Zn and Pb emissions from roofing materials – Modelling and mass balance attempt at the scale of a small urban catchment

Emissions de plomb et de zinc par le ruissellement des matériaux de toiture – Une tentative de modélisation et de bilan à l'échelle d'un petit bassin versant urbain

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RÉSUMÉ

De nombreux travaux de recherche ont montré que les matériaux de couvertures constituent une source importante de métaux dans les eaux de ruissellement urbaines. Dans le cadre de la mise en œuvre de la Directive Cadre Européenne sur l'eau (2000/60 CE), la quantification de ces émissions s'avère nécessaire, imposant le développement d'outils permettant une telle évaluation à grande échelle.

L'étude porte sur un petit bassin versant urbain (assaini en réseau séparatif), sur lequel des échantillonnages ont été réalisés: retombées atmosphériques, ruissellement de chaussées, de toitures et eaux pluviales à l'exutoire du bassin.

L'objectif est (1) de vérifier la contribution des matériaux de toitures aux émissions de Zn et de Pb à l'échelle du bassin et (2) de voir comment les modèles précédemment développés dans le cadre du programme de recherche TOITEAU (à l'échelle de bancs d'essais expérimentaux) peuvent être appliqués à des échelles spatiales différentes (toit et bassin versant) pour la quantification des ces émissions.

Les résultats obtenus confirment la forte contribution des matériaux de toitures aux flux de Zn et Pb dans les eaux de ruissellement à l'échelle de bassin. Dans le cas du Zn, les modèles mis en place à petite échelle ont pu être transposés et validés à l'échelle du toit et du bassin versant. La transposition des modèles d'émission du plomb est plus difficile, du fait de l'estimation délicate des surfaces concernées.

MOTS CLÉS

Contamination du ruissellement; Matériaux de couverture; Métaux; Modélisation; Retombées atmosphériques.

ABSTRACT

Many studies have shown that roofing materials are an important source of metals in urban runoff. Today, in the context of the European Water Directive (2000/60 CE), the quantification of these emissions is necessary, and thus the development of assessment tools is needed.

This study focuses on a small urban catchment (drained by a separative sewer system). Atmospheric fallout, road runoff, roof runoff and total runoff at the outlet of the catchment were sampled.

The aim is (1) to verify the contribution of roofing materials to metallic flows of Zn and Pb at the catchment scale and (2) to try to model emissions using some models previously developed at the test-bed scale. These models have to be tested at different spatial scales.

Results obtained confirm the strong contribution of roofing materials to Zn and Pb flows at the catchment scale. For Zn, models tested were successfully transposed and validated at the roof and the catchment scales, permitting a good quantification of Zn emissions. For Pb, the use of the models highlights some difficulties, especially concerning the identification and the quantification of lead surface areas implemented.

KEYWORDS

Atmospheric fallout; Metals; Modelling; Roofing materials; Runoff contamination

1 INTRODUCTION

Metallic materials are largely used in urban areas, especially for infrastructure, such as buildings or street furniture. Exposed to atmospheric conditions, including environmental pollutants and quite high relative humidity, these materials are progressively corroded and a part of the corrosion products formed on the surface will be released into the runoff and washed off during rain events.

Today, in the context of the European Water Directive (2000/60 CE), whose aim is to obtain a good ecological state of aquatic environments until 2015, it seems necessary to reduce the production of pollutants at their sources. Thus, major sources have to be identified and quantified. Several research programs lead since the 1990's have shown the very high trace metal contamination of runoff from metallic or partly metallic roofs (Gromaire-Mertz *et al.*, 2001; Bertling *et al.*, 2002; Faller *et al.*, 2005). Anyway, an assessment tool taking into account the kind of material used is needed to accurately quantify metallic emissions from roofs.

TOITEAU project has begun in 2005, with the aim of developing a methodology for the estimation of annual metallic flows from roofs at the catchment area scale. The first objective of this program was the evaluation of annual runoff rates for different roofing materials commonly used in Paris conurbation, in order to establish a prioritization of the runoff contamination risk considering the type of roof. The second objective concerned the transposition of results obtained to larger spatial scales, using roof surface areas data obtained form air photographs and image classification software.

Models developed for the estimation of metallic flows from roofing materials (Robert-Sainte, 2009), permit to obtained satisfactory results at the scale of the test bench and for quite long periods of exposure (some months to one year).

The aim of the work described in this paper is (1) to consider the different contribution to the total runoff at the catchment scale in order to verify the contribution of roof runoff to metallic flows, and (2) to try to model this metallic flows issued from roofs at the scale of the urban catchment. This paper describes the attempt of transposition of these models to larger spatial scales (real roof and urban catchment) and to shorter time-scales (rain event)

Results obtained for Zn and Pb are presented here, as well as the models used and the attempt of application of these models to the catchment.

2 METHODOLOGY

2.1 Zn and Pb runoff quantification at test bed scale

Zn and Pb runoff from metallic roofing materials was quantified on test benches (Figure 1) exposed during 14 months to real atmospheric and pluviometric conditions, on two different sites in Paris conurbation. Zinc materials were exposed as metallic roofing panels (1250 x 400 mm) and as metallic gutters (400 mm long gutters collecting water from 1250 x 400 mm Plexiglas panels), whereas lead materials were exposed as metallic tightness elements sticked on a Plexiglas panel. Atmospheric inputs were evaluated on reference Plexiglas panels.

Figure 1: test beds (zinc panel, zinc gutter, lead tightness elements, reference Plexiglas panel)

All runoff waters were collected in containers which were changed approximately once a month, acidified at pH 1 with HNO3, and analysed for metal concentrations using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

For each collection period i, the metal runoff rate Fi, expressed in g. m^{-2} yr^{-1}, is calculated as:

$$F_i = \frac{V_i}{S_{mat} \cdot T_i} \left(C_i - C_{0_i} \right),$$

with: Vi the volume of runoff water collected during the time period of exposure Ti,
S_{mat} the projected surface area of the exposed metallic material,
$C_{,i}$ and $C_{0,i}$ the measured concentrations in runoff waters respectively for the considered test bed and for the Plexiglas reference panel.

An annual metal runoff rate has also been calculated, based on the sum of the runoff masses from de 14 collection periods.

Based on these experiments, a model of Zn and Pb runoff, per m^{-2} of projected material, taking into account the duration of exposure and the pluviometric conditions, has been developed.

The standard deviation of the measured metal concentrations, due to both sampling uncertainties and analysis, has been evaluated to 0.5% for Zn concentrations from the zinc panel, 0.9% for Pb concentrations from the lead panel and respectively to 12.8% for Zn and 18.5% for Pb concentrations from the reference Plexiglas panel ($C_{0,i}$). This leads to a standard deviation on the calculated metal runoff rates Fi of less than 1.1% for Zn and less than 2% for Pb.

2.2 Model validation at catchment scale

2.2.1 Methodology

The Zn and Pb emission models developed from the test bed experiments were applied and validated in full scale conditions, at the scale of a building catchment and at the scale of an urban catchment. It was decided to work on a small scale catchment so as to avoid the effects of in-sewer processes. However, on an urban catchment roofing materials are not the only source of zinc and lead. The contribution from atmospheric fallout and from automotive traffic via street runoff had also to be estimated and deduced from the total loads measured at the catchment outlets.

2.2.2 Catchment description

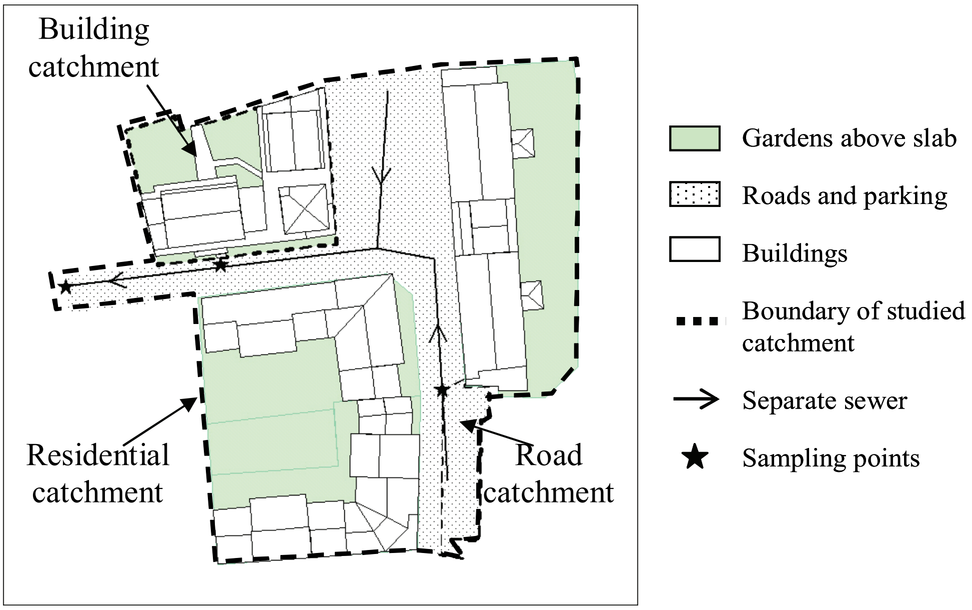

Figure 2: Map of studied catchments

A residential town-center catchment, located 3 km from one of the test bed exposure sites, and constructed 10 years ago, was selected. It is a low density traffic catchment without industrial activity nearby. The catchment area of 8210 m^2 consists of 28 % roads and parking, 42 % buildings (tile, zinc and flat roofs) and 30 % gardens (above slab) and is drained by a separate sewer. Two sub-catchments were also delimited: a 311 m^2 street and parking catchment which was used to quantify metal loads from street runoff and a 1288 m^2 building catchment which was used to validate the zinc runoff model from zinc roofs (Figure 2). This building catchment consists in 555 m^2 zinc roofing, 281 m^2 flat roofing, 396 m^2 garden and 56 m^2 other impervious surfaces.

The projected surface area of zinc roofing (603 m^2 for the residential catchment) was calculated with GIS (Mapinfo), based on both the air orthophotography of the catchment and the block plan of the buildings. Yet, zinc and lead materials may also be used for tightness purposes on all the singular points of the roof (valleys, ridges, penetrations...). These singular points have been identified via on-site observations and their length has been calculated on the GIS tool. It remains however difficult to evaluate with precision the type of metal used for these elements and the surface of contact with the runoff. Some information is given by the French reference documents DTU addressed to professional roofers (Robert *et al.*, 2007). This data remains however theoretical and concerns the total width of the material which differs from the width in contact with the runoff. Further information was given by a thorough field survey on 50 individual houses situated in the same district as the considered catchment (Weiss, 2009). The ranges of observed widths of singular elements are reported in Table 1. The median of observed values was used to evaluate an order of Zn and Pb surfaces involved with tightness elements. On this catchment zinc tightness materials represent less then 10% of the total zinc surface. But tightness elements are determinant for the lead surface estimation.

		Ridge against wall	Valley	Chimney penetration	Roof windows tightness elements	Total
Length (m)		320	169	32	91	611
DTU width	Zn	0.2 ± 0.05	0.19 ± 0.03	0.2 ± 0.01		
	Pb	**0.05**± 0.01	0	**0.05**± 0.01		
Field survey: width$^{(1)}$ (probable material)		0.01-**0.1**-0.2 (Zn)	0.08-**0.1**-0.14 (Zn)	0-**0.12**-0.32 (Zn)	0.18-**0.2**-0.24 (Pb or prepainted metal)	
Surface evaluation (m^2)	Zn	32	16.9	3.5	0	52.4
	Pb	0 to 16	0	0 to 1.6	0 to 18.1	0 to 35.7

Table 1 : evaluation of singular roofing element length, typical width, involved metal and estimation of involved metal surface ((1): 1rst quartile – median – last quartile, bold = width considered for surface calculations)

2.2.3 Runoff sampling

Rain events were sampled at 4 levels from the atmosphere to the catchment outlet. Bulk atmospheric deposition (dry and wet) was sampled from a 1 m² stainless steel collector located on the highest roof at almost 400 m from the site. The sampling period included the studied rain event and the preceding dry weather period. Runoff from the building catchment, the road catchment and the global residential catchment was sampled by automatic samplers to obtain volume averaged concentrations over the rain event. Runoff volumes were measured in the separate sewer, at the residential catchment outlet, with a Sigma 950 flow-meter (height measured by bubble pipe and velocity by Doppler Effect). Rain depth was given by a rain gauge situated on the same building as the atmospheric deposition collector.

This field work was lead from 07/04/08 to 04/06/08. During this 2 months period, 15 rain sequences (i.e. periods lasting from the end of the previous rain event to the end of the considered rain event) can be delimited, out of which 7 have been sampled. The characteristics of these rain sequences, in terms of total duration of the sequence (rain event + previous dry weather period) and rain depth, as well as the identification of the samples collected are given in Table 2.

Rain sequence n°	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
T (days)	6.4	5.4	1.9	3.3	5.5	1.4	13.4	0.5	1.2	1.8	7.6	0.6	1.4	5.1	2.0
H (mm)	9.4	7.8	6	1.8	11	1.6	7.2	1.4	20.4	36	7	2.8	20.4	4.2	6.8
Atmosphere	✓		✓						✓		✓		✓	✓	✓
Road catchment	✓		✓						✓		✓		✓	✓	✓
Build. catchment									✓		✓		✓	✓	✓
Resid. catchment	✓		✓								✓		✓	✓	

Table 2 : characteristics of the considered rain sequences and identification of the collected samples

2.2.4 Zn and Pb loads calculation at catchment scale

Experimental data from the building catchment was used to validate the Zn runoff models established on test beds. It was considered that Zn loads at the exit of this catchment only originated from atmospheric fallout and from zinc roofing runoff. The mass of zinc attributed to zinc roofing for each sampled rain event was calculated as:

$$M_{roof}1 = (C_{build} - C_{atm})(S_{roof} R_{roof} + S_{garden} R_{garden})H$$

with: C_{build} the Zn concentration in the event mean sample collected from the building catchment,
C_{atm} the concentration of bulk atmospheric fallout (note that here $C_{atm} << C_{build}$),
S_{roof} the surface of building,
S_{garden} the surface of garden,
R_{roof} the runoff coefficient of building surfaces,
R_{garden} the runoff coefficient of garden surfaces,
H the rain depth.

The same approach was applied at the scale of the global residential catchment, for both zinc and lead. The mass of Zn and Pb produced by the residential catchment during a storm period has been calculated as:

$$M_{storm} = (C_{storm} V_{storm})$$

with : C_{storm} the Zn or Pb concentration in the event mean sample collected from the separate sewer at the outlet of the residential catchment,
V_{storm} the volume of runoff measured at the same point.

The mass of Zn or Pb originating from atmospheric fallout on gardens and buildings is estimated as:

$$M_{atm} = C_{atm}(S_{roof} R_{roof} + S_{garden} R_{garden})H \ ,$$

and the mass attributable to road runoff is given by $M_{road} = C_{road}(S_{road} R_{road})H$.

The mass of Zn or Pb attributed respectively to the runoff from zinc roofs and the runoff from lead tightness elements is obtained by difference: $M_{roof} = (M_{storm} - M_{atm} - M_{road})$.

This last mass will be compared to the results given by Zn and Pb runoff models established on the test beds, when applied to the total metal roofing elements of the considered catchment.

3 RESULTS

3.1 Zn and Pb runoff at test bed scale

3.1.1 Measurements

Zinc runoff from new zinc roofing material and lead runoff from lead tightness material, calculated at an annual scale and per square meter of projected material area from test beds reached respectively 3.3 – 3.8 $g.m^{-2}.yr^{-1}$ for zinc and 7.2 – 7.6 $g.m^{-2}yr^{-1}$ for lead (Robert-Sainte *et al.*, 2009). For zinc, these values are consistent with those measured in Stockholm, under similar atmospheric conditions (Odnevall Wallinder *et al.*, 1998), when reported to the projected area and not to the material area. Indeed, previous research (Odnevall Wallinder *et al.*, 2000) showed that zinc runoff rate per m^2 of material area varies with the inclination of the material. This variation becomes negligible when considering projected areas. Literature data on lead runoff rates are scarce and fragmented: Schultze-Rettmer (1995) reported annual Pb runoff rates lying between 1 and 4 g.m^{-2}yr^{-1}, as calculated from a theoretical corrosion rate and Matthes *et al.* (2002) reported values between 2.9 and 4.1 g.m^{-2}yr^{-1}. Runoff rates evaluated in this study are higher in both cases.

Figure 3 shows the evolution of Zn and Pb concentrations in the runoff of the test beds, over the 13 exposure periods (covering 14 month). After a phase of rapid decrease in concentrations over the first 3 exposure periods, Pb runoff tends to a relatively stable Pb concentration. This phenomenon has already been noted by Matthes *et al.* (2002). Zinc runoff, on the contrary to what was suggested by He (2002), does not show any temporal trend on our test beds. Fluctuations in Zn concentrations could be mainly linked to rain depth and duration of exposure period (Robert-Sainte *et al.*, 2008).

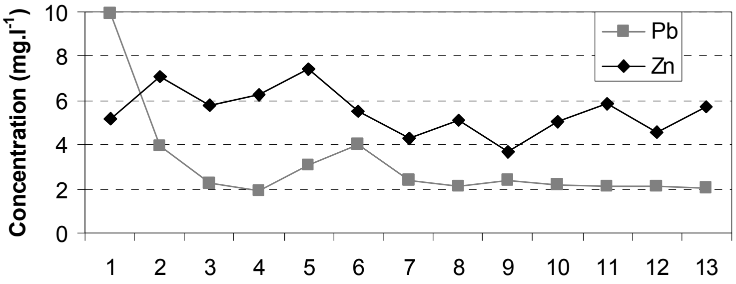

Figure 3: Evolution on Zn and Pb concentrations over the 14 months exposure of test beds

3.1.2 Models

Based on these observations, Zn or Pb runoff loads *Mi (g.m^{-2})* were tentatively modelled as a function of the duration T_i *(yr)* and the rain depth H_i *(mm)* of each sampling period *i*.

Three models were tested:

Model A: $M_i = K_1 H_i$, constant concentration model.

Model B: $M_i = \left(K_2 + K_3 \frac{T_i}{H_i} \right) H_i$, the concentration is considered to be a function of the T/H ratio, where T characterises the accumulation of corrosion products during the exposure period and H characterises the wash-off processes.

Model C: combines a linear accumulation model and an exponential wash-off model. It has been adapted from an accumulation / wash off model initially developed by Sartor *et al.* (1972) for street runoff. One of the main differences to model B is that it takes into account the mass of available corrosion products that remains on the material surface at the end of the previous sampling period.

$$M_i = M_{stock_i}\left(1 - \exp^{-K_4 H_i^{\alpha}}\right) \quad \text{and} \quad M_{stock_i} = K_5 T_i + (M_{stock_{i-1}} - M_{i-1})$$

Model A and B were used for Pb runoff and calibrated on sampling periods 7 to 13 of the lead test bed. Model B and C were used for Zn runoff and calibrated on the 13 sampling periods of the zinc test bed. Parameters values for the different models are given in Table 3. The comparison between measured and simulated loads for both metals is given in Figure 4 (Robert-Sainte, 2009).

	Model A	Model B	Model C
Zn runoff	∅	K2=3,2.10^{-3} K3=1,20	K4=0.032 α=0.65 K5=8,66.10^{-3} Mo=0.7
Pb runoff	K1 = 10,5.10^{-3}	K2=12,4.10^{-3} K3=-1,35	∅

Table 3 : calibrated model parameters values

Concerning Zn, it appears that the 2 models tested reproduce the general trend of runoff values from one period to another. Anyway, it is clear that Model C gives more precise results with slighter shifts observed around the experimental values. Thus, to model Zn runoff for successive exposure periods, it is important to take into account exposure duration, corresponding rainfall value and a parameter considering previous exposure period.

Concerning Pb, models A and B permit to obtain correct results, although some values obtained may differ from experimental points (period 8). For this element, Model C does not give satisfactory results, probably due to different processes of wash off.

In both cases, it appears that it is possible to properly model emissions from materials at the test bed scale and for different successive exposure periods.

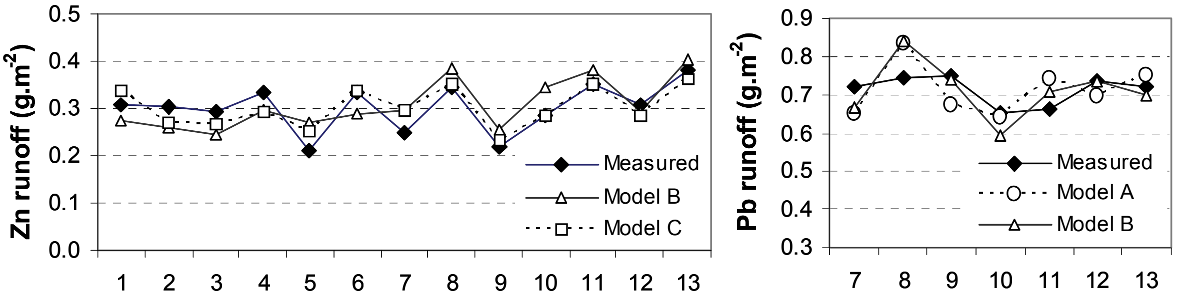

Figure 4: comparison of measured and simulated Zn and Pb runoff over the 13 exposure periods of the test beds

3.2 Zn and Pb runoff at catchment scale

3.2.1 Measured concentrations

The range of Zn and Pb concentrations measured on the different sampling sites are given in Table 4. For Zn much higher concentrations are measured in the building runoff, which is explained by the important fraction of zinc roofing on this building. The Zn concentrations measured on the building are in accordance to what is found in the literature for zinc roofing. More surprising is the fact that Zn concentration measured in atmospheric fallout is systematically superior to road runoff concentration. Zn concentrations measured on our atmospheric collector appear overestimated compared to other measurements in Paris conurbation (Azimi *et al.*, 2005). A blank test proved that this could not be explained by a contamination from the material of the collector itself (stainless steel). Yet, a local atmospheric contamination is suspected, induced by the galvanised furniture on the building where the collector is implemented, and the presence of a large zinc roof very closed to the collector building. Thus, in the further work, we will not use the measured atmospheric fallout for Zn but use an average Zn concentration of 60 µg/l which is the median value measured by Robert-Sainte (2009) on a nearby site.
Pb concentrations are in the range of values found in the literature for the different types of runoff (Davis et al., 2001; Gnecco et al., 2005). It is noticeable however that the highest concentrations are measured on the building runoff. This suggests that there is another source of lead than atmospheric fallout on this building. Even if we have not identified them, there might be some tightness elements on his building.

	Atmospheric fallout	Road runoff	Building runoff	Residential catchment stormwater
Zn (µg.l^{-1})	68 -196 - 285	47 - 83 - 360	2045 - 2988 - 3337	457 - 596 - 850
Pb (µg.l^{-1})	2.1 - 2.6 - 7.9	4.8 - 14.2 - 36.2	11.5 - 19.9 - 52.9	7.1 - 13.3 - 15.2

Table 4: Zn and Pb concentrations in the different types of runoff samples (minimum - median - maximum)

3.2.2 ***Relative contributions of different sources of Zn and Pb on the residential catchment***

Erreur ! Source du renvoi introuvable. gives the relative contribution of atmospheric fallout on garden and buildings, road runoff and other sources (mainly attributed to the corrosion of metallic roofing and tightness elements) to the total Zn and Pb masses measured at the residential catchment outlet.
Both atmospheric fallout and road runoff appear to be a minor source of Zn on this catchment, with 82% of the zinc attributed to the zinc runoff from roofing materials. For Pb, the contributions of atmospheric fallout (16%) and road runoff (30%) are more significant than for Zn. Yet most part of the lead runoff (54%) originates from another source, which we suppose to be the runoff from lead tightness materials.

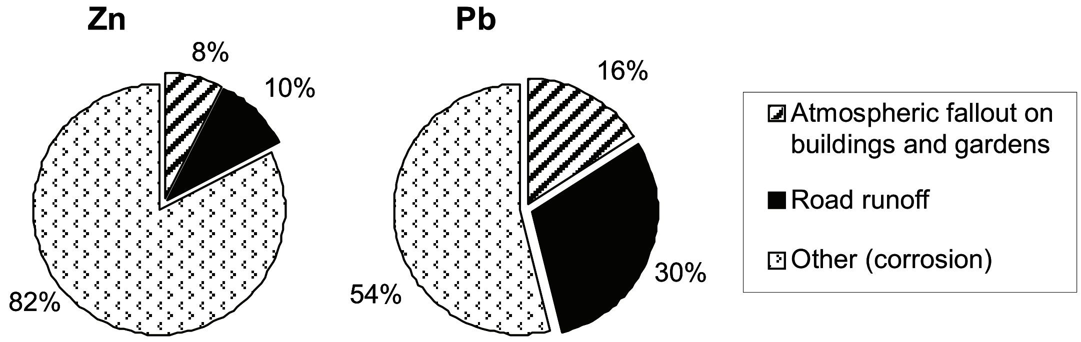

Figure 5: relative contribution of different sources to the Zn and Pb loads measured at the outlet of the residential catchment

3.2.3 *Validation of the Zn runoff models at roof scale*

Model B and C where applied to the 555 m^2 of zinc roofing of the experimental building catchment, for the 15 considered rain periods (Figure 6), and compared to values obtained experimentally for 5 rain events. The parameter values calibrated on the test bed where used, with exception to the initial mass Mo of model C, which has to be recalibrated.

Both models reproduce almost the same dynamic of Zn runoff evolution over the 15 rain periods even so model C is systematically superior to model B. The modelled Zn loads are in accordance with the values obtained experimentally. The total Zn mass estimated from the measurements over the 5 studied rain events is of 164 g, model B gives 136.5 g (-17%) and model C gives 186 g (+13%). This result is very promising if we consider that the models are here applied for a range of H and T values (H= 1.4 to 20.4 mm and T=0.6 to 13.4 days) that is very different from the ones used for model calibration on test beds (H= 34 to 80 mm and T=15 to 52 days).

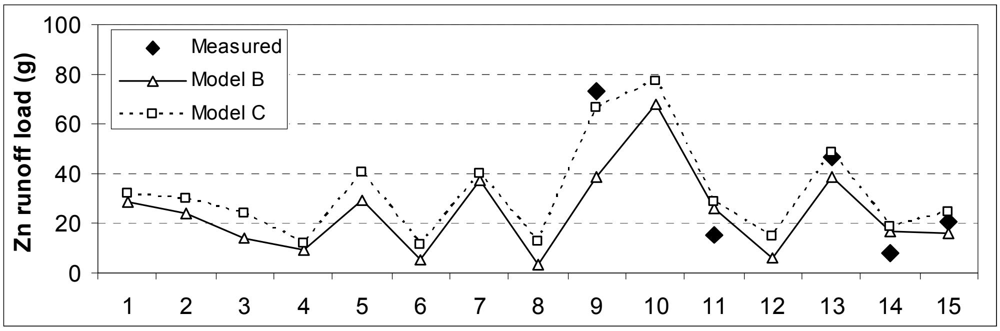

Figure 6: measured and modelled zinc runoff from the zinc roofing of the building catchment

3.2.4 *Evaluation of Zn and Pb runoff models at residential catchment scale*

Figure 7 compares the Zn masses attributed to the runoff from zinc surfaces at the residential catchment scale, either estimated from the measurements or modelled with the two zinc runoff models B and C. With exception of period 14 for which the simulated values a superior of a factor 3, the modelled values are in the same range as the estimation based on measurements (-18% to +63%). The total Zn mass estimated from the measurements over the 5 considered rain events is of 124 g, model B gives 145 g (+17%) and model C gives 173 g (+40%). The two models, and especially model C, tend to overestimate zinc realises at catchment scale. The difference with model B is however in the range of uncertainties linked to experimental and calculation methods.

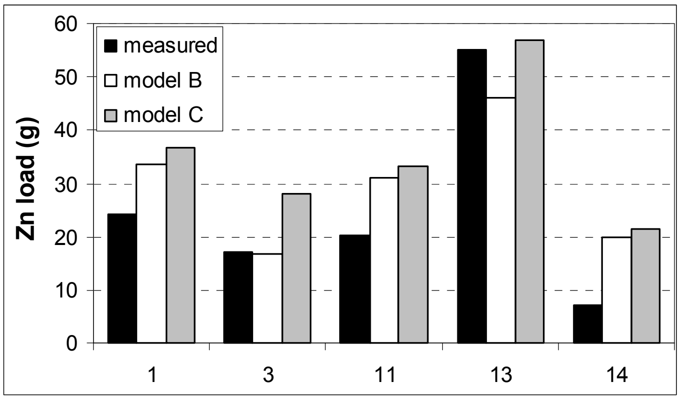

Figure 7: measured and modelled Zn runoff from zinc roofs of the residential catchment

For lead, the uncertainty on the involved lead material surfaces is too important for a real evaluation of the lead runoff model. Based on the evaluation from the runoff measurements on 5 rain periods, the quantity of lead that would originate from the corrosion of lead roofing elements is of 2 g. Applying model A, this would correspond to the runoff of 4 m^2 of lead material, which is in the possible range of lead surfaces given in Table 1. Thus most part of the lead runoff load on this residential catchment would originate from a very small surface of lead material (0.05% of catchment surface).

4 CONCLUSION

This work shows that the quantification of metallic emissions (Zn and Pb) from materials is possible, using different models taking into account the main characteristics of exposure conditions (rainfall value H, and exposure duration T).

The analysis of relative contributions of different sources of Zn and Pb in runoff has led to the conclusion that roofing materials constitute the major source of emission of these metallic species.

For Zn, models of quantification developed at the test-bed scale and applied to different spatial and temporal scales permit to obtain satisfactory results both at the roof scale and at the catchment scale. Thus, the transposition of models to others spatial scale is a success and is very promising for the quantification of Zn emission from roofing materials at larger spatial scales – using air photographs.

For Pb, results obtained are less promising, due to problems in the evaluation of the surface of materials implemented. Indeed, it appears to be difficult both to quantify the surfaces of lead involved (because of their small size), and to clearly identify the material used (in link with the recent appearance on the market of new materials used instead of lead).

In all cases, it remains important to improve the results of the quantification of these surfaces. To reach this goal, a work has to be done concerning the use of materials (especially concerning new materials), and the estimation of the widths of the singular elements (especially for the tightness elements implemented for roof windows). One possibility could be the improvement of the statistic analysis of widths for these kinds of elements through a larger field survey.

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