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## **Characterisation of atmospheric deposition and runoff water from a small suburban catchment**

### **Caractérisation des retombées atmosphériques et des eaux de ruissellement d'un petit bassin versant périurbain**

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#### **RÉSUMÉ**

Une étude a été menée dans le cadre de l'IRSTV (Institut de Recherche en Sciences et Techniques de la Ville) afin de caractériser les retombées atmosphériques et les eaux de ruissellement d'un petit bassin versant séparatif périurbain (31 ha) à Nantes. Les métaux traces, les hydrocarbures aromatiques polycycliques (HAP) et les pesticides ont été mesurés. La caractérisation des retombées atmosphériques montre une grande variabilité des concentrations en métaux, sans lien avec les caractéristiques de la pluie. L'abondance des métaux est la suivante :  $Zn > Cu > Cr \approx Ni > Cd$ . Les polluants organiques sont rarement détectés dans les retombées atmosphériques. Zn et Pb sont les principaux polluants des eaux de ruissellement, tandis que les concentrations en Ni, Cu, Cr, Cd, HAP et pesticides sont généralement faibles. D'une manière générale, les concentrations mesurées se situent dans la fourchette basse des concentrations rapportées dans la littérature. D'après le système d'évaluation de la qualité (SEQ-eau), la qualité des eaux de ruissellement est mauvaise à cause des fortes concentrations en Pb et Zn. Les observations au microscope électronique à balayage (MEB) montrent que les particules des retombées atmosphériques sont similaires à celles des eaux de ruissellement, avec prédominance du pollen, des bactéries et des particules issues de l'érosion des sols. Des particules organiques sphériques formées lors des processus de combustion des fuels sont aussi observées.

#### **ABSTRACT**

A study has been carried out in the frame of IRSTV (Institut de Recherche en Sciences et Techniques de la ville) a federative research network supported by the Pays de la Loire Region with the objective to characterize atmospheric deposition, roof runoff and street runoff from a small sub urban catchment (31 ha) equipped with a separative sewer system in Nantes. Trace metals, polycyclic aromatic hydrocarbons (PAHs) and pesticides were investigated. The characterization of atmospheric deposition shows a high variability of trace metal concentrations, which could not be explained from rainfall characteristics. The relative abundance of metals is as follows:  $Zn > Cu > Cr \approx Ni > Cd$ . Organic pollutants, i.e. PAHs and pesticides were rarely detected in atmospheric deposition. Zinc and Pb appear to be the major contaminants in runoff water, whereas the concentrations of Ni, Cu, Cr, Cd, PAHs and pesticides are generally low. As a whole, the concentrations are similar to the lowest range of those reported in the literature. According to the statutory values, runoff water quality is bad because of high Pb and Zn concentrations. From scanning electron microscopy (SEM) observations it appears that atmospheric particles are not different from runoff particles, with a predominance of pollen, bacteria and particles from soil erosion. Spherical organic particles formed during the combustion of fuels are also observed.

#### **MOTS CLÉS**

Atmospheric deposition, trace metals, PAHs, pesticides, runoff water, SEM

## 1 Context and objectives

Over the past several decades, stormwater runoff has been identified as one of the major causes of deterioration of receiving waters (Pitt *et al.*, 1995; Gromaire *et al.*, 2001; Gaspéri, 2006). Vehicle emissions, motor oil, tire and brake wear and road surfaces are diffuse sources of contaminants in urban environments. Other sources include heating, the corrosion of roofs and roof materials. During rainfall, the contaminants are washed from roofs and impervious surfaces into the stormwater system and then discharged into urban rivers or surface waterways (Brown and Peake, 2006). Heavy metals, polycyclic aromatic hydrocarbons (PAHs) and pesticides are of particular concern due to their prevalence, toxicity to aquatic organisms and persistence in the environment (Hoffman *et al.*, 1984; Walker *et al.*, 1999).

The reduction of urban stormwater pollution has become of major concern for water managers in order to meet the new European regulation. Indeed, the water framework Directive (Directive 2000/60/EC) fixes as objective the good ecological and chemical states of surface waterways and groundwater by 2015.

Most of the time, stormwater runoff from urban areas drained by a separative system is discharged into the environment without any treatment inducing a degradation of water bodies. Efforts to restore the quality of urban water resources degraded by contaminants from urban stormwater runoff are also of concern in the US and restoration programs have started in the early 90's (Bannerman *et al.*, 1993). The objective of our study carried out in the frame of IRSTV, a federative research network supported by the Pays de la Loire Region, is to characterize atmospheric deposition, roof runoff and street runoff from a small urban catchment equipped with a separative sewer system.

## 2 MATERIALS AND METHODS

### 2.1 The study site

This study was conducted in the Pin Sec catchment located in the East of Nantes city (France), between the Loire and Erdre rivers. The Pin Sec catchment has a surface of 31 ha with 2500 residents. The habitat is mostly constituted by personal households or collective buildings. The impervious surface represents 49% mainly roofs, streets, pavements and parking lots. Roof surface represents 18% of the total surface of the catchment. The mean slope of the catchment is about 1.1%.

### 2.2 Sampling and equipment

Bulk atmospheric deposition (dry and wet depositions) was sampled using a stainless steel funnel for samples aimed at organic pollutant analysis, whereas Owen gauges were used for samples aimed at heavy metal analysis. The collector surfaces were 0.034 m<sup>2</sup> and 0.066 m<sup>2</sup>, respectively. The samples were collected weekly during two months. Rainfall was measured continuously by three bucket rain gauges installed in this zone. Data validation is made by comparison between the 3 rain gauges.

Roof runoff samples were collected from four roofs representative of the study area (slate, tile, zinc sheets and bitumen flat). The gutters for tile and bitumen flat roofs are in polyvinyl chloride (PVC), whereas slate and zinc sheet roofs have galvanized gutters. Roof runoff was collected at the end of roof gutters proportionally to the flow. The samples for each roof are collected in 120-L plastic containers.

For street runoff the collected surface was 690 m<sup>2</sup> on Riveterie street, the mean slope is 0.9 %. Runoff water gets to a gully pot in which a pressure sensor and a triangular weir are set. The sensor allows measuring water height every minute with a precision of 1 mm.

### 2.3 Chemical analyses

The pollution parameters studied are: pH, conductivity, suspended solids (SS), total organic carbon (TOC), determined according to the French standards for water analysis (AFNOR, 1999). 15/16 polycyclic aromatic hydrocarbons (PAHs) recommended by the Environmental Protection Agency (US EPA). PAHs were analyzed by IDAC laboratory according to NF EN ISO 17993. The quantification limits for PAHs vary from 2.0 to 10 ng L<sup>-1</sup>. Heavy metals (Zn, Ni, Cd, Cr, Cu, Pb) were analyzed too. The analyses were made at the LCPC environmental and chemical laboratory by atomic absorption spectrometry according NF EN ISO 15586. The quantification limits were 0.10 µg L<sup>-1</sup> for Cd, 1.0 µg L<sup>-1</sup> for Pb, 2.0 µg L<sup>-1</sup> for Cu, 0.5 µg L<sup>-1</sup> for Cr, 8.0 µg L<sup>-1</sup> for Zn and 1.0 µg L<sup>-1</sup> for Ni.

### 3 RESULTS AND DISCUSSION

#### 3.1 ATMOSPHERIC DEPOSITION

##### 3.1.1 Pollutant concentrations

In this study, the pollutant concentration is presented in normalised concentration (NC). Normal concentration was calculated according to equation 1 (Scheyer et al., 2007). Where MMC is the mean monthly concentration,  $H_c$  is the total rainfall collected for each period and  $H_m$  is the total rainfall calculated from a mean between three bucket rain gauges.

$$NC = MMC \times \frac{H_c}{H_m} \quad (1)$$

##### Bulk Parameters

During the survey period pH values were low ranging from 5.3 to 6.8 (table 1). The highest values were obtained between July and September 2007.

Conductivity varies strongly between the years with values around  $100 \mu\text{S cm}^{-1}$  in 2007 and  $20 \mu\text{S cm}^{-1}$  in 2008 (table 1). This can be due to higher ion concentrations ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ) measured in the samples collected in 2007. These ions originate from anthropogenic sources ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) as well as from marine inputs ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ). (Celle-Jeanton et al., 2009)

Regarding suspended solids (SS) and total organic carbon (TOC) differences are observed according to the period of the year. Suspended solid concentrations range from 2 to  $35 \text{ mg L}^{-1}$ , whereas TOC concentrations vary from 0.5 to  $12 \text{ mg L}^{-1}$ . For both parameters, the highest values were measured in June and July 2008 and can be attributed to an increase in biological activities. This is corroborated by SEM observations showing mosquitoes, pieces of leaves and pollens.

year	Campaign	pH	Conductivity $\mu\text{S cm}^{-1}$	$\text{NO}_3^-$ $\text{mg L}^{-1}$	$\text{SO}_4^{2-}$ $\text{mg L}^{-1}$	$\text{Cl}^-$ $\text{mg L}^{-1}$	SS $\text{mg L}^{-1}$	TOC $\text{mg L}^{-1}$
2007	July-Aug	6.8	136	2.0	2.0	2.0	17.5	2.6
	Aug-Sep	6.5	102	1.0	2.0	2.0	4.0	1.7
2008	May-June	5.6	26	< 0.5	1.2	0.3	10.2	5.5
	June-July	5.8	20	< 1	1.4	1.3	35.0	12.3
	Aug-Sep	6.0	21	-	-	-	19.8	3.7
	Oct-Nov	5.3	22	1.1	0.9	2.1	< 2	0.5
	Nov-Dec	5.4	25	1.2	1.8	1.2	< 2	0.6

Table 1. Bulk parameter concentrations in atmospheric deposition at the Pin Sec catchment (Nantes, France).

SS: suspended solids, TOC: total organic carbon

##### Trace elements

Automobile traffic, incineration plants, domestic heating and airports are the main metal sources in urban environment (Sabin et al., 2005; Azimi et al., 2005). Due to its characteristics (residential area), traffic is the main source of metals in the Pin Sec catchment. However, other sources located near the catchment (such as the Valorena incineration plant and a nearby highway) could also play a role.

Figure 1 shows metal concentrations in total atmospheric deposition. Apart from cadmium (detected in 60 % of the samples only) the 6 surveyed metals were systematically detected. As can be seen on figure 1, metal concentrations are variable.

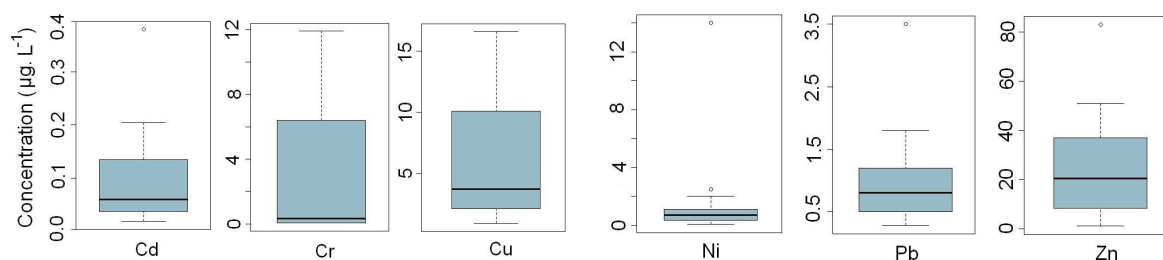


Figure 1. Metal concentrations in atmospheric deposition

Zinc constitutes 72 % of metals, which is in agreement with the literature. The relative abundance of other metals is as follows:  $Cu > Cr \approx Ni > Pb > Cd$ . According to the literature (Golomb et al., 1997; Garnaud et al., 2001; Azimi et al., 2005) this order was different before 2000 ( $Zn > Cu > Pb > Cr \approx Ni > Cd$ ). This difference can be explained by the decrease in the use of leaded gasoline since the year 2000.

The influence of meteorological conditions on metal concentrations has been evaluated using the Pearson coefficient. The only significant correlation that is observed is between Zn and max dry weather period duration. The bilateral test with  $\alpha \geq 0.05$  confirms this correlation.

It is well known that wind speed and direction have a strong influence on pollutant masses in the atmosphere (Garnaud et al., 2001). All over the campaigns carried out in this study wind with low to moderate speed ( $2$  to  $5 \text{ m s}^{-1}$ ) were dominant. Because of this homogeneity in wind speed, this parameter has not been taken into account. Wind direction was quite variable from one campaign to another and showed no correlation with metal fluxes.

#### Organic micro-pollutants

Polycyclic aromatic hydrocarbon and pesticide concentrations were generally low and in some cases close to the quantification limits. For PAHs, concentrations above the quantification limits were measured in 50 % of the samples, mostly at the end of the summer and during the winter. For the campaigns carried out in 2007 and in May-June 2008 no PAH was detected. Acenaphthylene and phenanthrene were the only one detected in the June-July campaign at a concentration of  $13 \text{ ng L}^{-1}$ . For the October-November 2008 campaign, fluoranthene, pyrene and chrysene concentrations range from 2 to  $14.5 \text{ ng L}^{-1}$ . Finally, for the 2008 winter campaign, the sum of the 15 PAHs is  $1090 \text{ ng L}^{-1}$ . The higher winter concentrations are due to domestic heating (which is not working during the summer) and to an increase in fuel consumption when vehicles start in cold periods. Similar observations were made in 2008 by Air Pays de la Loire (Air Pays de la Loire, 2008) for a survey campaign carried out on an urban site in Nantes. During cold periods, the sum of the 7 studied PAHs (B(a)An, B(j)Fl, B(b)Fl, B(k)Fl, B(a)Py, Db[a,h]An, In[1,2,3-cd]Py) was  $11 \text{ } \mu\text{g m}^{-3}$ , whereas in the warm period the total concentration ranges from 0.09 to  $0.8 \text{ } \mu\text{g m}^{-3}$ . Individual PAH concentrations are regularly below the quantification limit ( $0.014 \text{ } \mu\text{g m}^{-3}$  for a sample of  $720 \text{ m}^{-3}$ ).

Other similar studies also show variations in PAH concentrations and fluxes between cold and warm periods (Azimi et al., 2005). This difference is mainly due to heating, which is responsible for 85 % of winter PAH emissions in urban environment. In their study on atmospheric deposition of 2 French cities –one industrial (Le Havre), the other urban (Rouen)- (Motelay-Massei et al., 2006) measured max winter concentrations of  $1659 \text{ ng L}^{-1}$  (Rouen) and  $1012 \text{ ng L}^{-1}$  (Le Havre).

Regarding pesticides, none of the surveyed molecule was detected in the winter, whereas glyphosate and AMPA summer concentrations range from 60 to  $470 \text{ ng L}^{-1}$  for glyphosate and from 50 to 770 for AMPA. These concentrations are reported in table 2.

To our knowledge, glyphosate and AMPA have rarely been identified in atmospheric deposition. Though their volatility is low, these molecules are found in the atmosphere due to their transport by vaporisation when applied on the catchment and in the neighbourhood. For a typical wind speed of 3 to  $5 \text{ m s}^{-1}$  pesticides can cover a distance of 250 to 500 km per day. Quaghebeur et al. (2004) and Delaunay et al. (2006) report the detection of glyphosate and AMPA in about 10 % of the samples.

Pesticides (ng L <sup>-1</sup> )	2007		2008	
	July-Aug	Aug-Sep	May-June	June-July
Glyphosate	470	60	70	90
AMPA	150	50	660	120
Diuron	< 20	< 20	< 20	< 20
metaldehyde	< 100	< 100	123	< 100
mecoprop	-	-	< 50	< 50

Table 2. Pesticide concentrations in atmospheric deposition of the Pin Sec catchment (Nantes, France)

On the Pin Sec catchment the possible sources of glyphosate to the atmosphere are chemical weed killing by homeowners, the treatment of impervious surfaces by municipalities and external input from cultures around Nantes such as vineyards, orchards, market gardening (Air Pays de la Loire, 2002).

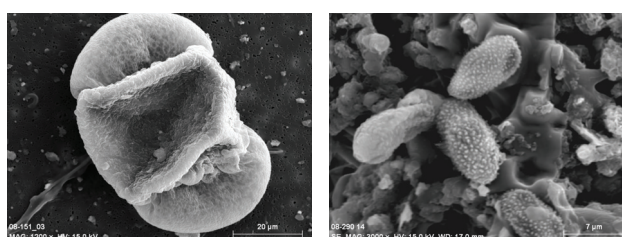
### 3.1.2 Identification and analysis of atmospheric particles

Urban dusts were collected between 16 May and 19 June and from 19 June to 3 July 2008 at the Pin Sec. Mean PM<sub>10</sub> concentration is 12 µg m<sup>-3</sup> for the first period and 13 µg m<sup>-3</sup> for the second. For SEM observation of rainfall particles the rain event of 15 June 2008 was collected; the characteristics of the rain were: total high 12 mm, antecedent dry period 9 days and max intensity at 5 min 31 mm h<sup>-1</sup>.

A classification of atmospheric particles based on their morphology, size and chemical composition was made. Four groups were defined: 2 groups for organic and mineral particles of natural origin and 2 groups including organic and mineral particles of anthropogenic origin (Lamprea, 2009).

70 % of the particles belong to the first group: organic particles of natural origin (figure 2) among which pollens are dominant though there is a large diversity of particles. Similar results were reported by Ebert et al. (2004) and Kim (2007).

In the second group are particles of mineral origin, either isolated or agglomerated. The most commonly observed are irregular particles with a smooth surface and with a size ranging from 5 to 10 µm. The size of the agglomerates varies from 30 to 230 µm. Due to the protocol used to collect the particles; it is unlikely that the agglomerates have been sampled. They were probably formed during the sampling period (15 to 34 days).



(a) Pollen (b) Bacteria  
Figure 2. Atmospheric particles of biological origin

Organic particles of anthropogenic origin are in the third group. These particles are mainly flying ash formed during fuel combustion. Figure 3a shows a spherical particle with a porous surface originating from the combustion of oil (Montelay-Massei et al., 2006). Figure 3b, shows shining fibres which are probably soot particles generated during the combustion of fuels (Wang et al., 2008). Shi et al. (2003) in their study on PM<sub>2.5</sub> and PM<sub>10</sub> report changes in the morphology of flying ash; when in contact with water, shining fibres get a sponge-like morphology. Such particles are observed in our samples (figure 3c).

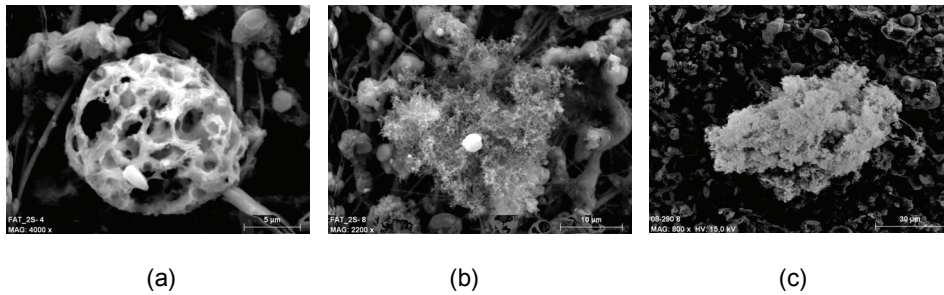


Figure 3. Organic particles of anthropogenic origin

In the last group are spherical particles of anthropogenic origin with a size ranging from 2 to 15  $\mu\text{m}$ . Elemental analysis of these particles as well as a cartography of the elements identified (Si, Al, Fe, Ba) were performed. Si and Al-rich particles probably originate from the combustion of fuels (Xie et al., 2005; Chôel et al., 2007). Microspheres enriched in Fe are probably iron oxides from industrial source (Jones et al., 2006) The cartography also shows two small particles containing barium. The presence of Ba mainly associated with S ( $\text{BaSO}_4$ ) was reported by El-Samrani et al. (2004) who consider that  $\text{BaSO}_4$  is generated by the abrasion of brakes or road paints. However, S was not detected in our samples, this hypothesis has then to be rejected.

## 3.2 Runoff water

Bulk parameters are discussed in detail in Lamprea (2009) and will not be presented here.

### 3.2.1 Trace elements

Large variations in metal concentrations are observed from one campaign to the other and between the different sites (table 2). An example is shown in figure 4 for Pb and Zn concentrations in roof runoff. In all cases Cd concentrations are low and often close to the quantification limits. These concentrations are rather similar for both roof and street runoff with a median ranging from 0.2  $\mu\text{g L}^{-1}$  (zinc roof) to 0.7 (slate roof).

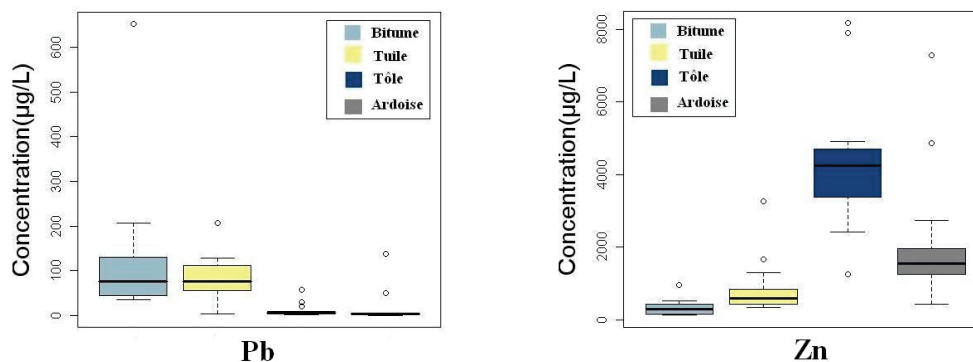


Figure 4. Lead and zinc concentrations in roof runoff water.

Copper, Cr and Ni concentrations in roof runoff are also low (table 2) ranging from 1.5 to 4.5 for Cr, 2.6 to 7.5 for Cu and 1.3 to 8.3  $\mu\text{g L}^{-1}$  for Ni. The Kruskal-Wallis test with  $\alpha = 0.05$  shows no difference between Cu and Cr concentrations for the different roofs, whereas Ni concentrations are twice higher for runoff water from the slate roof but similar for the 3 others. Nickel probably originates from roof accessories but this has not been verified. Chromium concentration in street runoff is similar to that of roof runoff. On the contrary Ni and Cu concentrations are higher (table 2) due to tire and brake wearing in street runoff (Legret and Pagotto, 1999; Thornton et al., 2001).

Mean Pb concentrations for zinc and slate roofs vary from 4.4 to 6.5  $\mu\text{g L}^{-1}$ , whereas they are 76 and 79  $\mu\text{g L}^{-1}$  for bitumen and tile roofs, respectively. This can be explained by Pb leaching from

accessories and PVC gutters. Indeed, lead is commonly used for tightness due to its malleability, stability and resistance to climatic conditions. It is also largely used in Europe as an additive in PVC (Al malack, 2001). In street runoff, Pb concentration is similar to that measured for zinc and slate roofs. Contribution of Pb from traffic is now very limited due to the decrease in the use of leaded gasoline since the year 2000.

Metals	Statistics	Bitumen	Tile	Zinc	Slate	street
Cd	Minimum	<QL	0.1	<QL	0.2	0.1
	Median	0.4	0.4	0.2	0.7	0.5
	maximum	2.6	4	0.8	28	0.8
Ni	Minimum	<QL	<QL	<QL	1.0	2.2
	Median	2.4	2.3	1.9	4.3	8.2
	maximum	5.4	4.1	7.3	17	12
Cr	Minimum	<QL	1.3	<QL	1.5	2.0
	Median	2.9	1.7	3.2	2.7	4.9
	maximum	9.7	6.5	11	6.2	5.1
Cu	Minimum	<QL	<QL	<QL	<QL	16
	Median	5.4	4.3	3.4	4.3	18
	maximum	25	14	11	14	23
Pb	Minimum	36	4.0	1.9	1.0	2.3
	Median	76	79	6.5	4.4	8.2
	maximum	652	208	58	137	18
Zn	Minimum	121	346	1 263	434	66
	Median	230	569	4 244	1 598	212
	maximum	958	3 256	8 174	7 300	350

Table 3 Median, max and min metal concentrations ( $\mu\text{g L}^{-1}$ ) in runoff water from the Pin Sec catchment

Zinc is the predominant metal in all roof runoff. The wilcoxon test with  $\alpha = 0.05$  shows that median concentrations are significantly different from one roof to the other. Unsurprisingly, the concentrations are higher for the zinc roof. Zinc concentrations are generally lower in street runoff, only the concentrations from the bitumen roof are lower.

The influence of meteorological conditions (total rainfall, antecedent dry period (ADP) and maximum intensity at 5' on metal and SS concentrations was studied using the Pearson correlation coefficient with  $\alpha = 0.05$  and principal component analysis (PCA). This study does not reveal any correlation.

### 3.2.2 Organic micro-pollutants (PAHs and pesticides)

Polycyclic aromatic hydrocarbons (PAHs) were detected in less than 25 % of the samples mainly in the winter as was the case for atmospheric deposition. Figure 5 shows the distribution of PAHs in roof runoff; naphthalene (Np), fluoranthene (Flu), pyrene (Py) and benzo(3,4)fluoranthene (B[b]Flu) are dominant. Due to the high variability of Np concentrations from one roof to another it was decided to calculate the relative PAH distribution without Np. Flu and Py percentages are then similar for the different campaigns as well as among the 4 roofs. The mean relative percentage is 26 % for Flu and 16 % for Py. Regarding B[b]Flu the percentages are quite variable between campaigns and roofs, ranging from 5 to 26 %. Flu and Py are likely to originate from combustion processes; this is confirmed by the Flu/Py ratio ranging from 1.2 to 2.0. However, in roof runoff, the pyrolytic origin of PAHs is not exclusive. Indeed, the B(a)/Chry ratio comprised between 0.33 and 0.8 and the Ip/B(a) ratio ranging from 0.75 to 1.33 testifies of a petrogenic origin.

High PAH concentrations were detected in one of the street runoff sample (October 2008), whereas in the 2 other samples concentrations were under the quantification limits. This difference can be explained by the meteorological conditions with an antecedent dry period of 8 days in the case of the October rain, whereas it was only a few hours in the other cases. In street runoff, Flu and Py are the main PAHs, with mean relative percentages of 20 and 14 %, respectively. Flu/Py, B(a)/Chry and Ip/B(a)/P ratios indicate a petrogenic origin. In street runoff, these sources are motor oil, grease and residues generated during tire abrasion.





in other catchments with similar characteristics. The relative abundance of metals is as follows: Zn > Cu > Cr  $\approx$  Ni > Cd. Organic pollutants, i.e. PAHs and pesticides, were rarely detected. PAHs were only detected in the winter, their origin is residential and collective heating. Glyphosate and AMPA were detected in the summer, they probably originate from the volatilisation and dispersion of herbicides on vineyards and other cultures in the Nantes region, as well as from the treatment of impervious surfaces.

Runoff from 4 roofs (tile, slate, zinc and flat bitumen) and a street was also studied. Zinc and lead appear to be the major contaminants, whereas the concentrations of Ni, Cu, Cr, Cd, PAHs and pesticides are generally low. The comparison of median concentrations in roof and street runoff shows that cadmium concentrations are similar, while Cu and Ni are higher in street runoff. Zinc and lead concentrations in street runoff are comparable to those of roofs without Zn or Pb accessories, whereas they are much lower than those of roofs with Pb or Zn accessories. As a whole, the concentrations are similar to the lowest range of those reported in the literature. According to the SEQ-eau, runoff water quality is bad because of high Pb and Zn concentrations.

From SEM observations it appears that atmospheric particles are not different from runoff particles, with a predominance of pollen, bacteria and particles from soil erosion. Spherical organic particles formed during the combustion of fuels are also observed.

Sampling of atmospheric particles and runoff water, as well as SEM observations on the Pin Sec catchment should be completed. This will be done in the frame of the national project INOGEV (innovations for a sustainable management of water in cities).

## ACKNOWLEDGEMENT

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