

Contribution of dry atmospheric deposition to the metal load in a small urban watershed (Nantes, France)

Contribution du dépôt sec atmosphérique à la pollution en métaux d'un petit bassin versant urbain (Nantes, France)

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RÉSUMÉ

Une méthode innovante mise au point pour la mesure du dépôt sec atmosphérique a été utilisée pour effectuer un bilan de masse des métaux traces à l'exutoire du réseau d'eaux pluviales du bassin versant du Pin Sec à Nantes (France). Cette méthode, qui prend en compte la nature des surfaces urbaines (tuile, ardoise, tôle en zinc, bitume, herbe, enduit de façade, verre), montre que la contribution du dépôt sec atmosphérique est inférieure à celle généralement rapportée dans la littérature (12% pour Zn, 18% pour Cu, 8% pour Pb). Les méthodes classiques semblent surestimer le dépôt sec.

Les charges en métaux varient d'un mois à l'autre, entraînant des variations dans la contribution relative de l'atmosphère et des eaux de ruissellement. Des pluies abondantes fin 2010 pourraient expliquer un lessivage plus important des surfaces urbaines et donc une contribution plus importante des eaux de ruissellement à la charge en métaux traces à l'exutoire du bassin versant du Pin Sec. A l'inverse, la sécheresse du printemps 2011 se traduirait par une contribution plus forte de l'atmosphère.

ABSTRACT

An innovating method developed for the measurement of dry atmospheric deposition was used to estimate metal mass balances at the outlet of the Pin Sec watershed in Nantes (France). This method, which takes into account the nature of urban surfaces (tiles, slates, zinc sheets, grass, bitumen, coatings, glass), showed that the contribution of atmospheric dry deposition is smaller than that estimated in previous studies, e.g.12% for Zn, 18% for Cu and 8% for Pb. The methods used classically seem to overestimate dry deposition.

Metal loads greatly vary from one month to the other inducing variations in the relative contribution of the atmosphere and runoff. Heavy rainfall at the end of 2010 could be responsible for a larger washout of urban surfaces, hence a larger contribution of runoff water to the metal load at the outlet of the Pin Sec watershed. On the contrary, dry conditions during the spring induced a higher contribution of the atmosphere.

MOTS CLES

Bassin versant urbain, Dépôt sec atmosphérique, Métaux traces, ONEVU, Pollution

1 BACKGROUND AND OBJECTIVES

Good quality air is considered essential for human health. However, air pollution continues to be an important problem all over the world [..]. More than 2 million people die prematurely each year because of bad indoor and outdoor air quality (WHO, 2000). The atmosphere is regularly contaminated by gaseous, liquid or solid pollutants. Atmospheric particles have a mixed origin either natural or anthropogenic (Slezakova et al., 2008; Thorpe and Harrison, 2008). Soil dust and evaporation of sea water (in coastal areas) are considered as the largest natural sources (Slezakova et al., 2008). In urban regions, vehicle related emissions including fuel combustion, tire abrasion, brake wear and the resuspension of road dust are among the most important sources (Song and Gao, 2011). Heating, industries and constructions are other important sources.

In most of the world, air quality is now regulated. At the European level, two directives (Directive 2008/50/CE and Directive 2004/107/CE) are implemented to control air quality. Pollutant deposition is also taken into account in the French decree 2010/1250 but the measurement methods are not identified. Though atmospheric deposition is recognized as a major vector of pollutants in the environment, there is a lack of knowledge regarding the relative contribution of dry and wet depositions. Indeed, recent studies (Roupsard et al., 2012) have shown that the nature of urban surfaces as well as meteorological conditions greatly influences dry deposition but until now this has not been taken into account.

A long-term study is currently carried out on the Pin Sec watershed (Nantes, France) in the frame of the Research Institute of Urban Sciences and Techniques (IRSTV), with the objective to assess water, pollutant and energy balances for a small urban watershed. In this context, special attention is paid to the estimation of dry deposition by means of beryllium 7 (^7Be). This paper presents the first results regarding the contribution of dry atmospheric deposition to the metal load in this small urban watershed.

2 MATERIALS AND METHODS

2.1 The study site

The sampling site was the small "Pin Sec" catchment located East of Nantes city which was urbanized mostly during the 20th century; it is limited on the Northeast by a tram line embankment. The habitat is mostly constituted of personal households and 5-storey collective buildings. The impervious surfaces estimated from the "Nantes Métropole" cadastral survey cover about 49 % of the watershed and the mean slope is about 1.1 %. The climate in Nantes (47°13'N, 01°33'W, 80 km far from the Atlantic coast) is oceanic. The prevalent wind directions are from the South-Southwest and North-Northwest sectors with the highest wind speeds typically from the Southwest, while moderate and low winds are most often from the West. The average annual precipitation during the survey was 809 mm.

2.2 Sampling

An original approach was developed in this long-term study (September 2010 to October 2011) to measure dry deposition. It combines particle collectors (Partisol 2000 FRM), a covered rain gauge and frames on which test samples of different urban materials are fixed (tiles, glass, bitumen etc...). A meteorological station and an ultrasonic anemometer supply meteorological and micrometeorological data. Measuring instruments have been installed on the roof of a 4-store building in the Pin Sec catchment; the data should be representative of the global quality of atmospheric deposition on this catchment. Particles were collected during one-week periods on quartz filters (47 mm \varnothing) at a flow rate of 1 m³ h⁻¹ avoiding the clogging of the filters. In order to have enough material to carry out the analyses the 4 weekly filters were gathered together each month.

Regarding storm water, samples were collected for each rain event during the same period to an extent proportional to the actual discharge flow at the outfall. Mean monthly samples were then constituted.

2.3 Chemical analyses

Trace metal analyses (As, Cd, Cr, Cu, Ni, Pb, V, Zn) were carried out at the IFSTTAR Nantes Environmental and Chemical laboratory. The analyses were performed after mineralization of the samples using a mixture of HF and HClO₄ acids. Determination of the chemical element contents was performed by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS; Varian 820-MS). In order to assess the validity of the mineralization protocol as well as the quality of the analytical data, a reference sample was used (CRM 1648a, urban atmospheric sample). The quantification limits ranged from 0.1 ng m⁻³ to 0.2 ng m⁻³ depending on the element. The analytical uncertainty varies from 5% (Cu, V) to 8% (Cr); it is 6% for Cd and 7% for As, Ni, Pb and Zn.

2.4 Flux and mass calculation

The detailed calculation is reported in Percot (2012).

The dry velocity V_d (m S⁻¹) is defined as $V_d = \frac{-F}{C}$ (1)

with -F the flux (g m⁻² S⁻¹) measured on a given surface and C (g m⁻³) the pollutant concentration in the air nearby this surface.

The wet deposition flux is given by $F_{RH} = \frac{M_{Rh}}{S_a}$ (2)

with $M_{RH} = C_{tot}.H.S_a.10^{-6}$ and $S_a = S_{tot}.C_r$. M_{RH} is the pollutant mass (g), S_a the active surface of the catchment (m²), C_{tot} the pollutant concentration, H the rainfall depth (mm), and C_r the run-off coefficient.

Finally, the flux at the outlet is $F_{out} = \frac{M_{out}}{S_a}$ (3)

with $M_{out} = C_{out}.V.10^{-3}$. M_{out} is the pollutant mass in run-off water at the outlet (g), C_{out} the mean monthly pollutant concentration during wet weather at the outlet (mg L⁻¹), and V (L) the monthly water volume transported in the collector during wet weather.

The pollutant mass brought by atmospheric dry deposition is given by , $M_{Rs} = F_{surf}.Surf$ (4)

where F_{surf} is the dry deposition flux for a given surface (e.g. bitumen) and Surf the corresponding surface estimated on the Pin Sec.

3 RESULTS AND DISCUSSION

3.1 Dry deposition fluxes

Monthly fluxes were obtained by multiplying dry deposition velocities measured for the different urban surfaces (i.e. bitumen, glass etc.) with pollutant concentrations in atmospheric particles. These fluxes are then applied to the corresponding surfaces estimated for the Pin Sec watershed. The monthly Zn flux is presented as an example in figure 1.

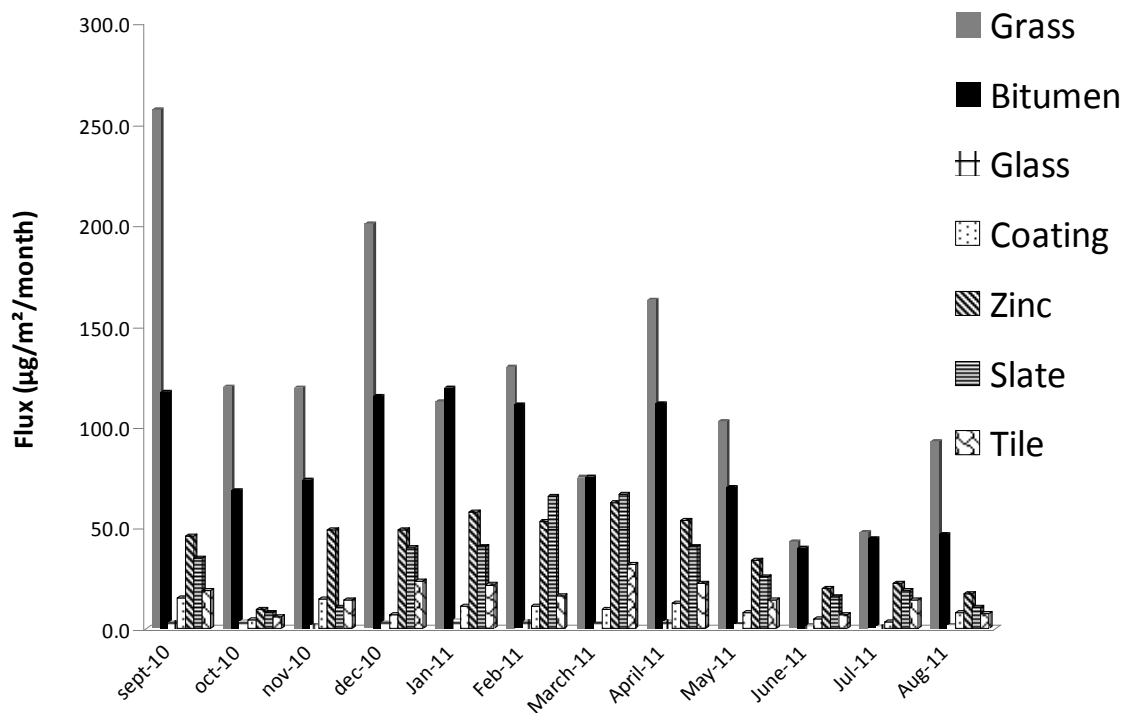


Figure 1. Mean monthly variations of zinc dry deposition flux.

As can be seen on figure 1, the flux is highly variable from one month to the other and it strongly depends on the nature of the surfaces. For all trace metals, the flux is the highest on herb surfaces (e.g. $258 \mu\text{g m}^{-2} \text{ month}^{-1}$ for Zn) and bitumen ($140 \mu\text{g m}^{-2} \text{ month}^{-1}$). Whatever the metal, the smallest flux is observed for vertical surfaces such as glass ($4 \mu\text{g m}^{-2} \text{ month}^{-1}$ for Zn in January) and façade coatings ($15 \mu\text{g m}^{-2} \text{ month}^{-1}$ in September). It appears, therefore, that surface roughness is a major factor in atmospheric dry deposition.

Roupsard et al. (2012) showed that deposition velocities do not vary much throughout the year, therefore, the seasonal variation can be attributed mainly to variations in metal concentrations. The influence of wind speed and direction was also studied but no correlation could be observed (Percot, 2012).

For each metal, the monthly flux for the 7 urban surfaces (grass, bitumen, glass, façade coating, slate, zinc sheet and tile) were summed up to determine the global flux; all the monthly fluxes were then totalized yielding the annual dry deposition flux ($\mu\text{g m}^{-2} \text{ year}^{-1}$). Literature data on dry fluxes are scarce; the few available studies (Sabin et al., 2005; Becouze, 2010) show that the fluxes calculated for the Pin Sec watershed are generally lower, which is not surprising as Pin Sec is an urban residential watershed whereas the other sites are industrial (Becouze, 2010) or suburban (Sabin et al., 2005).

3.2 Wet deposition fluxes

Wet deposition fluxes were calculated as described in 2.4. As shown in figure 2, metal fluxes vary throughout the year and are higher during the winter months and especially in December (e.g. $1200 \mu\text{g m}^{-2} \text{ month}^{-1}$ for Zn). The smallest flux ($113 \mu\text{g m}^{-2} \text{ month}^{-1}$ for Zn) is observed in April (except for Cu which is minimum in May) when rainfall is the lowest.

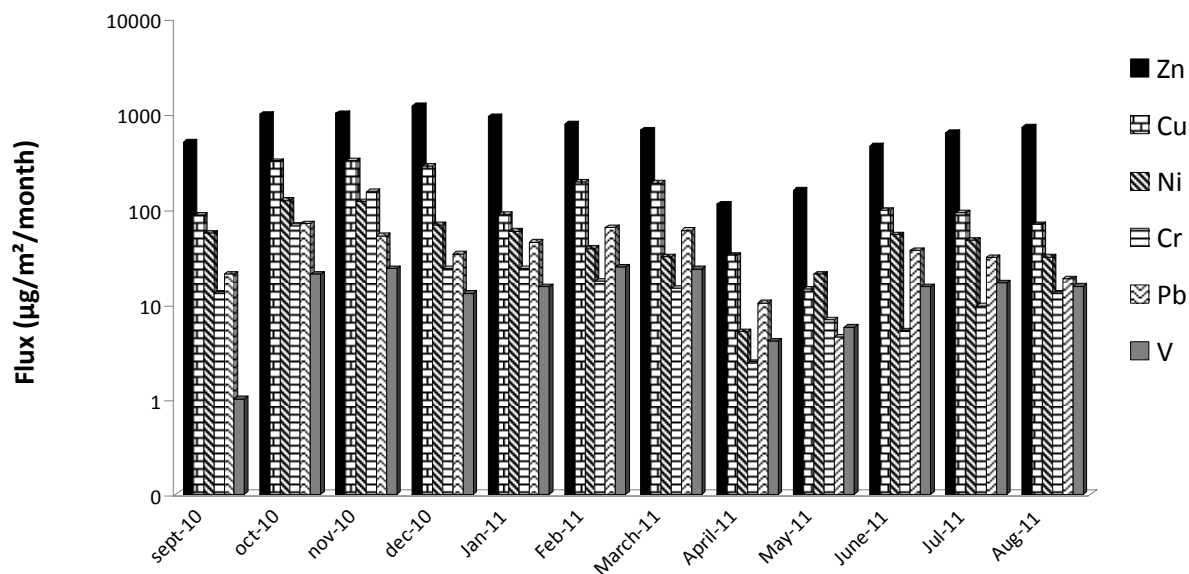


Figure 2 Monthly variations of metal wet deposition flux.

In order to understand these yearly variations, different correlations with meteorological parameters were studied. The highest correlation ($R^2 = 0.88$) was observed between total rainfall and Cr but correlation coefficients are generally low and do not allow explaining variations. This was already mentioned by Lamprea (2009) and Azimi (2005) who explained that as metal sources in the urban environment are the same all over the year, fluxes do not depend on the seasons.

The relative abundance of trace metals is generally as follows: $Zn > Cu > Ni > Cr \approx Pb > As > Cr$.

3.3 Metal fluxes at the outlet

Metal fluxes at the outlet of the Pin Sec watershed were calculated as described in 2.4. Zinc, Cu and Pb were the most abundant elements. Fluxes were high in December (fig. 3) because of heavy rainfall inducing high volumes transported in the collector: $16\,884\ \mu\text{g m}^{-2}\ \text{month}^{-1}$ for Zn, $2\,755\ \mu\text{g m}^{-2}\ \text{month}^{-1}$ for Cu and $2\,374\ \mu\text{g m}^{-2}\ \text{month}^{-1}$ for Pb. Minimum values were observed during the driest months, especially in April. Zinc flux was then $960\ \mu\text{g m}^{-2}\ \text{month}^{-1}$, Cu and Pb 228 and $131\ \mu\text{g m}^{-2}\ \text{month}^{-1}$, respectively.

Copper and Pb fluxes were slightly higher than those reported by Lamprea (2009), whereas Zn flux is twice as high because of higher concentrations. These, however, are difficult to explain as Zn sources remain the same as in the previous study. Rainfalls are similar as those registered for the last 30 years. Copper and Pb fluxes were also comparable to those reported by Bressy (2010) for Noisy le Grand, whereas the Zn flux is lower in our study, probably due to different sources.

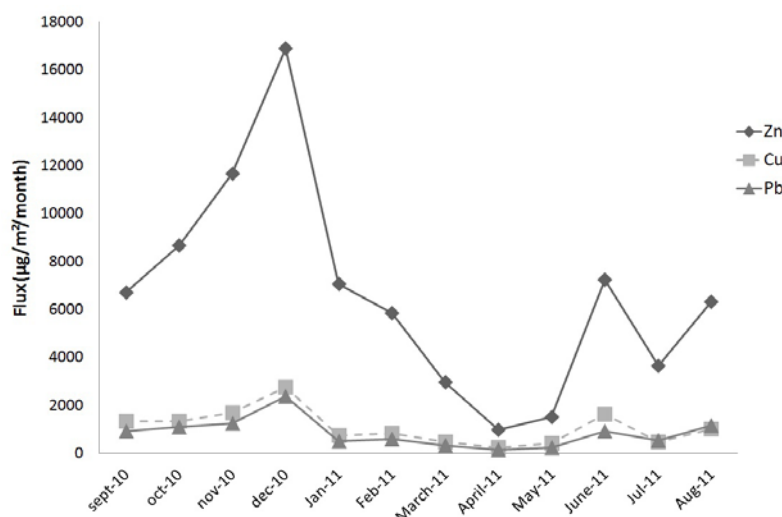


Figure 3. Monthly variations of Zn, Cu and Pb at the outlet of the Pin Sec watershed.

3.4 Metal loads contributed by the atmosphere and at the outlet

In order to estimate atmospheric deposition a pollutant mass balance has been calculated. The hypothesis that all the impervious surfaces are connected to the storm water network was made. Furthermore, according to our estimation 51% of the Pin Sec watershed is grass, a permeable surface. Therefore, in our calculation we decided not to take grass into account as no soil saturation was observed during the survey period, which could have induced water runoff.

Table 1 shows the estimation of the Pin Sec surfaces (m²) taken into account for the calculation the metal mass contributed by dry deposition. The mass was obtained by multiplying the flux (as calculated in 3.1) by these surfaces.

Table 1. Urban surfaces taken into account for the calculation of atmospheric dry deposition on the Pin Sec watershed

Nature of the surfaces on the watershed	Surfaces (m ²)
Bitumen	97 700
Glass	16 500
Coating	86 454
Zinc	1 000
Slate	12 600
Tile	21 000
Total	394 254

Zinc mass is the highest with a monthly mean of 10 g and a maximum of 14 g in January. The mean Cu load comes second with 5 g (maximum 9 g in November), followed by Pb (3 g, maximum 5 g in July). Vanadium, Ni, As, Cd and Cr masses are very low (< 1 g). The annual variations of metal masses contributed by the atmosphere seem to depend mainly on variations in concentrations (Percot, 2012). Meteorological conditions could also play a role. Indeed, lower winter temperatures could limit pollutant dispersion, hence an increase in dry deposition. During the Summer, the deposition is lower due to thermophoresis processes limiting the deposition.

As already seen for the fluxes, wet deposition is higher than dry deposition. Zinc deposit is the highest (80 g as a monthly average) with a maximum of 140 g in December. The mean monthly Cu load is 17 g, with a maximum of 37 g in November, while the Pb monthly load varies from 1 to 4 g. The Ni load is much higher than dry deposition, with a mean monthly value of 6 g (0.7 g for dry load). As for dry deposition the monthly variations are not easy to explain, in particular there is no significant correlation between rainfall and the decrease in trace metals in PM₁₀.

Table 2 shows the total metal mass contributed by atmospheric deposition (dry + wet loads).

	Zn (g)	Cu (g)	Ni (g)	Cr (g)	Pb (g)	V (g)	As (g)	Cd (g)
September 2010	71	16	7	2	7	1	0	0
October 2010	121	43	14	8	12	3	0	0
November 2010	125	46	14	17	10	3	0	3
December 2010	152	38	9	4	8	2	1	0
January 2011	121	15	7	4	9	2	0	0
February 2011	121	29	6	3	12	4	0	0
March 2011	93	26	4	2	10	4	0	0
April 2011	26	9	1	1	5	2	0	0
May 2011	27	6	3	1	3	2	0	0
June 2011	57	15	7	1	6	3	0	0
July 2011	78	14	6	1	6	3	0	0
August 2011	89	12	5	1	4	3	0	0
Total	1081	269	83	45	92	32	1	3

These total loads will allow us estimating the atmospheric contribution to the pollution at the outlet.

The metal loads at the outlet of the Pin Sec watershed were calculated. As expected, Zn, Cu and Pb loads are the highest, e.g. 2000 g for Zn, 320 for Cu and 272 for Pb in December (Fig. 4).

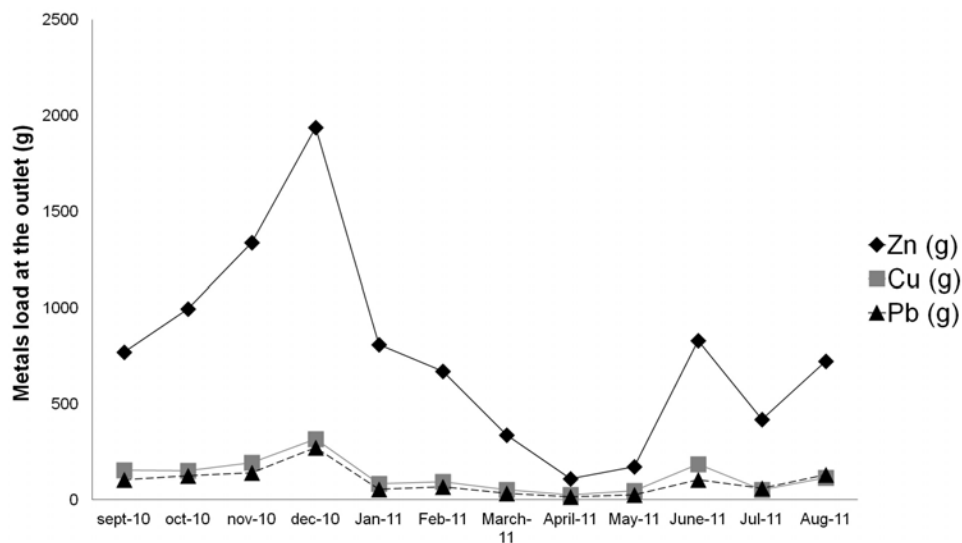


Figure 4. Monthly variations of metal loads at the outlet of the Pin Sec watershed

3.5 Contribution of atmospheric deposition to the metal pollution at the outlet of the Pin Sec watershed

The flux at the outlet of a watershed is the sum of the atmospheric flux plus the flux generated by runoff water (Zgheib, 2009). Therefore, the load at the outlet (M_{out}) is the sum of the atmospheric load (M_{atm}) and the runoff load (M_{run}):

$$M_{out} = M_{atm} + M_{run} \quad (5)$$

The monthly contribution of the atmosphere to the metal load is presented in figure 5. As can be seen,

the loads are highly variable from one month to the other. However, it has to be noted that due to the very low concentrations in some elements (As, Cd, Cr, Ni, V) one must be cautious regarding their contribution. Zinc contribution ranges from 8% in December to 40% in April, with a mean of 12%. The mean Cu contribution is 18% with a minimum in June (10%) and a maximum (55%) in March, whereas the Pb average contribution is around 2%.

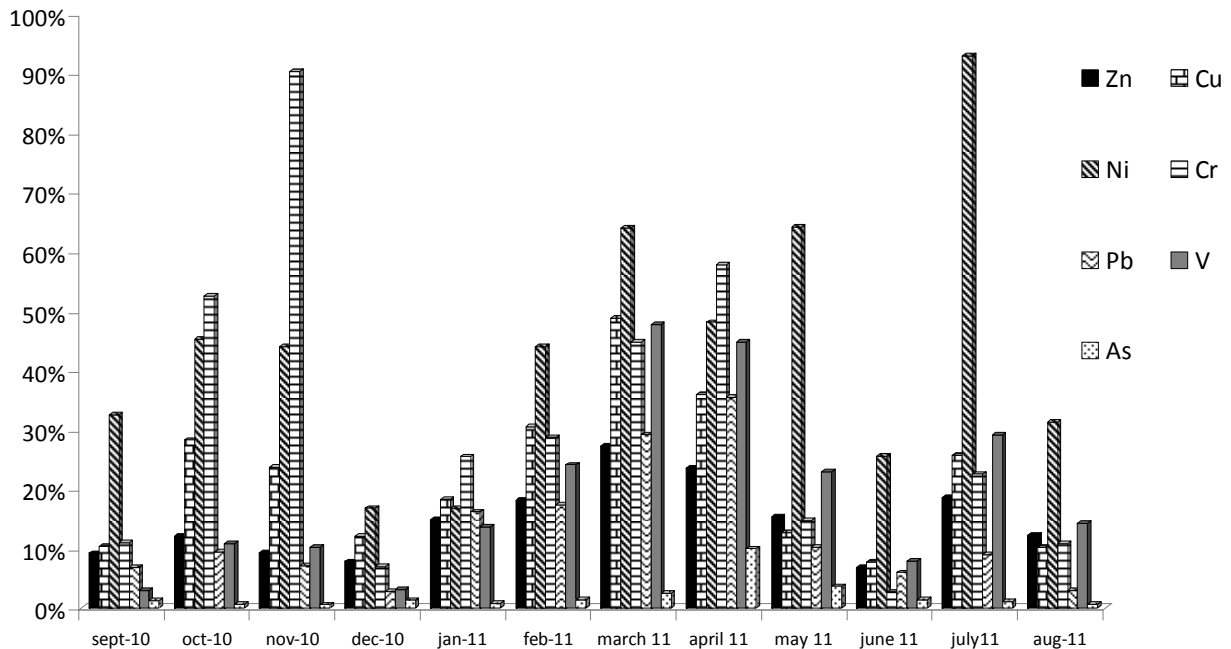


Figure 5. Monthly variations of the contribution (%) of atmospheric deposition to the metal load at the outlet of the Pin Sec watershed.

Metal loads greatly vary from one month to the other due to large variations in PM_{10} concentrations, which are influenced by meteorological factors (e.g. relative humidity, temperature). However, the influence of these factors is dependant on metals. As shown by Percot (2012) rainfall does not seem to influence the deposition of some metals but do play a role for others (Ni, V). For example, the contribution of atmospheric deposition is larger in November 2010 (a rainy month) than in December, when rainfall is less abundant. It is possible that the heavy November rain has washed out the pollutants brought by atmospheric deposition, inducing a decrease in the pollutant loads deposited on surfaces and increasing the relative contribution of metals released from these surfaces. Therefore, the contribution of runoff water is much larger and the metals at the outlet are mainly released from urban surfaces (Zgheib, 2009). On the contrary, dry deposition contribution increases in spring due to low rainfall during this period. It has to be noted that the large contribution of Ni and Cr shown in figure 5 may not be significant because, as already mentioned, the concentrations of these elements are very low.

The annual contribution of atmospheric deposition and runoff water at the outlet of the Pin Sec watershed was then estimated. An example is presented in figure 6 for Zn, Cu and Pb. The atmospheric contribution is 12% for Zn, 18% for Cu and 8% for Pb. This contribution is 1% for As, 11% for V, 25% for Cr and 33% for Ni and Cd. It has to be noted again that the concentrations of some elements (especially Cd) was very low, resulting in uncertainties on the relative contributions.

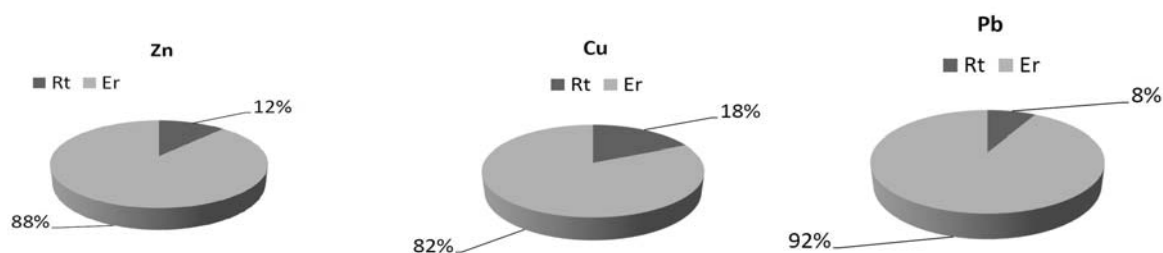


Figure 6. Annual relative contribution of atmospheric deposition and runoff water at the outlet of the Pin Sec watershed (Rt : total atmospheric deposition ; Er : runoff water)

The atmospheric contribution determined in our study is always smaller than those estimated in previous studies (Lamprea, 2009). Different sampling devices in both studies can explain these differences. Indeed, as already mentioned, dry deposition fluxes are greatly influenced by the nature of urban surfaces. However, these were not taken into account in previous studies and the fluxes estimated by means of plastic funnels (as in Lamprea, 2009) are probably overestimated.

4 CONCLUSION

An innovating method developed for the measurement of dry atmospheric deposition was used to estimate metal mass balances on the Pin Sec watershed. This method, which takes into account the nature of urban surfaces, showed that the contribution of atmospheric dry deposition is smaller than what was estimated in previous studies.

Metal loads greatly vary from one month to the other inducing variations in the relative contribution of the atmosphere and runoff. Heavy rainfall at the end of 2010 could be responsible for a larger washout of urban surfaces, hence a larger contribution of runoff water to the metal load at the outlet of the Pin Sec watershed. On the contrary, dry conditions during the spring induced a higher contribution of the atmosphere.

In our study allowing an estimation of dry atmospheric deposition on different urban surfaces we made the hypothesis that because grass is not an impervious surface, the deposition on this surface does not contribute to the pollution at the outlet (though grass surfaces represent 51% of the total surface of the watershed). This, however, could not be quantified and should be verified by lixiviation on test samples.

Finally, this new methodology should be implemented on other watersheds with different characteristics, and other pollutants should be studied.

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