over original sandy subsoil. Depending on stormwater input, the basin remains usually flooded during 2 to 4 days. The groundwater level is between 1.5 m and 3.5 m below the bottom of the basin when the level of water table is high and can in some rare hydrological periods come up to the basin bottom. In 1993, no vegetation was observed in the basin. Thereafter, the basin has progressively been overgrown with spontaneous vegetation. In 2001, only weeds were found. Since 2003, the presence of trees, shrubs and weeds was noticed. An inventory of plants observed in the Cheviré basin was proposed by Coulon et al. (2013).

### Django Reinhardt infiltration basin

The second site is located in Chassieu in the Eastern suburbs of Lyon, France. The DjR detention–infiltration basin collects stormwater from an industrial area of 185 ha, which is densely urbanized (about 75 % of imperviousness).

The catchment is drained by a stormwater separate system. However intermittently, the pipe network collects "clean" water (or supposed to be clean) that comes from cooling of industrial processes. The detention–infiltration system placed at the outlet is composed of two compartments (Fig. 1b): (1) a detention and settling basin of 32,000 m<sup>3</sup> covering 11,000 m<sup>2</sup> and (2) an infiltration basin of 61,000 m<sup>3</sup> and 8,000 m<sup>2</sup>.

Stormwater and dry weather effluent from the catchment enters the detention-infiltration system via (1) two 160-cm circular pipes, then flows successively through: (2) the detention/settling basin, (3) a 350 l/s flow control device, (4) a 60-cm circular pipe connecting the two compartments and (5) the infiltration basin. During maintenance of the settling compartment water is diverted to the infiltration basin and discharged directly in the infiltration part by a 60-cm pipe. The aquifer is located approximately 13 m under the bottom of the infiltration basin. Infiltration occurs through quaternary fluvial and glacial deposits. The soil beneath the infiltration basin is mainly composed of coarse material (30 % pebbles, 45 % gravels, 20 % coarse sand and 5 % fine sand). The groundwater level is 13 m below the bottom of the infiltration basin (Barraud et al. 2002). The bottom of the basin was designed to be bare.

The basin has been operating for more than 30 years. It was rehabilitated in 2002. The initial three compartment system was transformed into a more simple two compartment system as described in Fig. 1b. The basin was then totally scraped in April 2004 (sediments and the topsoil completely removed except in its south east corner where a thick layer of sediments was left). From the end of 2006 to the beginning of 2007, the bare bottom of the basin has progressively been overgrown with spontaneous vegetation qualified by Saulais et al. (2011).

### Sampling methodology and purposes of the studies

For each basin, various sampling campaigns were conducted with one or several objectives. Only sampling campaigns aimed at the physical and chemical characterizations of contaminated sediments were taken into account in this paper, even if other issues were addressed within the last years, such as infiltration performances or microbiology for example. Table 2 presents the parameters analyzed and/or the studies conducted on samples collected during the selected sampling campaigns for Cheviré and DjR basins, the stormwater sediments being characterized according to soil standards.

### Cheviré infiltration basin

The site has been studied since 1993 (IFSTTAR-ONEVU). Seventeen sampling campaigns have been conducted since that year. Five campaigns devoted to several characterizations were selected: 1993, 2001, 2003, 2005 and 2009.

Fig. 1 Schemes of a Cheviré (from Coulon et al. 2013) and b DjR basins (A, B and C are the points in areas most often sampled and cited in the text)



32 000 m<sup>3</sup>

The 1993, 2001, 2003 and 2009 sampling campaigns were conducted on three zones. These zones were selected based on their location within the basin (entrance and outlet) (Fig. 1a). Zone (CH1) is located at the entrance of the basin, zone 2 (CH2) corresponds to the middle area and zone 3 (CH3) is situated near the outlet. In 2005, another area, P1, situated between CH1 and CH2 was sampled (Fig. 1a).

The sampled sediment layer can be distinguished from the underground soil by its black color, its texture and its structure. The thickness of this layer varies depending on the zones: from 9 cm (CH3) to 21 cm (CH2). In zone 1 (CH1), the surface layer is composed of a succession of sediment and sand layers that resembles a deltaic deposit. This particular texture could be explained by the fact that when heavy rainfall events occur, coarser particles settled in the entrance pipe are swept into the basin. Between 1993 and 2009, the thickness of the sedimentary layer increased from about 10 mm (0.6 mm/ year) to about 200 mm (12.5 mm/year) in zones 2 and 3. The sediment sampling was conducted on the entire thickness and

on each zone of the basin. For each sampling zone, a representative sample was composed of a homogeneous mixture shots within a grid system distribution. According to the analyses and studies carried out, the samples obtained were preserved in adapted containers (glass or plastic). At the laboratory these sediments were 2-mm sieved and dried at 40 °C or freeze-dried.

2001

2009

The samples were regularly analyzed for the bulk parameters: pH, dry and volatile matter, water content, grain size and total organic carbon (TOC). Trace metals were also systematically quantified by chemical analyses. Less data on organic pollutants were collected but the organic matter was specifically characterized and analyzed (Durand et al. 2004a; El-Mufleh et al. 2013; Coulon et al. 2013). Finally, several studies were devoted to the characterization of the bearing phases of pollutants and to their potential mobility either by extractions (Durand et al. 2004a; El-Mufleh Al Husseini et al. 2013) or by analyses of pore waters (Béchet et al. 2007).

Table 2 by more than the		תואלעא מוות העלהווו		sampung van	vin ito engindu	CITICBU UNI						
	ONEVU	- Cheviré				OTHU — Django	Reinhardt					
	1993 Legret et al. (1995)	2001 Durand (2003), Clozel et al. (2006)	2003 Durin (2006)	2005 Pétavy (2007)	2008–2011 El-Mufleh (2011)	1999–2000 200 Winiarski et al. (2001)	11 2005 Le Cou (200	2 1stumer E 18)	006–2007 ładin (2009)	2005–2010 Le Coustumer et al. (2007), Le Coustumer	2008–2011 Saulais et al. (2011)	2009–2011 Gonzales- Merchan (2012)
Sediment thickness					×					× (2008) ×		×
Trace metals	×	×	×	×	×	×	×	×		$\times$ (Cu, Pb, Zn)	×	
PAHs		×		×	×		×	×				
Total hydrocarbons			×		×		×	×				
Hq	×		×		×	×	×	×			×	
Mineralogy		×			×			×				
Major elements	$\times$ (AI)	×	×	×	×			×			×	
Total organic matter (TOM)		×	×	×	×	×	×	×			×	×
Total organic carbon (TOC)			×		×		×	x			×	
Organic matter study		×						×				
Particle size analyses		×	×	×	×	×	×	×		$\times$ (10 pts)	×	×
Size fractionation		×	×	×	×			×				
Study of aggregation					×			×				
Single metal e×traction											×	
Sequential metal extraction		×			×							
Kinetic extraction					×							
Magnetic/density fractionation		×			×							

 Table 2
 Synthesis of the performed analyses and experiments for the sampling campaigns on the two basins

### Django Reinhardt infiltration basin

More than 20 campaigns were carried out on the DjR basin since 1999 in the OTHU observatory.

The different campaigns were dedicated to answer different specific questions. pH, water content, loss on ignition, TOC and heavy metal content were systematically measured either on mean samples constituted from a mixture of 10–20 random or regular sub sampling strategy or on localized samples. The samples are generally homogenized and stored at 4 °C before analyses or freeze-dried for organic characterization. Different objectives were dedicated to the different campaigns (as described in the following paragraphs).

Winiarski et al. (2006) collected samples (1999–2001) on three different locations in the basin form the surface to 4 m depth. Physico-chemical measurements were carried out at every 10 cm until 50 cm depth and then at every 20 cm. These studies show that the main pollution accumulation was found in the topsoil. In 2005 and in three representative points, samples were taken at different depth (from 0 to -1 m) to corroborate the reports of Winiarski et al. 2006 and Dechesne et al. 2004 for another basin located in the east of Lyon. The 2005's campaign were then analyzed in terms of pH, dry and volatile matter, water content, grain size, TOC, trace metal, total hydrocarbons (THCs) and PAHs (benzo[*a*]pyrene, benzo[*b*]fluoranthene, fluoranthene, benzo[*g*,*h*,*i*]perylene, benzo[*k*]fluoranthene, indeno[1,2,3-*c*,*d*]pyrene) contents.

This campaign was carried out in May 2008 and April 2010. The measures show that sediment thickness is higher in areas regularly exposed to runoff water (in particular in the area near the inflow point) and in the lowest parts in terms of topography. In these zones, the thickness layer reached 14 cm (May 2008) and more than 20 cm (April 2010). The accumulation was therefore about 10 mm/year mainly coming from stormwater total suspended solids (TSS) (from 63 % to 74 %) compared to other sources (Gonzalez-Merchan et al. 2013).

On April 2005, February 2006, July 2007, April 2008, April 2009 and July 2010, 100 points were collected, according to a  $10 \times 10$  m grid, taken in the top 5 cm of the infiltration systems. All the samples were then oven dried at 105 °C and 2-mm sieved before the determination of Zn, Pb, and Cu concentrations with an X-ray fluorescence (XRF) portable analyser Niton XLt 700 Series Instrument calibrated with ICP-MS (inductively coupled plasma-mass spectrometry) analyses. The spatio-temporal results from 2005 to 2006 were published by Le Coustumer et al. (2007), and those from 2005 to 2007 were reported by Le Coustumer (2008). Since that time, two other similar campaigns were carried out one in 2008 and one in 2010 (Gonzalez-Merchan 2012).

Badin et al. (2008, 2009) collected the surface of the same zone at five different periods during 1 year in order to study the evolution of aggregation and the consequences on the localization of hydrocarbons, heavy metals and natural organic matter were taken from a  $2\text{-m}^2$  area (samples of 1 kg each). They were kept at 4 °C for 5 weeks before fractionation experiments, and aliquots were frozen at -18 °C. Sampling and conservation were performed in glass bottles for hydrocarbons analysis (Badin et al. 2008, 2009). Saulais et al. (2011) studied samples collected at three different periods corresponding to the different plant growth phases under three different vegetation covers (a mixture of sample on a  $2\text{-m}^2$ area). The potential mobility of Zn, Cu and Cd was also carried out.

#### A sediment presenting a mixed and complex pollution

These sediments are characterized by their high mineral and organic pollutants contents. This is why they have been deeply studied. Concerns have been expressed about the environmental impacts that may be exerted by the trapped pollutants on groundwater, soils and ecosystems. We thus begin this review by the description of pollutant loads.

Trace metal content evaluation methods

For the analysis of trace metals, one important analytical point is the dissolution phase, i.e., total attack with a HF-HClO<sub>4</sub> mixture or pseudo-total attack with aqua regia (HCl-HNO<sub>3</sub>), referring to NF X 31-147 (1996) and NF ISO 11466 (1995) standards, respectively. NF ISO 11466 (1995) standard points out that the majority of soils are not completely dissolved by aqua regia and the effectiveness of extraction differs from one element to another. A close attention must be paid to this analytical point.

Moreover, the instrumental techniques of trace metal analysis have evolved. In two decades, successive techniques were used: the atomic absorption spectrometry, inductively coupled plasma atomic or optical emission spectroscopy (ICP-AES or ICP-OES) and then ICP-MS. The benefits brought by the development of these techniques are in terms (1) of limit of quantification and (2) panel of elements analyzed at the same time. The comparison of the results obtained by these techniques is easy if the dissolution reagent is the same.

Major and trace metal analyses for Cheviré sediments were always carried out in the same laboratory and after dissolution by total attack. For DjR sediments, the analyses were not always carried out in the same laboratory nor under the same conditions of dissolution. Table 3 specifies the dissolution method used (total or pseudo-total) for the analyses carried out between 2001 and 2009. Moreover, for the campaigns of 2005 to 2010, Cu, Pb and Zn determinations were carried out directly on the solid sample (without dissolution pre-stage) using an XRF spectrometer. The limits of quantification of the elements by this technique were thus relatively high. They are 5, 10 and 12 times higher than that of the ICP-MS for Zn, Cu

		Major and tra	ce elements	Polycyclic aromatic l	nydrocarbons			Total hydrocarbon co	ntent
		Attack	Analytical method	Extraction solvent	Soxhlet	ASE	Analytical method	Extraction solvent	Analytical method
Cheviré	Legret et al. 1995	HF/HClO <sub>4</sub>	AAS						
	Durand (2003)		ICP-OES/ICP-MS	CC14	×		GC-MS		
	Durin (2006)								
	Pétavy (2007)			C <sub>6</sub> H <sub>6</sub> /(CH <sub>3</sub> ) <sub>2</sub> CO	×		LC-Fluo	CFC	FTIR
	El-Mufleh (2011)			CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> OH		×	GC-MS	C <sub>6</sub> H <sub>6</sub> /(CH <sub>3</sub> ) <sub>2</sub> CO	GC-FID
DjR	Le Coustumer (2008)		XRF						
	Le Coustumer (2008) in 2005		ICP-AES						
	Badin (2009)	Aqua regia	ICP-OES/AAS	$CH_2Cl_2$		×	GC-MS		
	Saulais et al. (2011)	Aqua regia	ICP-OES and AAS						

ionization detector, ICP-AES inductively coupled plasma atomic emission spectroscopy, ICP-OES inductively coupled plasma optical emission spectroscopy, ICP-MS inductively coupled plasma mass spectrometry, XRF X-ray fluorescence

and Cd, respectively. Thus Cd quantification was not carried out by this technique in DjR basin. Table 3 synthesizes the methodologies used for each campaign.

Total hydrocarbons and PAH content evaluation methods

The first stage for THCs ( $\Sigma C_{10} - C_{40}$ ) and PAH analysis is the extraction from the matrix. This extraction was carried out using an organic solvent by a Soxhlet or Accelerated Solvent Extractor (ASE) systems. After extraction, PAHs were analyzed either by gas chromatography coupled to mass spectrometry (GC-MS) or high-performance liquid chromatography (HPLC) according to EPA 8270 US standard and NF ISO 13877 (1999), respectively. For THC, until the end of 2008, their analysis was carried out by infra-red spectroscopy according to the X31-410 standard. At present, the analysis is performed by gas chromatography coupled to flame ionization detector (GC-FID) according to the X31-431 standard. A characterization campaign of THC content in road residues was carried out, in 2008 by the CETE-IF, on 25 samples coming from stormwater basins and ditches of Paris and Lyon regions (France). The study aimed to compare THC concentrations obtained by IR or GC-FID. The range concentrations were from 100 to 8,400 mg  $\rm kg^{-1}.$  The results show an average concentration ratio of 3,1 between IR and GC-FID techniques. Table 3 synthesizes the type of solvent of extraction, the extraction and analytical methods used for each campaign.

### Pollutant levels and spatial distribution

Table 4 presents the concentrations of trace metals, PAHs and THCs in the different areas of the basins for Cheviré and DjR. Compared to the Dutch intervention thresholds, used as reference (refer to: Ministry of Housing, Spatial Planning and Environment (1994). Intervention Values and Target Values - Soil Quality Standards. The Hague (the Netherlands): Directorate-General for Environmental Protection, 19 p. Ministry of Housing, Spatial Planning and Environment, The Netherlands 1994; Spierenburg and Demanze 1995), sediments from infiltration basins are mostly polluted with trace metal and hydrocarbons. Despite a low content, cadmium is always taken into account because of its high toxicity. The concentrations of trace elements must indeed be compared to those of the local geochemical background. As an example, even if chromium content of the Cheviré sediment was near or over 100 mg kg<sup>-1</sup>, this value was in good agreement with the underlying soil and the local geochemical chromium contents.

Trace metal concentrations ranged from 0.5 to 2,500 mg kg<sup>-1</sup>, depending on the element, with the following order of concentration: Zn>Pb>Cu>>Cd (Durand et al. 2004b; Le Coustumer 2008; Mermillod-Blondin et al. 2008; El-Mufleh Al Husseini et al. 2013) (Table 4). On Cheviré basin, the concentrations of pollutants increased from the entrance (CH1) to the outlet (CH3). The comparison of the levels of pollutants between 1993 and

				Cd	Cu	Pb	Zn	THC	∑РАН
				(mg kg <sup>-1</sup> )					$(\mu g \ kg^{-1})$
Cheviré	Legret et al. (1995)	CH1		1.2	90	300	683		
		CH2		1.5	84	292	833		
		CH3		3.7	208	819	1,980		
	Durand (2003)	CH1 CH2		1.6 1.7	237 297	359 376	1,576 1,894		2206 (mean)
		CH3		2.0	279	522	2,070		
	Durin (2006)	CH1 CH2		1.1 1.6	206 308	254 319	1,447 1,787		
		CH3		2.6	317	445	2,463		
	Pétavy (2007)	P1 (near CH1)		1.1	281	30	1,526	7,674	1,752
	El-Mufleh (2011)	CH1		0.5	190	70	784	1,300	2,344
		CH2		0.9	320	250	1,714	2,056	4,340
		CH3		1.2	366	368	1,863	1,686	4,283
Django Reinhardt	Le Coustumer (2008)								
		А	2005	7.1	313	167	2,500	4,389	4,654
		В		3.5	265	105	1,338	14,171	32,893
		С		1.5	117	57	704	2,173	36,40
		Mean (SD %)	2005		97 (83)	56 (64)	703 (85)		
			2006		178 (59)	186 (103)	1,128 (65)		
			2007		213 (34)	234 (37)	1,299 (36)		
			2008		247 (16)	210 (23)	1,384 (22)		
	Badin (2009)	С		11.4 (2.0)	115 (40)		1,156 (70)		
	Saulais et al. (2011)	A–B		4.2 (0.4)	213 (22)		1,465 (112)		
Dutch standard									
		Polluted soil <sup>a</sup>		0.8	36	85	140	50	1,000
		Intervention three	shold <sup>b</sup>	12.0	190	530	720	5,000	

2009 in Cheviré sediments shows that the concentrations are almost unchanged for trace metals except for Pb and Cu. The sharp decrease in lead content, already observed in 2003 by Béchet et al. (2007), corresponds to its prohibition in gasoline fuels in France (since 2000). In DjR, the spatial heterogeneity characterized through Zn, Pb and Cu concentrations in 100 points, was important at the beginning of the basin life. The zones that were most often flooded had higher concentration of heavy metals. Some specific parts also presented high concentrations in particular the oldest area of the basin that had not been correctly scrapped during renovation phases (Fig. 2a-f). As time passes the concentrations tends to be more constant all over the basin, the sediments being highly polluted according to Dutch standards. The accumulation of metals is also significant with time. An increase in pollutant mass was observed for copper, lead and zinc with a factor of 2.6, 3.8 and 2, respectively, from 2005 to 2010 (Gonzalez-Merchan 2012). The sum of PAHs appears to be constant with time (for Cheviré basin). PAHs are, as trace metals, accumulated near the outlet (Table 4) (El-Mufleh et al. 2013). For DjR basin, PAHs accumulate, as copper, in the middle part of the basin (point B). THCs for both basins accumulate in the middle part of the basin. As mentioned in Table 3, the analytical methodology differs between the two studies. The difference is in good agreement with the study conducted in 2008 by the CETE IF (see 3.2).

The monitoring of heavy metals and hydrocarbons contents shows an accumulation with time and in specific areas of the basin. To understand this distribution, a mere analysis of the total content is not sufficient. A more complete physicochemical characterization of the sediment was thus required. The next part of this article is dedicated to the characterization of this anthropogenic sediment.

## Physical and main chemical characterization of stormwater sediments

The total parameters such as pH, major elements, grain size, total organic matter (TOM) and TOC contents are parameters easily and usually obtained. Further studies on the solid phases (mineral and organic phases) were thus undertaken after the strong aggregation tendency within the sediments



Fig. 2 Concentrations of Cu, Pb and Zn in 2005 after 1 year of operation and in 2010 after 6 years

was described. The relation between organic matter and infiltration properties was investigated.

Global parameters analyses in relation to pollutant loads

Tables 5 and 6 summarize the main physical and chemical characteristics. The pH value was measured, at 20 °C, on a soil suspension prepared by mixing dried sediment and ultra-pure water with a V/V ratio of five (NF ISO 10390 (2005)). The suspension was let to settle for 2 h before the measurement. Major element analyses were performed following trace metal

methods (see Section 3.1). In the two observatories, ONEVU and OTHU, grain size analyses were performed using a laser diffractometer for the fraction below 500 or 1,600  $\mu$ m, respectively (Malvern<sup>®</sup> Mastersizer 2000 and 2000.G). The TOM content was measured by weight loss at 550 °C during 2 h (NF EN 12879 (2000)). TOC content was evaluated by sulfochromic oxidation at 900 °C (NF ISO 14235 (1998)).

The pH values of sediments are relatively constant within the basins and over time, for example pH values ranged from 6.5 to 7.9 and from 6.9 to 7.6 in Cheviré and DjR basins, respectively (Tables 5 and 6). Despite different geological

Table 5 Main physicochemical characteristics of Cheviré sediment

		Legret	et al. (199	95)	Durand (2003)			Durin (2006)		Pétavy (2007)	El-Muf	leh (2011)		
		CH1	CH2	CH3	CH1	CH2	CH3	CH1	CH2	CH3	P1 (near CH1)	CH1	CH2	CH3
pН		6.9	6.5	6.8				7.9	7.5	7.2		7.5	6.7	6.3
TOM	%	6	6	14				12	14	14	12	9	12	18
TOC								8	8	9		8	11	16
D10	μm				7	5	4				5	14	4	3
D50					37	27	24				92	411	69	20
D90					193	997	612				1,044	1,339	1,155	1,110
Al	$\mathrm{g}~\mathrm{kg}^{-1}$	53	50	69	56	64	62	56	62	66		49	63	68
Ca					14	10	11	16	12	11		18.0	10.0	10.0
Fe					33	37	34	30	27	38		23.6	29.3	36.5
Mg					8	8	8	8	8	9		6.0	7.1	8.9

Table 6 Main physicochemical characteristics of Django Reinhardt sediment

		Le Coi	istumer (20	008)	Badin (2009)	Saulais et al. (2011)	Gonzalez-Merchan (2012)		
		2005			2007	2008	2009–20	011	
		А	В	С	C Mean on five samples	Between A and B Mean on 13 measurements	А	В	С
pН		7.1	7.3	7.6	7.3	7.6			
TOM	%	17	13	14	10	20	11 (mea	n)	
TOC		32	15	59	40	12			
D10	μm	5	5	5			43	44	8
D50		25	25	25		300	155	136	75
D90		67	95	231		432	420	527	370
Al	${ m g~kg^{-1}}$				16	15			
Ca					122	86			
Fe					24	24			
Mg					8	7			

contexts (sandy alluvial deposit for Cheviré and carbonated fluvio-glacial deposit for DjR), pH values are close. Major element contents mimic (except for Ca) trace metal distribution. The texture analyses showed that 75 % of the particles (sonificated fraction <2 mm), was less than 100 µm in diameter both at Cheviré and DjR (Legret et al. 1995; Durand 2003; Pétavy 2007; Badin et al. 2009; El-Mufleh 2011; Gonzalez-Merchan 2012). Therefore, stormwater sediments are fine materials, classified as silt, in the soil texture classification. For Cheviré basin, the finest particles are found near the outlet of the basin. For DjR basin the texture of the particles is more homogenous and finer because of the retention/settling basin placed prior to the infiltration compartment. The TOM contents are globally high, from 4 % to 27 % of dry weight (Bedell et al. 2004; Winiarski et al. 2006; Pétavy 2007, Gonzalez-Merchan 2012). The comparison of TOM between 1993 and 2009 in Cheviré basin shows no significant evolution for the sediment near the entrance (6-7 %) and the outlet (14-16 %) of the basin, whereas TOM content in the central area has doubled (6 % and 12 %, respectively) (Table 5). This difference could be related to the larger development of vegetation in this latter area. In the same way, DjR shows a higher organic matter concentration near the inlet where vegetation has also grown (Table 6). TOC values reported for the two sediments ranged from 56 to 198 g  $kg^{-1}$  (Durand 2003; Badin et al. 2009) (Tables 5 and 6). Cannavo et al. (2010) reported mean TOC values of 66, 90 and 121 g kg<sup>-1</sup> for zones 1, 2 and 3, respectively, in Cheviré basin. The TOC values of stormwater sediments are up to 40 times higher than those of agricultural soils (Deport 2002) and comparable to alpine humus soils (130 g kg<sup>-1</sup>) (Baldock and Neslson 2000).

Furthermore, stormwater sediment present high hydrophobicity related to the nature and content of OM, which influences soil properties, particularly hydraulic properties when considering infiltration processes (Franzluebbers 2002; Lassabatere et al. 2007; Cannavo 2010; Arye et al. 2011). In stormwater infiltration basins, unlike natural soils, the high hydrophobicity of organic matter induces a low hydraulic conductivity of sediment and a high water retention capacity. A positive correlation between the OM content and the increase in microporosity was suggested by Coulon et al. (2013). The hydrophobicity of the sediment was measured and related, along with the high microporosity, to the clogging of the basins.

Two parameters appear to be significantly linked to pollutant contents: texture and organic matter contents. However, global analyses are not sufficient to explain these tendencies. Researches were then conducted in order to characterize the structure and solid phase nature of these sediments more precisely.

A highly aggregated material: distinction between structure and texture

The texture of the sediments is a characteristic of both the nature of the material and its origin. This measurement helps to know what kind of primary solid phases particles are responsible for the retention of pollutants of are subjected to aggregation. An aggregate is a cluster (or group) of soil/sediment particles in which the forces holding the particles together are much stronger than the forces between adjacent aggregates (Tisdall and Oades 1982). The different methodologies used to characterize the aggregation state came from soil sciences. As the surface of the basins is a "Technosol", we deduced that this physical parameter was essential to evaluate in order to understand the infiltration properties of the surface, the accessibility of water to the solid phases and the pollutants.

The aggregation was characterized on wet samples thanks to a comparison of the particle size distribution curves before and after an ultrasound treatment (during 2 to 10 min). Fractions above 500 or 1,600  $\mu$ m were analyzed using a series of sieves. For each sample three volumetric proportions were given: those of the >160- $\mu$ m fractions without sonication (PnoUS), after sonication (PafterUS), and those of the macroaggregates (=ultrasound sensitive aggregates): Pmacroaggregates=PnoUS-PafterUS). Ultrasound sensitive aggregates accounted for 53 % of the DjR material and for 31 % of the Cheviré. Both DjR and Cheviré materials showed a high percentage of aggregation. The aggregates are formed by particles that measure from 10 to 60  $\mu$ m.

Badin et al. (2009) characterized more precisely the aggregation properties of sediments from Cheviré and DjR basins. A low water content and organic matter have been shown to control mainly the stability of aggregates (Fig. 3a). SEM observations (Fig. 3b) highlighted that sediments were composed of single particles and aggregates, sized between 10 and 300  $\mu$ m, 10  $\mu$ m being the minimal size of aggregates (Badin et al. 2009; El-Mufleh 2011). The microaggregates <160  $\mu$ m appeared to be very stable and were not destroyed with chemical treatment or sonication.



**Fig. 3** a Cumulative curves of the laser diffractometry grain size analyses of <1,600  $\mu$ m Cheviré particles untreated and after elimination of OM by H<sub>2</sub>O<sub>2</sub> oxidation (*bold lines*) (*solid line:* unsonicated materials; *dotted lines:* 1 min sonicated material; from Badin et al. 2009) and **b** SEM image of an aggregate from Cheviré sediment

The sediment structure is highly variable with time and especially with the water content and depends on the initial sampling conditions. This characterization is very relevant for hydrodynamic and modeling purposes because it will influence directly the macro and microporosity of the sediment. The laser methodology can be easily used and helped us to compare both sediments. If the purpose is to identify and fractionate the elementary particles, then aggregates have to be destroyed thanks to a sonication/friction process or a chemical treatment.

## The distinction between natural and anthropogenic organic matter

Durand et al. (2005) characterized the organic matter of Cheviré sediment by fractionation of lipid, fulvic acid, humic acid and humin fractions. These fractions were obtained following the IHSS procedure, according to their solubility properties (Calderoni and Schnitzer 1984), except that the final "humin" residue was not treated with HF/HCl to prevent loss of organic matter.

The humin fraction was the main organic fraction corresponding to 46.6-75.7 % of TOM (57.6 % for Cheviré). The humic acids fraction represented 2.6 to a maximum of 18.0 % for Cheviré. The lipid fraction was 11.4-35.4 % of the TOM (19.9 % for Cheviré). The fulvic acids fraction represents 4.5 (for Cheviré) to 10.3 % of TOM in the three sediments. Humic acid and humin fractions were characterized using pyrolysis techniques in presence of alkylating agents (TMAH and TEAAc thermochemolysis) (Durand et al. 2004a). The sediments from infiltration basins were compared with natural (peat) sediments to identify the origin of organic matter. A minor plant origin was superimposed in the humic acid fraction. The structures identified are mainly fatty acids, linear and polycyclic alcohols from bacterial origin and methyl esters from higher plants. Anthropogenic organic matter was mainly found in the lipid fraction. Hydrocarbons were characterized by a large unresolved complex mixture (UCM). Hydrocarbons and PAHs at high concentrations were mainly located in the neutral lipid fraction (Durand et al. 2004b). A part of the hydrocarbons was derived from diesel and motors lubricating oils. Many pyrolytic products from fuel combustion have also been identified.

Badin et al. (2008) study aimed to understand the chemical specificity of aggregates in DjR sediment and more precisely the role of the anthropogenic organic matter on aggregation properties. A soft grain size fractionation was performed. OM of sediments and isolated fractions were characterized by measuring organic carbon content and isolating aromatic hydrocarbons, saturated hydrocarbons and polar compounds extracted with Dichloromethane. The organic compounds observed were, as pointed out by Durand et al. (2004b), petroleum byproducts (steranes and terpanes, UCM and

PAHs). However, the occurrence of natural biomarkers (phytol and derivatives, sterols) confirms the dual natural and anthropogenic contribution in stormwater sediment. OM distribution between grain size fractions and in aggregated ones, suggests that organic macromolecules take part in the aggregation of sediments and prevent fine particles (<10  $\mu$ m) from being leached. Moreover, the association of organic molecules with soil constituents makes them less accessible to biodegradation (Coulon et al. 2013).

The nature and content of organic matter are thus key parameters as regard sediment properties: sediment structure (aggregation), organic compound biodegradation, hydrodynamic properties and specially pollutant retention and mobility.

### Mineral phases characterization

In order to characterize the mineral solid phases of sediments, the single and aggregated particles were analyzed by X-ray diffractometry (XRD). Minerals such as quartz, feldspar, mica and clays were usually identified by XRD analyses in stormwater sediment (Badin et al. 2009; El-Mufleh Al Husseini et al. 2013). These natural mineral phases (quartz, feldspar, mica or clay) were identified by SEM observations, as single particles or in aggregates (Fig. 3b). They are easily related to the local geochemical context of the basin. In the case of Cheviré sediment, quartz, albite (Na feldspar), microcline (K feldspar), mica, clays (clinochlore [chlorite], kaolinite, smectite, illite) and amphibole are identified, in relation with the geology of the area (altered mica-schists). In the case of DjR basin, calcite and illite were also identified, but no amphibole was detected. The mineralogy of DjR sediment was in good agreement with carbonated fluvio-glacial deposit. Furthermore, the comparison of major element contents in the sediment within the same basin and over the time for Cheviré and DjR basins shows no much difference, neither within the basins nor over time (Tables 5 and 6).

Natural crystallized mineral phases are characterized by XRD analyses. However anthropogenic particles, highly polluted, could not be detected by this method. Microscopic observations and microanalyses methods were thus implemented to visualize and analyze these particles.

Anthropogenic particles characterization by observations and microanalyses

Bulk sediments were first observed by optical or SEM microscopes. However, anthropogenic particles were not detected. Then fractionations, by grain size and/or particle densities, were carried out on Cheviré sediments and the fractions were characterized. The observations on the sediment were related to those carried on particles of runoff waters collected at the entrance of Cheviré basin. SEM observations of magnetic particles from Cheviré sediment underline the presence of fragments of slag and filamentous and oblong fragments of various alloys: cuproaluminium with Ni, Fe, Mn; Fe–Cr–Ni stainless steels, etc., coming from industrial refining (Clozel et al. 2006, see 4.3.1). Observations were carried out under optical combined to microscope coupled to micro X-ray fluorescence ( $\mu$ XRF) analyses (M4 Tornado, Bruker) on fractions resulting from grain size fractionation. These observations highlighted the presence of black color particles of various sizes. The  $\mu$ XRF spectra of these particles pointed out the presence of Cu and/or Zn (Fig. 4a). These particles could be residues of tire or brake pads and road asphalt identified as pollutant sources by Legret and Pagotto (1999).

Stormwater TSS are the main components of the sediments and bearing phases of pollutants. As for sediments, the observations were carried out under optical microscope coupled to  $\mu$ XRF analyses on particles from runoff water, collected at the entrance of Cheviré basin. This study showed the presence of many particles of natural origin: organics particles (i.e., plant debris, fragments of insects) and especially mineral particles (aluminosilicates, silicates or iron oxides). The presence of macro and micro-aggregates were noted (Fig. 4b), which shows that aggregation can occur before the entrance of the basin. Particles of anthropogenic origin were also observed: i.e., particles of polystyrene, glass and ball lens (used in road infrastructures as reflecting device) (Fig. 4c). Metal particles of alloys (Fig. 4d) and black color particles similar to those noticed in sediments were observed.

The main limit of these kinds of analyses is that only global or at best semi-quantitative contents are given. However, helpful information was obtained. Some hypotheses were confirmed, and these techniques could be used to study the behavior of particulate pollution focusing on specific particles considered as tracers.

These studies showed that due to the anthropogenic origin of some particles and the aggregation phenomenon, these technosols are very specific and cannot be described as sediments or natural soils. However, as mentioned in the introductive part, decision-making processes cannot only rely on total pollutant contents. The objective of the researches was then to understand pollutant behavior and distribution, in order to reduce volumes to be treated.

### Pollutants distribution within solid phases

When the environmental impact of sediments is considered, the potential mobility of pollutants has to be documented. Chemical extractions performed in several studies were devoted to the distribution of trace metals between operationally defined solid phases. But these methods have drawbacks. Moreover, they are no more so relevant due to the new



Fig. 4 Optical microscope images of: a black color particle and its  $\mu$ XRF spectrum, c a macroaggregate, d glass beads, d metal fragment and its  $\mu$ XRF spectrum

information obtained on the nature of solid phases and on the aggregation state. Other techniques were recently applied to define the pollutant bearing phases. The objective is to propose a specific treatment of sediments aimed at reduction of volumes to be treated.

### Single and sequential trace metal extractions

Despite criticisms (Etcheber et al. 1983), sequential extractions are the most frequently used method for trace metal location in sediments. The most widely applied being those proposed by Tessier et al. (1979). The European Community Bureau of Reference (BCR) has proposed an optimized threestep procedure, including an application for sediment with the production of a Certified Reference Material (Quevauviller et al. 1993; Rauret et al. 1999). This BCR protocol was applied by Durand et al. (2004b) on sediments from three urban infiltration basins (including Cheviré basin) to study trace metal speciation. The results on Cheviré basin (Table 4) show that Cd is mainly in the exchangeable fraction and Ni and Cr are in the residual fraction. Cu is in both the reducible and oxidisable fractions, Pb is in the oxidisable fraction, whereas Zn is in both exchangeable and reducible fractions. Each trace metal has its own behavior, which is homogenous within a same basin. It is thus considered that metal speciation may have already been acquired when the water and associated suspended matter arrived in the pond (Clozel et al. 2006).

Saulais et al. (2011) studied the distribution of Cd, Cu and Zn within exchangeable, carbonate and organic matter fraction in DjR sediment. The chemical extractions were performed in parallel (successive single extractions). This experiment was carried out at different spatial and temporal points. The study underlines that Zn is stable with time and is mainly associated to carbonate and organic matter fractions. Cd and Cu vary with time and space and are also associated to carbonate and organic matter fractions. Cu is over 50 % associated to organic matter fractions which is in good agreement with sequential extractions results.

### Distribution of pollutants among grain size fractions

Several research groups have investigated the location of trace metals in sediment by size fractionation using a series of sieves. Lee et al. (1997) argue that trace metals are mainly accumulated in fine fractions due to their higher binding sites comparing to those of coarse sands. On rough sediment, contrary to conventional results, no significant difference in trace metal concentration was observed between fine particles and coarser particles (often aggregated ones) within Cheviré sediment by Durand (2003), Durin (2006) and Pétavy (2007). Badin (2009) observed the same specificity for DjR sediment.

To illustrate the pollutant distribution within grain size fraction, three studies are presented here (Pétavy 2007, only trace metal distribution was studied; Badin 2009; El-Mufleh 2011). Three grain size classes are considered, large, medium and fine particles. The cut-offs were quite different from one study to another. Pétavy (2007) and Badin (2009) studies were performed on untreated sediments. The fractions correspond to >1,250, 250–1,250 and <250  $\mu$ m and >1,000, 160–1,000 and <160  $\mu$ m, respectively. For Cheviré analyses with a sonication pre-stage, the fractions correspond to >500, 63–500 and <63  $\mu$ m (El-Mufleh 2011).

### Role of aggregates

In the studies of Pétavy (2007) and Badin (2009), care was taken to avoid serious disturbance of sediment structure (especially aggregates). Figure 5 shows the mass, trace metal and PAH distribution within the three grain size classes. Contrary to Lee et al. (1997) results, trace metal and PAH distribution is quite similar. Most of the pollutants are bound to large and medium particles (Fig. 5). The hypothesis to explain this behavior is that these pollutants are indeed associated with finer particles, but these fine particles by physico-chemical interactions, form aggregates with sizes of up to 300  $\mu$ m.

### Disaggregation pre-stage

To verify the aggregation retention role hypothesis, size fractionation of Cheviré sediment was carried out with a preliminary disaggregation phase. Three fractions were studied:  $>500 \mu m$  (large), 63–500  $\mu m$  (medium) and <63  $\mu m$  (fine), according to sediment size distribution after sonification. The results confirm the proposed hypothesis, 90 % of total trace metals are in the <63- $\mu m$  fraction as well as 85 % of PAHs (Fig. 5).

These results partly explain the distribution of pollutants within Cheviré basin with higher contents in finer size sediments (zones 2 and 3). In fact, finer particles, which hold the pollutants, are more easily transported and thus are found in the outlet area of the basin. Then these fine particles may form aggregates due to physicochemical process (van der Waals forces, Brownian movement, etc.), and pollutants are trapped in the sediment.

### Pollutants in density fractions

#### Trace metals on heavy and light magnetic particles

Clozel et al. (2006) identify metal-bearing phases and contribution to total metal amount by combining SEM-EDX observations and analyses on light and heavy magnetic particles of the 40-80 µm fraction on Cheviré sediment. These heavy magnetic particles are composed of spheroids Fe oxides (probably magnetite spinel [Fe<sub>3</sub>O<sub>4</sub>]), fragments of slag and filamentous and oblong fragments of various alloys (cuproaluminium with Ni, Fe, Mn; Fe-Cr-Ni stainless steels, etc.). Both the spinel spheroids and the slag fragments come from industrial refining. No trace metal was associated to the spheroids Fe oxides. Copper and zinc spheroids were contained in slag fragments. Lead has been observed in porous Fe oxyhydroxydes in the form of small clusters (less than 10 µm). These clusters were usually observed in particle surfaces. The light magnetic particles are mainly particles that have defied storing. They include some porous oxyhydroxydes and chlorite flakes in which with Zn has occasionally been observed.

A mass estimation of the particles of interest was performed. The observed metal-bearing phases account for no more than 10% of Cu, Pb and Zn. It could be assumed that the unexplained metal content in the total mass is present in the light non-magnetic fraction that was not studied. Another methodology, increasing the number of fractions should be performed. To do so, a five-density-fractions method was carried out.

### PAHs and trace metals in five density fractions

The distribution of trace metals (Cd, Cr, Cu, Ni, Pb, Zn) and PAHs within five density fractions was evaluated for three urban stormwater basin sediments, including Cheviré sediment. After a preliminary sonication stage in order to destroy aggregates, five density fractions: d<1.9, 1.9 < d<2.3, 2.3 < d<2.6, 2.6 < d<2.8 and d>2.8 g cm<sup>-3</sup> were obtained by successive additions of sodium polytungstate solutions (LST Fastfloat; Na<sub>6</sub>[H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>]) with 1.9, 2.3, 2.6 and 2.8 g cm<sup>-3</sup> densities (Basile-Doelsch et al. 2007). Each fraction thus obtained was characterized using XRD and Scanning Electron Microscopy. In addition to the micropollutant





analysis, trace metals were investigated in each fraction using energy dispersive X-ray spectroscopy (EDX spectroscopy) microprobe.

Figure 6 shows the mass, trace metal and PAH distribution within the five fractions. The lightest fractions, d < 1.9 and 1.9-2.3 present the highest organic matter contents 42 % and 21 %, respectively. Thus, most of these fractions are not organic which is confirmed by the detection of mineral phases, i.e., quartz, feldspar and clays, by XRD analyses. Plant elements and mostly micro- and macro-aggregates in the fractions are observed by SEM microscopy. These aggregates are composed of mineral particles surrounded by organic matter (natural and anthropogenic origin). The presence of mineral particles, despite their high density in these light fractions could be explained by the incomplete destruction of the aggregates in the prior stage of sonication. The heaviest fractions have low organic matter contents which is consistent with their high mineral content. Some microaggregates are still observed by SEM microscopy in the 2.3-2.6 fraction, whereas very few of them are present in the two heaviest fractions. These observations confirmed the conclusions of Badin et al. (2009), i.e., organic matter plays a major role on aggregation.

PAHs are mainly contained in the d < 2.3 g cm<sup>-3</sup> fractions, which means that PAHs are bound to the organic matter (OM). Trace metals losses globally represent about forty percent. However, for Ni and Cr mass balance is about 100 %. Cu, Pb, Zn and especially Cd are pH-sensitive and thus could be solubilized during the fractionation stage. This dissolution concerns two density fractions, 2.6 < d <2.8 and d>2.8, especially the fraction 2.6 < d <2.8 because its contact with the solution of low pH was longer. Due to this solubilization and comparing to Clozel et al. (2006) results, we can assume the distribution of trace metals as follows, namely a quarter in the fractions <2.3 g cm<sup>-3</sup>, without the impact of the pH, trace metal would represent in the heaviest fraction around 10 % of the total content and most of trace metals would be detected in the 2.6–2.8 g cm<sup>-3</sup> fraction. Thus, OM, clays and calcite (observed for another sediment of the study) seem to be important trace metal bearing phases.

### **Conclusions and perspectives**

Conventional physical and chemical methods of characterization are applied to sediments in most of the studies in the literature to determine global parameters (pH, conductivity, grain size analysis...), trace metal and PAH loads, mineralogy (DRX) and OM content. These characterizations are always relevant but additional techniques of characterization are now recommended to implement better management practices.

Real progresses of knowledge were obtained by using microscopic observations to visualize the aggregation state, combined with grain size or chemical analyses and to the origin of the particles. The anthropogenic origin of a large part of particles and the aggregation phenomenon contribute to the assessment that the stormwater sediments strongly differ from what is classically called "sediment" and should be classified as a technosol. We propose to now systematically call these materials technosols.

The aggregation level of the sediment which is permanently variable is also an interesting information as it can be linked to infiltration properties of the basin surface. Moreover, the hydraulic performance assessment would take advantage of coupling the classical infiltration tests to the characterization of organic components.

Even if the two basins are very different (intrinsic characteristics, geological and urban context), the comparison of the results on the two sediments underlines that the bulk properties are often close (aggregation, grain size, pollutant content...). The differences lie mainly in the experimental protocols, such as analytical techniques and methods. In terms of maintenance strategy, using portable XRF appears as a costeffective method to evaluate the trace metals contamination at the basin scale, instead of performing several expensive

Fig. 6 Mass, trace metal and PAH distribution between the five density fractions of Cheviré sediment. \* not analysed



chemical analyses, even if some calibration and validation analyses are required.

Analytical techniques have evolved with influence on analytical procedures or detection and quantification limits. In case of organic analyses, as these data collection required more advanced techniques, they were mainly developed during the last 10 years. In terms of mobility, the implemented methods underline again the role of aggregation, pollutants (trace metals and PAHs) being mostly associated to fine particles aggregated. This observation raises the question of the stability of these pollutants in the sediment. Traditional chemical extractions could always be used as an operational method (rapid and relatively low cost) but density fractionation was found to be one of the most promising technique to identify the bearing phases of pollutants. However the longterm behavior of these pollutants cannot be evaluated by such experiments and dynamic experiments or in situ experimentations have to be performed.

Further investigations are currently in progress or are needed to contribute the management practices: (1) they will concern priority substances to take into account the European water framework; (2) some major substances (S and P) should also be more studied for their impact on quality of sediments; (3) geochemical modeling could be an useful tool to validate the chemical mechanisms in the sediment and to evaluate the evolution of sediments but strong developments are to be performed to implement the specificity of the materials.

Plants could be studied as regards the capacity of retention of pollutants. They could have a strong influence on biodegradation and could contribute to the stabilization of trace metals and organics. Will it be possible in the future to use the native plants of the basins or to implement plants to stabilize or improve the biodegradation of organic pollutants in the technosol? The long-term performance of the basin relies on the evolution of the sediment properties. The functions of this particular technosol have to be studied. Finally, the microbial compartments (both phototrophic and heterotrophic ones) have to be investigated further as their influence on the fate of OM in basins was underlined.

In terms of sediment management, the first main recommendation is to take care that the analytical methods used for the various experimental campaigns will remain the same. The second one contributing to improve maintenance practices, as previously mentioned noted by Weinstein et al. (2010), is to periodically remove the sediment to reduce both in situ and ex situ risks resulting from pollutant exposure. The monitoring of the sediment quality over the basin could reduce the surface concerned by the removal and decrease the cost of the cleaning out. The knowledge of the distribution of pollutants among solid phases, by methods described in this paper, could help in determining the appropriate method of disposal. The development of a multidisciplinary and harmonized methodology to study stormwater sediment characterization makes sense when considering the conceptual integrative approach prone since a few years in the domain of urban water management (Tixier et al. 2011). The ecological risk assessment could therefore benefit from more relevant physical and chemical data on the contaminated sediments.

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