**Cite this ariticle as:**

*Gnecco, I., Palla, A. and Sansalone J.J. (2019). Partitioning of zinc, copper and lead in urban drainage from paved source area catchments. Journal of Hydrology, 578, 124128. DOI: 10.1016/j.jhydrol.2019.124128*

# Partitioning of zinc, copper and lead in urban drainage from paved source area catchments

Gnecco I.[a*], Palla A.[a] and Sansalone J.J.[b]

*a. Department of Civil, Chemical and Environmental Engineering, University of Genova, Via Montallegro 1, 16145 Genoa, Italy.*

*b. University of Florida, Engr. School of Sustainable Infrastructure and Environment, Gainesville, FL, 32611, USA*

*E-mail addresses: anna.palla@unige.it; ilaria.gnecco@unige.it; jsansal@ufl.edu*

*[*]Corresponding author: Tel.: ++39-010-353-2485; Fax: ++39-010-353-2481.*

## 1 Introduction

Anthropogenic activities in paved source areas such as modern transportation whether from vehicular, industrial or air traffic can be a significant source of constituents including particulate matter (PM) pathogens, nutrients and metals that are mobilized and transported during urban drainage wet weather events (Lee and Bang, 2000; Zhao et al., 2010). As part of antecedent dry intervals these constituents have a temporal build-up profile within transportation systems and appurtenances (Huber et al., 2016; Wijesiri et al., 2016). Metals transported in runoff partition between PM and the solution phase. For paved source areas with conditions of low rainfall pH at low pavement residence times in terms of minutes, metal partitioning can be predominately dissolved at the time of interception by a source area control strategy (Sansalone and Buchberger, 1997). Previous research has examined the characteristics of metals in runoff from paved source areas, including total (dissolved plus particulate-bound) concentration profiles, dissolved fractions and speciation (Dean et al., 2005; Huber et al., 2016). Separately, PM, as the primary substrate and vehicle for metal partitioning has been characterized in terms of both transported PM in runoff and dry deposition metal concentration (Djukic et al., 2016; Lau and Stenstrom, 2005; Sansalone and Ying, 2008). The build-up, wash-off, partitioning and equilibrium distribution across the PM gradation has been indexed through the metric of a particle size distribution (PSD) (Sansalone and Tribouillard, 1999; Sansalone et al., 2010). Subsequent research demonstrated that the PSD and even more simply, PM dry mass, are reasonable surrogates for more fundamental measurements such as specific surface area (SSA), surface area (SA) and charge of PM (Sansalone and Cristina, 2004).

Partitioning of metals, between dissolved and particulate phases of runoff, is complex. While partitioning can be described on an event basis, partitioning is likely to vary significantly between events, paved source areas and within event. The variable nature of partitioning is due to variable PM concentrations, PSD, pH, alkalinity, residence time, hydrologic phenomena and urban surface conditions. Partitioning is typically defined as an interaction between the dissolved metal fraction, and the particulate-bound fraction; irrespective of the colloidal fraction. These interactions can be forward (nominally sorption) or reverse reactions (desorption) that occur during the partitioning reaction as shown conceptually in Figure 1. This is the conceptual model of partitioning in this study. The partitioning includes specific mass transfer mechanisms such as ion exchange, surface complexation and precipitation. Chemical species in complex environmental systems eventually attain different equilibrium concentrations in the phases comprising these systems. The concentrations in theory should be quantifiable as PM phase to aqueous phase and partitioning is a reasonable estimate of the distribution of a solute between two phases. Furthermore, during the wash-off process the equilibrium partitioning has also been shown to be a function of hydrologic response (indexed by pavement residence time for rainfall-runoff), pavement type as well as rainfall-runoff pH and redox (Huber et al., 2016; Turer et al., 2001).

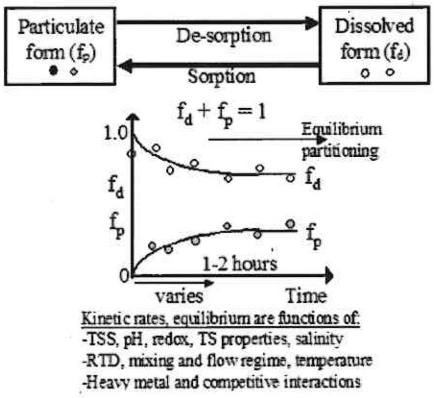



Figure 1. Two-partition model of partitioning between dissolved and particulate metals

While partitioning in this study is examined through a two-partition model, there is a very hetero-disperse PSD in source area runoff that varies from colloidal (< 1 μm) to suspended (< 25 μm, as total suspended solids, TSS) to settleable (< 75 μm) to sediment PM (< 4750 μm nominally) with PM larger than sediment classified as gross solids. For urban paved source areas, on a gravimetric basis, the sediment fraction generally dominates all other PM fractions, the colloidal fraction is less than several percent and the suspended fraction is in the range of 20 to 30% of the total (e.g. Kuang et al., 2007). However, on a number basis the fine suspended fraction (< 10 μm) dominates all other PM fractions. While specific surface area ($m^2/g$) of PM increases with decreasing PM diameter, the total surface area ($m^2$) is dominated by the sediment fraction because this fraction gravimetrically dominates PM transported in paved source areas.

Under conditions where a number of metals are present in runoff (common analytes are Cu, Cd, Pb and Zn), the competitive order of partitioning (sorption) can be compared to bonding preferences as predicted using covalent theory, electrostatics, or hydrolysis followed by sorption. According to covalent theory for divalent metal ions, the bonding preference is Cu > Pb > Cd > Zn (McBride, 1994). However, based on electrostatics, bonding preference for divalent metals is Cu > Zn > Cd > Pb (McBride, 1994). Finally, based on the tendency to hydrolyse, the bonding preference of selected metal ions is Pb > Cu > Zn > Cd (McBride, 1994).

Knowledge of the partitioning and the relative fractions of dissolved and particulate-bound mass are of fundamental importance for in-situ treatments where residence times on the source area surface in the presence of entrained PM are on the order of minutes to less than an hour. In these urban paved source areas there is competitive partitioning and the distribution of metal mass as a function of particle size across the PSD. Despite the complexity of partitioning, this study takes a two-partition approach, lumping the metal distribution across the PSD as a single particle-bound partition, irrespective of distribution across the PSD.

Beyond transport of metals phases and the distribution across the PSD for the PM-bound fraction of metals, knowledge of partitioning is needed at the point of treatment. As an example, small in-situ unit operations such as adsorptive-filter exfiltration (Teng and Sansalone, 2004; Sansalone and Teng, 2004), engineered permeable pavement systems as adsorptive-filters (Kuang et al., 2007) and large-scale unit operations such as retention/detention systems are primarily focused on the sedimentation of PM thus the abatement of PM-bound constituents (Fletcher et al., 2013; Koch et al., 2014). Knowledge of metal partitioning, in particular at the point of treatment or discharge represents needed regulatory and design inputs in stormwater management.

This study has a number of objectives related to partitioning and transport of metals from paved surfaces of four differing urban land uses: three transportation facilities (highway, airport, port) and the heterogeneous paved areas including roads, parking lots and residential buildings .The first objective is to compare data collected from catchments located within urban paved source areas in order to characterize the pollutant load associated with runoff as a function of the specific anthropogenic activity/land use. For this purpose, the site characteristics as well as the monitoring programme (i.e. monitoring period, sampling method, etc.) are considered. The second objective is to compare the equilibrium concentrations of metals and PM using a non-parametric analysis on sample bases for a series of six paved surface area catchments within transportation facilities. In particular, two American highway sites, and four Italian sites located in the Liguria Region (two port terminal sites and two aviation sites) are examined. Finally, the third objective is to analyse the transport of metal phases on an event basis thus relating hydrology and PM mass delivery with metal partitioning. For this purpose, two among the six investigated sites are selected as representative catchments in terms of catchment size and PM concentration.

# 2 Material and methods

## 2.1 Sites description

### *2.1.1 Urban paved source areas*

Nineteen source area catchments are examined in order to characterize the pollutant load associated with storm runoff in different urban land-use areas, focusing specifically on the delivery of PM and metals. The selected paved source area catchments belong to four land-use categories: three transportation facilities (highway, airport, port) characterized by intense anthropogenic activities and the heterogeneous paved areas (including roads, parking lots, residential buildings, etc.).

In order to consistently compare water chemistry data collected at different locations, the specific catchment characteristics (in terms of drainage area, land-use category, drainage system, etc.) and the monitoring campaign features (such as monitoring equipment, sampling procedure and protocol, monitoring site location, etc.) have been considered.

Table 1 illustrates the nineteen selected source area catchments, in particular it provides a description of each land-use paved source area catchment together with the sampling and the analytical methodology employed for the measurement of PM and total metals concentrations associated with rainfall-runoff events. In detailed, the following specific information are reported:

- The site description in terms of the land-use category, the drainage area size, the pavement type, the percentage of imperviousness, the slope of the surface area and the Average Daily Traffic (ADT);
- The precipitation regime as annual rainfall depth;

- The monitoring programme characteristics by means of the whole monitoring period, the number of rainfall events sampled, the sampling procedure and the chemical analysis protocol.

It has to be noticed that nine over nineteen sites refer to experimental studies documented in the literature (they are labelled in Table 1 with the following reference numbers: 3, 4, 7, 8, 10, 11, and 12). Such experimental results allow to provide a more comprehensive characterization of the investigated urban paved source areas thus including different site characteristics as well as precipitation regime. Therefore, the information presented in Table 1 are organized in order to supporting the discussion on the pollution load associated with runoff resulting from different sites and land-uses.

### *2.1.2 Transportation facilities*

In order to deeply investigate the water chemistry data in pavement runoff and examine the delivery behaviour of PM and metal (including the partitioning process), a limited number of paved source area catchments are picked out among the previous investigated four urban paved land-use categories. The selection criterion is based on the relevance of metal load being a major concern due to their impact on receiving waters arising from the potential to cause acute or chronic toxic effects in the aquatic environment. Based on the above considerations, six source area catchments (two American and four Italian sites) belonging to transportation facilities are considered within the following categories: highway, parking lot (landside) and apron terminal (airside) within aviation site, commercial and tourism terminals within port area.

In the below section a more detailed description of the six sites located within transportation facilities is provided.

Two American experimental catchments are selected as representative sites of the highway land-use (labelled in the Table 1 with the reference numbers 1 and 2 respectively). The first site is located in urban Cincinnati (Ohio), along an asphalt paved section of Interstate 75, hereinafter named as highway I-75. This major north-south interstate carries an ADT load of 135,000 passenger vehicles and 15,000 commercial vehicles; the monitored catchment drainage area is 300 $m^2$ (15 m long by 20 m wide). The second highway-land-use site is located along an elevated section of Portland cement concrete (PCC) paved Interstate 10 in urban Baton Rouge (Louisiana), hereinafter named as highway I-10. The monitored catchment with a drainage area of 544 $m^2$ is characterized by an ADT equal to 70,400 vehicles. A full description of both Cincinnati and Baton Rouge sites, including sampling and analysis methodology can be found elsewhere (Sansalone and Buchberger, 1997; Sansalone et al., 1998; Cristina and Sansalone, 2003; Sansalone et al., 2005).

Regarding aviation land-use, two distinctly different land uses, respectively airside and landside, from the same commercial aviation facility in Genoa (Italy) are examined (labelled in the Table 1 with the reference number 5). The apron terminal catchment site is located within the boarding area of the airport, hereinafter named as airside–airport. Specifically, this study area is a concrete pavement apron employed for boarding and refuelling operations. The monitored catchment drainage area is about one hectare. The second aviation site is located within a parking area connected to the airport terminal, hereinafter named as landside–airport. The monitored area is an asphalt pavement with partial zones of concrete pavement for an extension of about 1.4 ha. Detailed description of the monitoring site and equipment can be found elsewhere (Gnecco et al., 2008).

As for the port terminal land-use, two experimental sites instrumented within the industrial ports of Liguria Region (Italy), on the Tyrrhenian Sea, are selected to investigate storm runoff pollutants as a function of different port activities (labelled in the Table 1 with the reference numbers 13 and 14). In particular, the container terminal site is located within the Port of La Spezia. The site is used for container handling and storage and has a total watershed area of ten hectares, hereinafter named as container–port. The monitored area is an asphalt surface of about one hectare suitably selected within the terminal. The tourism terminal site is located within the car ferries terminal of the Port of Genoa (Italy) and includes the access road for private and commercial vehicles to/from the car ferries embarkation point and the parking lot for vehicles and trucks, hereinafter named as car ferry–port. The monitored area is a concrete-paved surface with an area of about 5 ha. A full description of the port terminal catchment sites is provided elsewhere (Gnecco et al., 2006; Gnecco et al., 2007a).

### 2.2 Rational and basis for data analysis

The monitoring campaigns carried out to characterize runoff, point out the significant temporal variation of the pollutant load across the wash-off process of a single rainfall-runoff event: the concentration values may vary even by several orders of magnitude within the same pollutograph (e.g. Gnecco and Lanza, 2013). Therefore, a single index, the Event Mean Concentration (EMC), is generally used to evaluate the pollutant load associated with each rainfall-runoff event, thus it allows comparing pollutant concentration values from different storm events and sites. The EMC is a flow averaged concentration defined as the total pollutant load (mass) divided by the total runoff volume (Sansalone and Buchberger, 1997).

Focusing on the six sites within transportation facilities, after the event-based analysis, water chemistry data are statistically examined on sample basis by using a non-parametric analysis in order to illustrate the variability of the pollutant load associated with storm runoff. Quality data are presented as box plots providing statistical results on a sample basis. The lower and upper boundary of each box indicate respectively the 25$^{th}$ and 75$^{th}$ percentiles, while the continuous line and the dash line within the box mark respectively the median and the mean values. Whiskers above and below each box indicate the 90$^{th}$ and 10$^{th}$ percentiles; individual crosses/circles showed in the plot represent the 5$^{th}$ and 95$^{th}$ percentiles.

Similarly, the partitioning indices investigated in the present study are examined both on sample and event basis.

## 2.3 Description of partitioning parameters

The partitioning model is based on Glenn (2002) who defined two partitions, for a given constituent, in the dissolved and particulate-bound fractions. The dissolved fraction is defined as $C_d$ in [M/L$^3$], where M indicates the mass of constituent and L$^3$ is the volume of aqueous solution (or non-aqueous solution). The particulate form is defined as $C_p$ in [M/L$^3$], where M indicates the mass of constituent and L$^3$ is the volume of PM plus water (the bulk volume). Therefore, the form $C_p$ is the mass of the metal "sorbed" to PM relative to the volume of water (Thomann and Mueller, 1987). For a given concentration of PM, $C_p$ can also be expressed as $C_p$

$= C_s \cdot m$ where m is the PM concentration in [M/L$^3$], L$^3$ is the bulk aqueous volume with PM and $C_s$ is the metal concentration expresses on a dry weight basis [M/M] (i.e. mass of metal on or in the PM/mass of dry PM). Units for $C_s$ are typically μg/g; noting the μg/g is equivalent to a part per million.

To assess the dominant phase of each metal, the metal mass indices, $f_d$ and $f_p$, are calculated through the following expressions:

$$f_d = \frac{C_d}{C_d + C_p} = \frac{M_d}{M_d + M_p} \quad (1)$$

$$f_p = \frac{C_p}{C_d + C_p} = \frac{M_p}{M_d + M_p} \quad (2)$$

where $M_d$ and $M_p$ are respectively the dissolved and the particulate-bound masses. Therefore, $f_d$ and $f_p$ are dimensionless indices and their sum is equal to 1; $f_d$ value greater than 0.5 ($f_p$ < 0.5) corresponds to a higher affinity for the dissolved fraction of metals.

Assuming linear kinetics (Thomann and Mueller, 1987), the equilibrium partition coefficient, $K_d$, is defined as followed:

$$K_d = \frac{C_s}{C_d} = \frac{C_p/m}{C_d} \quad (3)$$

$K_d$ is usually expressed as litre per kilogram (l/kg). Figure 2 shows a representation of the partitioning balancing the mechanism of sorption of the metal to PM and desorption from the PM back into the dissolved phase where $K_d$ represents the slope.

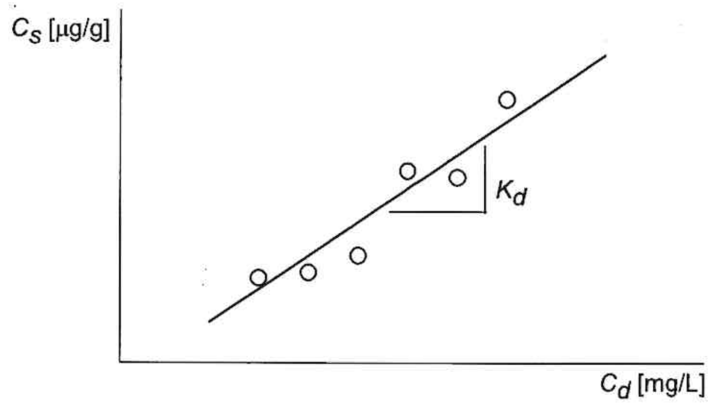



Figure 2. Definition of $K_d$ and conceptual relation of PM and dissolved metals.

# 3 Results and discussion

## 3.1 Urban land-use characterization

Table 2 illustrates water chemistry data monitored in the nineteen paved source area catchments with respect to the four different land-use categories. In particular, Table 2 focuses on PM (measured as total suspended solids, and herein designated as TSS) and three metals (Zinc, Copper and Lead) as constituents typically produced by vehicular traffic primarily and by other related anthropogenic activities (Dean et al., 2005; Huber at al., 2016). The concentration values are reported as EMC values thus providing a measure of the constituent load on rainfall-runoff event basis; for each parameter, the mean, median and standard deviation values of the EMC observed across the whole monitoring campaign are illustrated. Metals are illustrated referring to the total concentration value (both dissolved and particulate-bound fractions).

As for the highway land-use, all sites reveal similar TSS concentration values, except for Denver site whose concentration values exceed, at least, twice the values measured at the similar land-use sites. It has to be noticed that at the latter site the annual rainfall depth is at least one third of the other American sites. Lead concentration values are consistent with results reported in the literature for highway runoff. Indeed, Kayhanian (2012) observed that the average total lead EMC in runoff generated from 34 California highways is about 0.50 mg/l. Furthermore, Kayhanian (2012) pointed out that the concentration of lead in highway runoff reveals a significant decrease due to the phase-out leaded gasoline started in the USA in the mid-1980s. Consistently, only Denver and Nashville sites show significant concentration values of lead since the monitoring campaign were carried out in the 1970s (Discroll et al., 1990), while the concentration values observed at Cincinnati and Baton Rouge sites are below 0.1 mg/l. Among the investigated metals, zinc reveals the most relevant concentration values as reported by Preciado and Li (2005) that identified zinc as a metal of future concern. Significantly high zinc loads are recorded at both Cincinnati and Denver sites, characterized by a traffic count of 150,000 vehicles/day, even if a linear correlation between pollutant load and the corresponding ADT load does not emerge due to the numerous site and hydrologic characteristics affecting the pollutant mass delivery behaviour. Huber et al. (2016) highlighted that concentrations of metals in urban road runoff can be higher than most values observed in highway runoff because of braking and acceleration activities at traffic signals.

By comparing the port terminal land-use sites with the highway ones, results show a similar TSS mass delivery; on the contrary, metals are predominant in port areas, in particular, the most significant concentration values are measured at the container terminal site, due to both the heavy traffic and the storage of metal shipping containers.

Looking at the airport land-use sites, TSS concentration values are limited when compared to the other land-use sites because of lower traffic for airport traffic compared to highways; while metal concentrations are comparable to the highway sites, thus confirming the relevance of transportation facilities in altering the runoff quality.

Finally, the urban heterogeneous land-use sites that include both small catchments characterized by single paved area (such as roads or parking lot) and large catchments including both pervious and paved areas, show a wide variability in loads for metals and PM pointing out the difficulty in characterizing the constituent load associated with runoff from non-point sources in urban heterogeneous catchments.

In order to further investigate the delivery behaviour mainly focusing on metal partitioning, a limited selection of paved source area catchments is considered to analyse water quality data on sample basis. Therefore, in the following sections, the analysis of water quality data as well as the investigation on the metal partitioning process concern a series of six transportation facilities sites: two American highway sites, and four Italian sites located in the Liguria Region (two port terminal sites and two aviation sites).

### 3.2 Water chemistry data

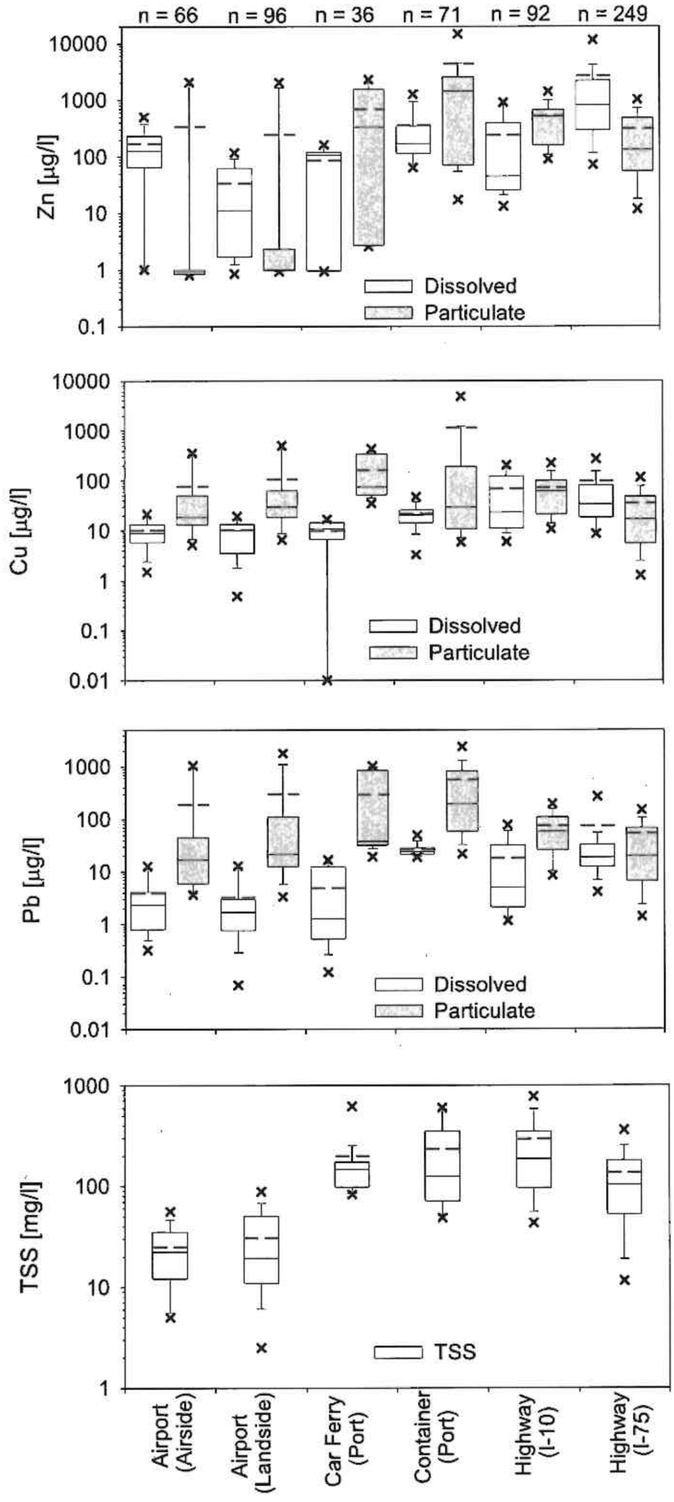
In Figures 3, non-parametric distribution of dissolved (white boxes) and particulate-bound (grey boxes) concentrations for zinc, copper and lead with respect to Italian (port and airport land-use sites) and American (highway land-use) paved source area catchments are illustrated; in addition, the last graph shows non-parametric distribution of TSS for each site.

As for PM, results show a large difference in terms of TSS load associated with runoff from airport sites with respect to the values measured at the port terminal and highway sites. In particular, both airport catchments show median TSS of 20 mg/l, while the median concentration values, observed at the other sites, range from 100 to 200 mg/l consistently with values reported in the literature: Charters et al. (2016) reported a mean value of 176 mg/l for TSS in urban asphalt road.

In spite of the wide range of TSS concentration values measured at the six paved source area catchments of concern, metals associated with storm runoff reveal significant concentration across the different sites. Such result points out that even if TSS can be assumed as a good marker of the general water quality conditions, TSS may be not sufficient as the sole index parameter to fully describe total loads including both dissolved and particulate phases, such as metals.

Among metals, copper shows comparable distribution and limited interquartile range across the different sites. In particular, referring to the median data, the dissolved fraction ranges between 10 and 20 μg/l; the particulate phase varies between 20 and 70 μg/l. Figure 3 clearly illustrates that, on sample basis, copper data has lower variability compared with lead and in particular zinc. In addition, a more balanced distribution between the aqueous and particulate phases of copper with respect to the other metals emerges. On the contrary, the aqueous phase of lead is significantly lower than the particulate one, except for Cincinnati highway (I-75) site (Sansalone and Buchberger, 1997; Dean et al., 2005). Furthermore, lead which is predominately particulate-bound (Sansalone and Cristina, 2004) can be indexed to the TSS delivery behaviour: the higher TSS load the higher concentration values of particulate lead are observed. Note that the median concentration values of the lead particulate fraction range from 20 μg/l observed at the airport sites to 200 μg/l measured at the container terminal site.

Finally, zinc reveals a wide range of concentration values for both the aqueous and particulate fractions across the monitored catchments as already observed in previous studies (Gnecco et al., 2005). Dissolved zinc shows median concentration values ranging between 10 and 800 μg/l, for the particulate-bound fraction, the median values vary across three orders of magnitude (from 1 μg/l to 1 mg/l). In addition, zinc shows a wider interquartile range (varying across several orders of magnitude at each site of concern) when compared with copper and lead, and such behaviour points out the zinc variability in terms of partitioning process, as illustrated in the following sections. Similarly, Huber et al. (2016) observed the high variability of zinc concentrations in traffic area runoff if compared with other heavy metals (particularly with copper).




355

356 Figure 3. Non-parametric distribution of dissolved and particulate-bound

357 concentrations for zinc (Zn), copper (Cu) and lead (Pb) with respect to the Italian

and American experimental sites (airside and landsite at the airport of Genova, Italy; car ferry, Port of Genova, Italy; container terminal, Port of La Spezia, Italy; highway I-75 Cincinnati, Ohio USA; highway I-10 Baton Rouge, Louisiana USA). Non-parametric distribution of the TSS for the different sites are illustrated in the bottom graph. Note that the n-value at the top of the figure refers to the number of samples collected at each site.

### 3.3 Metal partitioning

By examining the delivery behaviour of both aqueous and particulate fraction of metals, the role of metal partitioning as factor impacting the corresponding mass transport of each metal phase emerges. Therefore, to fully understand the transport of metals across the runoff hydrograph, metal partitioning between solution and PM needs to be examined.

Figure 4 illustrates the non-parametric distribution of the dissolved fraction index, $f_d$, for zinc, copper and lead on sample basis with respect to Italian and American experimental sites within transportation facilities.

At all catchment sites, copper and even more primarily lead reveal the greatest affinity for the particulate-bound fraction: $f_d$ for copper ranges between 0.12 and 0.4 on average and for lead the average is below 0.2. The exception occurs for the highway I-75 site that revels a dominant dissolved phase with respect to all investigated metals (Zn, Cu and Pb). It has to be noticed that such paved catchment is characterized by the smallest drainage area (equal to 300 $m^2$) therefore the rainfall-runoff process is extremely limited in time (as well as the residence time) and consequently the tendency toward the particulate fraction is reduced. In addition, Cincinnati is located in an industrial urban valley and rainfall and runoff pH values are highly acidic (Sansalone and Buchberger, 1997).

Zinc shows significantly different partitioning behaviour that may be partially depending on the specific site characteristics. The aviation sites (both airside and landside) that are characterized by limited TSS load show the marked predominance of aqueous zinc as confirmed by the median $f_d$ values larger than 0.9. On the other hands a wide interquartile range is observed for both aviation sites and mainly the container one characterized by a significant variation in concentration values between the rainfall-runoff events (see also Table 2).

Irrespective of the specific distribution of $f_d$ values observed at the six transportation facility sites, the same sequence of the average $f_d$ values (Zn > Cu > Pb) emerges thus showing the different affinity of each metal for the aqueous phase. Kayhanian (2012) highlighted that Pb exists predominately in particulate forms as largely documented in the literature and Huber at al. (2016) that examined a large datasets of heavy metal pollution in traffic area runoff pointed out that Pb is mostly in particulate phase while Cu and Zn exhibit an intermediate behaviour.

By comparing the differing land-use sites, the marked predominance of the particulate phase with respect to zinc, copper and lead, is recorded at the car ferry site. Looking at the TSS load observed on sample basis (see Figure 3), the car ferry site is characterised by high concentration values similarly to the ones observed for the other port and highway sites. However, differently from the other sites, this shows fairly consistent concentration values across the whole monitoring programme as confirmed by the limited interquartile range. In addition, the larger the catchment, the higher the residence time therefore the tendency toward the particulate fraction is enhanced due to the increasing contact time between metals and PM.

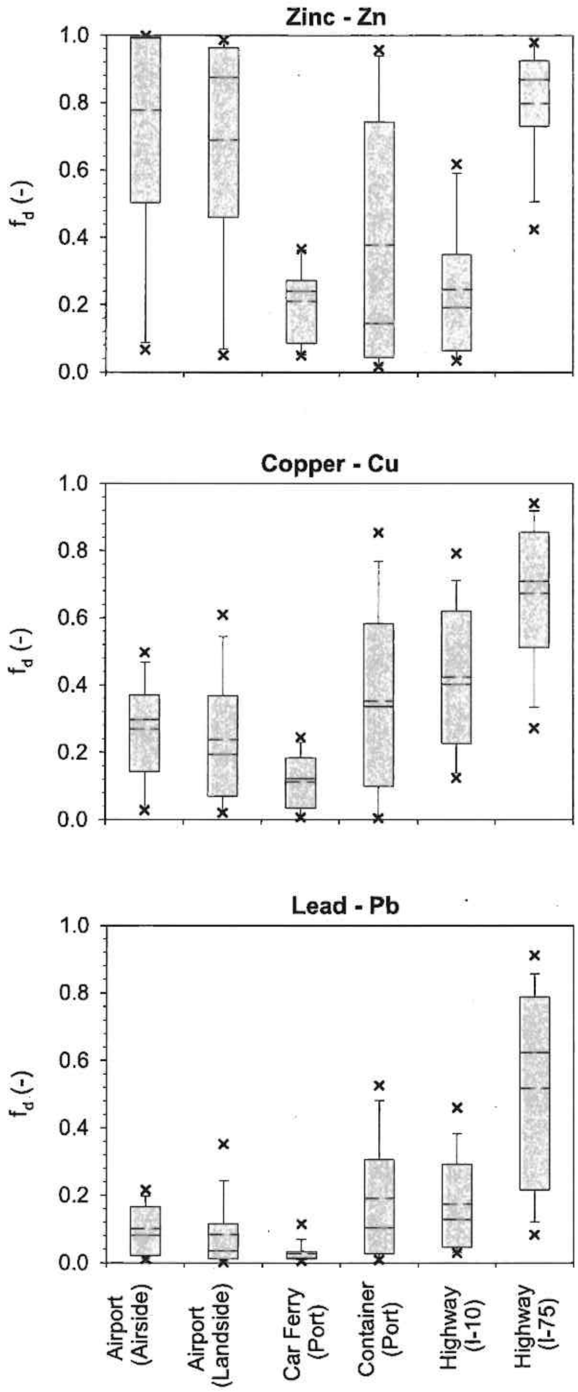


Figure 4. Non-parametric distribution of the dissolved fraction, $f_d$, for zinc (Zn), copper (Cu) and lead (Pb) with respect to the Italian and American experimental sites (airside and landsite at the airport of Genova, Italy; car ferry, Port of Genova, Italy; container terminal, Port of La Spezia, Italy; highway I-75 Cincinnati, Ohio USA; highway I-10 Baton Rouge, Louisiana USA).

In the following section the transport of metal phases is examined on an event basis and within each rainfall-runoff event in order to relate hydrology and PM mass delivery to metal partitioning. At this aim, the airside site within the Genoa Airport and the car ferry site within the Port of Genova have been selected as representative catchments. Both catchments are located in Genova (Italy) thus characterized by the same climatic condition and precipitation regime, on the other hand they differ in PM mass delivery (see Figure 3) and partitioning behaviour (see Figure 4).

In Tables 3 and 4 the dissolved fraction index, $f_d$, with respect to zinc, copper and lead (in terms of mean values and standard deviations) are summarized for each rainfall-runoff event monitored at the airside-airport and car ferry-port sites. In addition, the corresponding EMC values for TSS and pH are reported.

Partitioning indices analysed on event basis at the airside-airport and car ferry-port sites confirmed the partitioning behaviour observed on a sample basis: copper and largely lead reveal the greatest affinity for the particulate-bound fraction with mean $f_d$ values ranging from 0.11 to 0.26 for copper and from 0.03 to 0.12 for lead.

Zinc shows significantly different partitioning behaviour first depending on the specific site characteristics: the mean dissolved fraction index evaluated on event basis is respectively equal to 0.65 at the airside-airport site and 0.23 at the car ferry site. However, zinc shows a wide range of variation (as confirmed by the corresponding standard deviation) even across the different rainfall-runoff events at each catchment.

As previously observed, the airside-airport catchment is characterized by limited TSS concentration values, thus aqueous zinc generally dominates (see Table 3). However, due to the limited TSS mass delivery, ranging between 13 and 36 mg/l, the influence of pH in metal partitioning emerges. The strongly predominance of the dissolved fraction is observed in rainfall-runoff events when the mean pH values are below 7, while the increasing mean pH value above 7.5 determines $f_d$ lower than 0.5 (note that pH = - log[H+] thus pH variation equal to one corresponds to one order of magnitude in terms of proton concentration).

Looking at zinc data reported for the car ferry site (see Table 4), it can be observed that the dissolved fraction of zinc increases with decreasing TSS concentration thus confirming the influence of TSS in the partitioning of zinc: $f_d$ ranges from 0.06 to 0.35 corresponding to a TSS variation between 392 and 95 mg/l. On the contrary, particulate lead seems to dominate over the dissolved fraction irrespective of the TSS concentration and pH values.

To account for the TSS concentration, the temporal variation of the equilibrium partition coefficient, $K_d$, is examined.

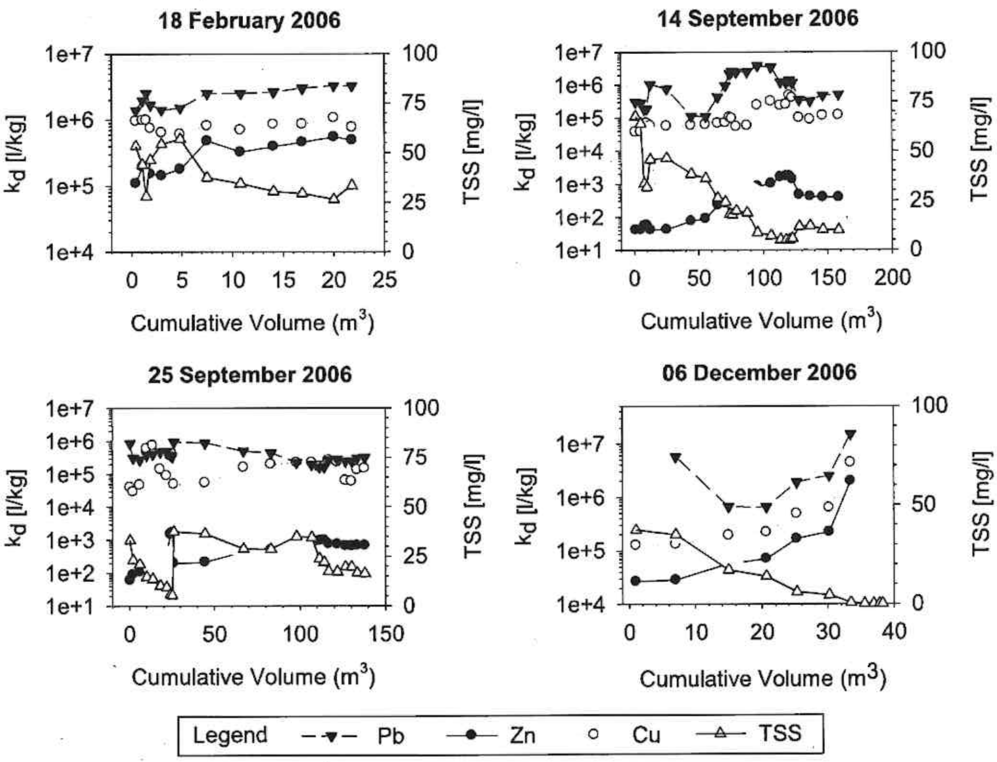



Figure 5. The equilibrium partition coefficient, $K_d$, for zinc (Zn), copper (Cu) and lead (Pb) as a function of the cumulative runoff volume at the airside site located within the Airport of Genova. Total Suspended Solids (TSS) concentration is also plotted in each graph.

In Figures 5 and 6 the equilibrium partitioning coefficient for Zn, Cu and Pb is plotted vs. the cumulative runoff volume observed at the airside–airport and car ferry–port sites. The coefficient $K_d$ ranges between $10^4$ to $10^7$ [l/kg] at the car ferry–port site, thus confirming the predominance of the particulate fraction. It is interesting to observe that $K_d$ values in the range of $10^4$ to $10^5$ [l/kg] are typical for rivers and large lakes where conditions such as the flow rate and TSS concentration can be assumed as constant (Thomann and Mueller, 1987; Glenn et al., 2001).

At the airside–airport site, for the events of 14 September and 25 September, results indicate the coefficient $K_d$ for zinc is several orders of magnitude lower than for copper and lead, in particular this varies between $10^1$ to $10^3$ l/kg due to the pronounced dissolved fraction when compared to Pb and Cu.

At both sites the $K_d$ pattern tends to mimic the TSS delivery behaviour, as clearly emerges for the event of 18 February (see Figures 5 and 6) and generally such behaviour is more pronounced for zinc whose partitioning is strongly influenced by the TSS concentration. Finally, the magnitude of $K_d$ for Zn, Cu and Pb tends to follow the same sequence that is observed when divalent metals hydrolyse: Pb > Cu > Zn (Glenn et al., 2001).

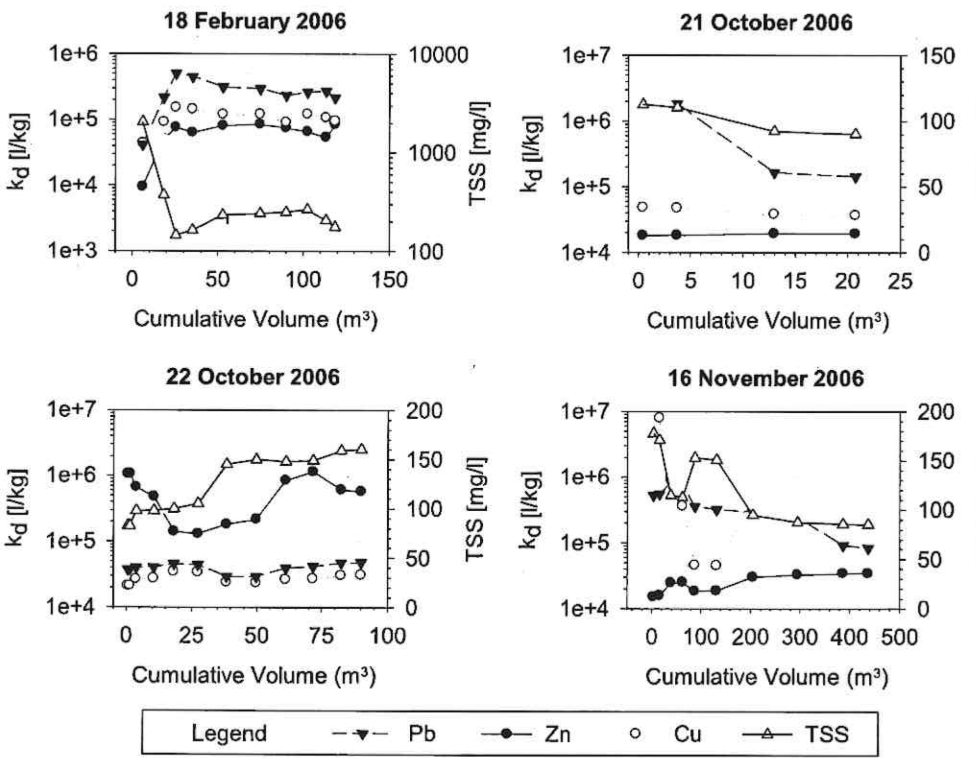



Figure 6. The equilibrium partition coefficient, $K_d$, for zinc (Zn), copper (Cu) and lead (Pb) as a function of the cumulative runoff volume at the car ferry site

located within the Port of Genova. Total Suspended Solids (TSS) concentration is also plotted in each graph.

An example of the kinetics of partitioning for metals is shown in Figure 7 for the Cincinnati highway (I-75) site. Figure 7 illustrates a consistent increase in $K_d$ for all metals across this source area runoff event. At the same time, PM illustrates a mass-limited washoff response; which is expected for a source area where PM and metal build up are dominated by traffic sources before the rainfall-runoff event (Sansalone et al., 1998; Cristina and Sansalone, 2003). Furthermore, the partitioning changes by orders of magnitude across this event, consistent with other results from the American source areas (Dean et al., 2005). A $K_d$ condition in the range of $10^4$ to $10^5$ L/kg appears to be approached for all metals as elapsed time (a surrogate for transported flow volume) increases despite significant variations in other parameters such as PM (suspended + settleable + sediment PM fraction) and flow. As in previous results described herein, $K_d$ values in the range of $10^4$ to $10^5$ L/kg are typical for rivers and large lakes where the residence time is in terms of days and conditions such as PM and flow are constant (Thomann and Mueller, 1987). The variations in flow and PM are shown to illustrate that these variations are mirrored shortly afterwards by resulting changes in $K_d$. Finally, the variation in the relative magnitude of $K_d$ for Zn, Cd, Cu and Pb tends to follow similar trends that can be explained by covalent bonding theory or tendency to undergo hydrolysis.

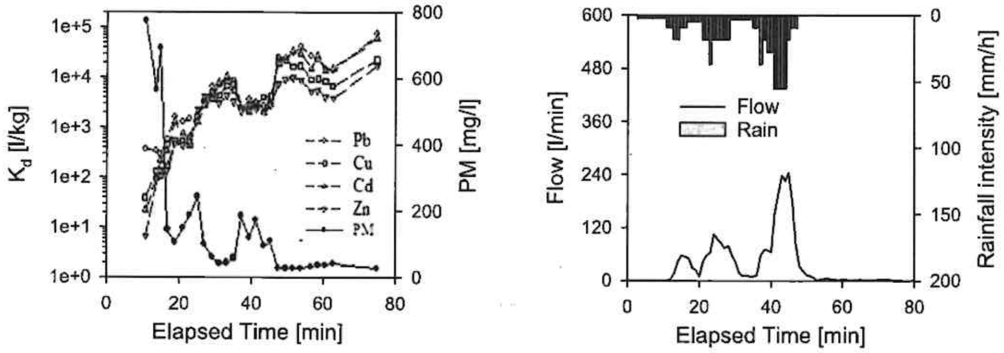



Figure 7. Metal partitioning, PM transport and hydrology for Cincinnati, OH (I-75).

The results in Figure 7 captured the role of flow and PM variability that are reasonably mirrored by partitioning variability because of the close temporal spacing of samples during the hydrograph for several reasons (Sansalone and Buchberger, 1997; Sansalone et al., 1998). The I-75 highway catchment is a high traffic paved source area with short residence times in terms of minutes, with low runoff alkalinity, hardness and pH. Since partitioning kinetics is a temporal process, upon completion of a runoff event the samples were immediately transported by the researchers to their nearby laboratory for fractionation and preservation which was completed within several hours as well as subsequent PM analysis (Sansalone and Buchberger, 1997).

While Figure 7 illustrates the intra-event variability of metal partitioning kinetics that reasonably mirror variations in flow and PM during the event, Figure 8 illustrates both the large inter-event variability of partitioning for a given site as well as the inter-site variability of partitioning for selected metals.

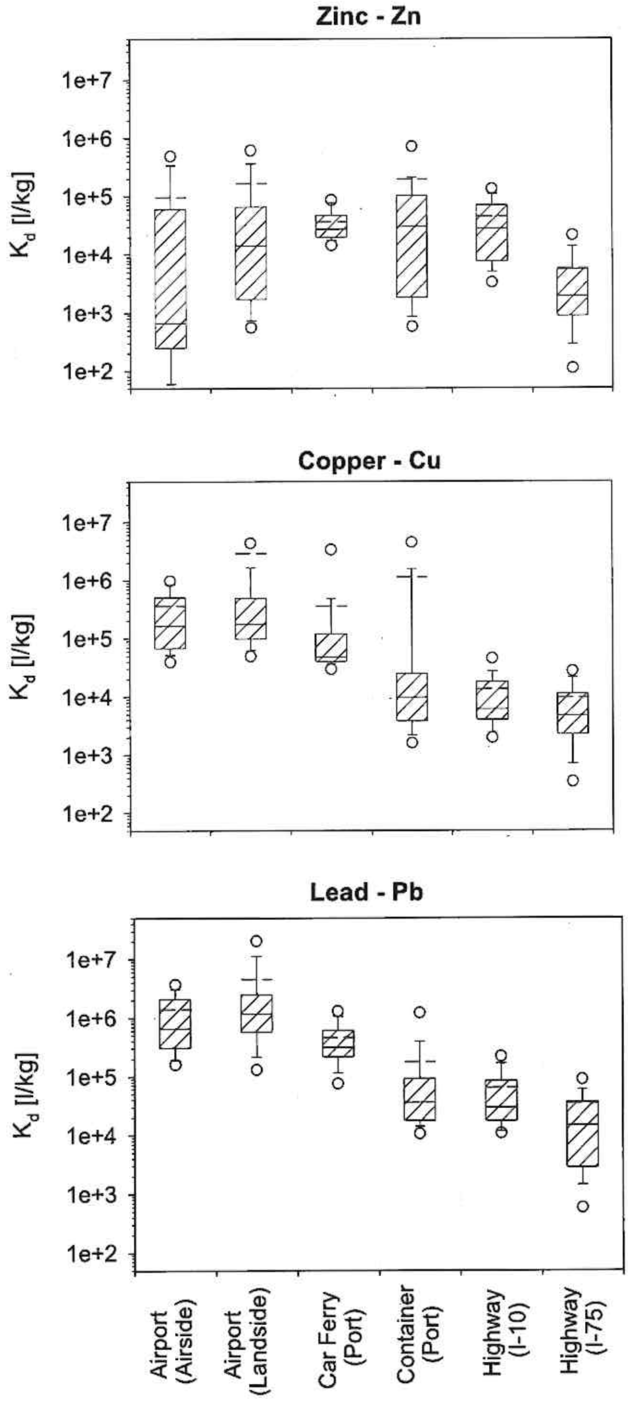



Figure 8 Non-parametric distribution of the equilibrium partition coefficient, $K_d$, for zinc (Zn), copper (Cu) and lead (Pb) with respect to the Italian and American experimental sites (airside and landsite at the airport of Genova, Italy; car ferry,

Port of Genova, Italy; container terminal, Port of La Spezia, Italy; highway I-75 Cincinnati, Ohio USA; highway I-10 Baton Rouge, Louisiana USA).

The intra- and inter-event variability of partitioning that vary by orders of magnitude as shown in Figure 7 and 8 has direct implications for source area treatment by unit operations and processes (UOPs). This variability points out that effective treatment requires a combination of filtration for the particulate-bound fraction and adsorption for the dissolved fraction.

The need for a combination of filtration and adsorption is re-enforced by the results in Figure 8 that indicate the variability of partitioning between metals also drives the need for filtration and adsorption as shown for the airside of the airport. Across sites, zinc partitions towards the dissolved phase while lead is strongly particulate-bound; also indicating the need for filtration and adsorption. Beyond the two-phase partitioning results, the distribution of metal as a function of particle diameter or size class should be examined when designing filters and clarifiers whether for source area or downstream drainage area treatment.

## 4 Conclusions

Representation of metal partitioning in urban drainage is required when determining loadings, treatment, maintenance, regulatory compliance and toxicity. This is particularly the case for urban paved source areas where, if a first-flush exists, the design volumetric capture and treatment will be based on such regulatory requirements. However, such treatment for metals requires partitioning information if metals are to be effectively separated from flows from paved source areas.

A two-partition model has been used to examine metal partitioning for a series of paved source areas belonging to transportation facilities: highway, parking lot (landside) and apron terminal (airside) within aviation site, terminals within port area.

Results from data collection and analysis identify differences in terms of TSS load associated with runoff ranging 20 mg/l at airport sites to 150 mg/l at the port terminal and highway sites. In spite of the wide range of TSS concentration values measured at the six paved source area catchments of concern, metals associated with runoff reveal significant concentration throughout the different sites.

Partitioning indices analysed on both sample and event basis show that copper and largely lead reveal the greatest affinity for the particulate-bound while zinc shows significantly different partitioning behaviour firstly depending on the specific site characteristics. Furthermore, zinc reveals a wide range of partitioning variation even across the different rainfall-runoff events at each catchment.

Results demonstrate that partitioning can vary by orders of magnitude across a runoff event, from largely dissolved to approaching a particulate-bound asymptote similar to receiving waters of much higher residence times. Results suggest that for on-line and real-time treatment of source area runoff, a combination of sedimentation, filtration and adsorption is required. For off-line storage and treatment before discharge, sedimentation and filtration may be sufficiently robust to achieve discharge goals.

## References

American Public Health Association, APHA (1992). Standard methods for the examination of water and wastewater, 18th Ed., A. D. Eaton, L. S. Clesceri, and A. E. Greenberg, eds., American Public Health Association, American Water Works Association and Water Environmental Federation, Washington, D.C

American Public Health Association, APHA (1998). Standard methods for the examination of water and wastewater, 20th Ed., A. D. Eaton, L. S. Clesceri, and A. E. Greenberg, eds., American Public Health Association, American Water Works Association and Water Environmental Federation, Washington, D.C.

APAT IRSA/CNR (2003). Metodologie Analitiche per il controllo della qualità delle acque (in italian). Manual 29/2003; ISBN 88-448-0083-7.

Barrett, M.E., Zuber, R.D., Collins, E.R., Malina Jr., J.F., Charbeneau, R.J. and Ward, G.H. (1995) A Review and Evaluation of Literature Pertaining to the Quantity and Control of Pollution from Highway Runoff and Construction. 2nd Edition, CRWR, University of Texas, Rep. 239.

Charters, F.J., Cochrane, T.A. and O'Sullivan, A.D. (2016). Untreated runoff quality from roof and road surfaces in a low intensity rainfall climate. Sci. Tot. Env. 550, 265-272, doi: 10.1016/j.scitotenv.2016.01.093.

Cristina, C.M. and Sansalone, J.J. (2003). 'First Flush', power law and particle separation diagrams for urban storm-water suspended particulates. J. of Env. Eng. 129(4), 298-307, doi: 10.1061/(ASCE)0733-9372(2003)129:4(298).

Dean, C.M., Sansalone J.J., Cartledge, F.K. and Pardue, J.H., (2005). Influence Of Hydrology On Rainfall-Runoff Metal Element Speciation. J. Env. Eng. 131 (4), 632-642, doi: 10.1061/(ASCE)0733-9372(2005)131:4(632).

Discroll, E., Shelley, P. and Strecker, E. (1990). Pollutant loadings and impacts from highway stormwater runoff: volume IV, research data appendix. FWHA-RD-88-009, Fed. Hwy. Admin., U.S. Dept. of Transp., Washington D.C., 1-39.

Djukić, A., Lekić, B., Rajaković-Ognjanović, V., Veljović, D., Vulić, T., Djolić, M., Naunovic, Z., Despotović, J. and Prodanović, D. (2016). Further insight into the mechanism of heavy metals partitioning in stormwater runoff. J. Environ. Manage. 168, 104–110, doi:10.1016/j.jenvman.2015.11.035

FDOT - Florida Department of Transportation (2005). Technical Report for the Florida statewide airport stormwater study.

Fletcher, T.D., Andrieu, H. and Hamel, P. (2013). Understanding, management and modelling of urban hydrology and its consequences for receiving waters: A state of the art. Adv. Water Resour. 51, 261–279, doi:10.1016/j.advwatres.2012.09.001.

Glenn III, D.W., Liu, D. and Sansalone, J.J. (2001). Influence of highway runoff chemistry, hydrology, and residence time on nonequilibrium partitioning of heavy metals implications for treatment at the highway shoulder. Transp. Res. Record 1755, 129-140, doi: 10.3141/1755-14.

Glenn III, D.W. (2002). Heavy metal distribution for aqueous and solid phases in runoff, snowmelt and soils, Louisiana State University, Baton Rouge, LA USA.

Gnecco, I., Berretta, C., Lanza, L.G. and La Barbera P. (2005). Storm water pollution in the urban environment of Genoa, Italy. Atmos. Res. 77(1-4), 60-73, doi: 10.1016/j.atmosres.2004.10.017.

Gnecco, I., Berretta, C., Lanza, L.G. and Sansalone J.J. (2006). Stormwater contaminant transport from italian shipping terminals implication for BMPs. In Proceedings of StormCon06, The North American Surface Water Quality Conference, 24-27 July 2006 Denver, Colorado (USA)

Gnecco, I., Lanza, L.G. and Sansalone, J.J. (2007a). Transport of metals in storm water runoff, Proc. 32nd Congress of IAHR, Harmonizing the Demand of Art and Nature in Hydraulics, Venice, Italy.

Gnecco, I. Palla, A., and Lanza, L.G. (2007b). Study for the characterization of the storm water runoff of aprons in the port of Savona-Vado. Technical Report (in Italian).

Gnecco, I., Sansalone, J.J. and Lanza, L.G. (2008). Speciation of zinc and copper in stormwater pavement runoff from airside and landside aviation land uses. Water Air Soil Pollut. 192(1-4), 321-336, doi:10.1007/s11270-008-9659-2.

Gnecco, I. and Lanza, L.G. (2013). Review of hydrologic processes and transport of pollutants operated by stormwater runoff in urban environment. In: Overland Flow and Surface Runoff, Nova Science Publishers, Inc., New York, NY, 287-320.

Gromaire-Mertz, M.C., Garnaud, S., Gonzalez, A. and Chebbo, G. (1999). Characterisation of urban runoff pollution in Paris. Wat. Sci. and Tech., 39(2), 1-8, doi:10.1016/S0273-1223(99)00002-5.

Huang, J., Du, P., Ao, C., Ho, M., Lei, M., Zhao, D. and Wang, Z. (2007). Multivariate analysis for stormwater quality characteristics identification from different urban surface types in Macau. Bulletin of Environmental Contamination and Toxicology 79(6), 650-654, doi: 10.1007/s00128-007-9297-1.

Huber, M., Welker, A. and Helmreich, B. (2016). Critical review of heavy metal pollution of traffic area runoff: Occurrence, influencing factors, and partitioning. Sci. Total Environ. 561, 895–919, doi:10.1016/j.scitotenv.2016.04.051.

Kayhanian, M. (2012). Trend and concentrations of legacy lead (Pb) in highway runoff. Environ. Pollut. 160, 169–177, doi:10.1016/j.envpol.2011.09.009.

Koch, B.J., Febria, C.M., Gevrey, M., Wainger, L.A. and Palmer, M.A. (2014). Nitrogen Removal by Stormwater Management Structures: A Data Synthesis. J. Am. WATER Resour. Assoc. 50(6), 1594-1607, doi:10.1111/jawr.12223.

Kuang, X., Kim, J.-Y., Gnecco, I., Raje, S., Garofalo, G. and Sansalone, J.J. (2007). Particle separation and hydrologic control by cementitious permeable pavement. Transp. Res. Record 2025, 111-117, doi: 10.3141/2025-11.

Lau, S.L. and Stenstrom, M.K. (2005). Metals and PAHs adsorbed to street particles. Water Res. 39, 4083–4092, doi:10.1016/j.watres.2005.08.002.

Lee, J.H. and Bang, K.W. (2000). Characterization of urban stormwater. Water Res. 34(6), 1773–1780, doi: 10.1016/S0043-1354(99)00325-5.

Legret, M. and Pagotto, C. (1999). Evaluation of pollutant loadings in the runoff waters from a major rural highway. Sci.Tot Env. 235, 143-150, doi: 10.1016/S0048-9697(99)00207-7.

McBride, M. (1994). Environmental Chemistry of Soils. Oxford University Press, New York, pp. 406.

Memon, F.A. and Butler, D. (2005). Characterization of pollutants washed off from road surfaces during wet weather. Urban Wat. J. 2(3), 171-182, doi: doi.org/10.1080/15730620500235437.

Preciado, H.F. and Li, L.Y. (2005). Evaluation of metal loadings and bioavailability in air, water and soil along two highways of British Columbia, Canada. Water Air Soil Pollut. 172, 81–108, doi: 10.1007/s11270-005-9063-0.

Sansalone, J.J. and Buchberger, S.G. (1997). Partitioning and first flush of metals in urban roadway storm water. J. Environ. Eng. 123(2), 134-143, doi: 10.1061/(ASCE)0733-9372(1997)123:2(134).

Sansalone, J.J., Koran, J.M., Smithson, J.A. and Buchberger, S.G. (1998). Physical characteristics of urban roadway solids transported during rain events. J. of Env. Eng. 124(5), 427-440, doi: 10.1061/(ASCE)0733-9372(1998)124:5(427).

Sansalone, J.J. and Tribouillard, T. (1999). Variation in Characteristics of Abraded Roadway Particles as a Function of Particle Size. Transp. Res. Rec. 1690, 153–163, doi: 10.3141/1690-18.

Sansalone, J.J. and Cristina, C.M. (2004). Prediction of Gradation-Based Heavy Metal Mass Using Granulometric Indices of Snowmelt Particles. J. Environ. Eng. 130, 1488–1497, doi:10.1061/(ASCE)0733-9372(2004)130.

Sansalone J.J. and Teng, Z. (2004). In situ partial exfiltration of rainfall runoff. I: Quality and quantity attenuation. J. Environ. Eng. 130(9), 990-1007, doi: 10.1061/(ASCE)0733-9372(2004)130:9(990).

Sansalone, J.J., Hird, J.P., Cartledge, F. and Tittlebaum, M.E. (2005). Event-based stormwater quality and quantity loadings from elevated urban infrastructure affected by transportation. Wat. Environ. Res. 77(4), 348–365, doi: 10.2175/106143005X51932.

Sansalone, J. and Ying, G. (2008). Partitioning and granulometric distribution of metal leachate from urban traffic dry deposition particulate matter subject to acidic rainfall and runoff retention. Water Res. 42, 4146–4162, doi:10.1016/j.watres.2008.06.013.

Sansalone, J., Ying, G.X. and Lin, H. (2010). Distribution of Metals for Particulate Matter Transported in Source Area Rainfall-Runoff. J. Environ. Eng. 136, 172–184, doi:10.1061/(asce)ee.1943-7870.0000139.

Taebi, A. and Droste, R.L. (2004). Pollution loads in urban runoff and sanitary wastewater. Sci.Tot Env. 327(1-3), 175-184, doi: 10.1016/j.scitotenv.2003.11.015.

Teng Z. and Sansalone J.J. (2004). In situ partial exfiltration of rainfall runoff. II: Particle separation J. Environ. Eng. 130(9), 1008-1020, doi: 10.1061/(ASCE)0733-9372(2004)130:11(1289).

Thomann, R. and Mueller, J. (1987). Principles of surface water quality modeling and control. Harper & Row, Publishers, Inc., New York, NY, 1-644.

Turer D., Maynard B.J. and Sansalone J.J. (2001). Heavy metal contamination in soils of urban highways: Comparison between runoff and soil concentrations at Cincinnati, Ohio. J. of Water, Air and Soil Pollution, 132 (3-4), 293-314 , doi: 10.1023/A:1013290130089.

USEPA (1990). Test Methods for Evaluating Solid Waste. Physical/Chemical Methods, SW 846, 3rd edition, final update, Washington, D.C., pp. 312.

Wijesiri, B., Egodawatta, P., Mcgree, J. and Goonetilleke, A. (2016). Understanding the uncertainty associated with particle-bound pollutant build-up and wash-off: A critical review. Water Res. 101, 582–596, doi:10.1016/j.watres.2016.06.013.

Zhao, H., Li, X., Wang, X. and Tian, D. (2010). Grain size distribution of road-deposited sediment and its contribution to heavy metal pollution in urban runoff in Beijing, China. J. Hazard. Mater. 183, 203–10, doi:10.1016/j.jhazmat.2010.07.012.

Table 1. Summary of paved source area catchment descriptions and sampling/analytical methodology employed for the measurement of PM and metals in runoff events.

| Location | Land-use | Area[a] | Pave-ment[b] | Imp.[c] | Slope[d] | ADT[e] | Monitoring Period | Rain | n[f] | Sampling method[g] | Standard Method[h] | Ref[i] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $m^2$ | | % | | x $10^3$ | | mm/yr | | | | |
| Cincinnati (OH, USA) | Highway (I-75) | 300 | A | 100 | <0.004 | 117 | Oct 95 – June 97 | 1,020 | 11 | GS | APHA | *(1)* |
| Baton Rouge (LA, USA) | Highway (I-10) | 544 | C | 100 | 0.0018 | 70 | June 02 – July 02 | 1,460 | 6 | GS | APHA | *(2)* |
| Little Rock (AR, USA) | Highway (I-30) | 6,070 | A | 90 | n.a. | 42 | May 83 – May 84 | 1,237 | 17 | AS | APHA | *(3)* |
| Denver (CO, USA) | Highway (I-25) | 142,859 | A | 37 | n.a. | 149 | Aug 76 – July 77 | 376 | 16 | AS | APHA | *(3)* |
| Nashville (TE, USA) | Highway (I-40) | 225,013 | C | 37 | n.a. | 88 | Oct 76 – Sep 77 | 1,143 | 21 | AS | APHA | *(3)* |
| Loire-Atlantique (France) | Highway (A-11) | 3,200 | A | ~100 | n.a. | 12 | Mar 95– Feb 96 | 656 | 49 | AS | n.a. | *(4)* |
| Airport (Genova, Italy) | Apron Terminal | 10,000 | C | 100 | 0.003 | n.a. | Nov 05 – Dec 06 | 1,035 | 10 | AS | APAT | *(5)* |
| Airports (Florida, USA) | Apron Terminal | 187,700 | C | 100 | 0.02 | n.a. | Sept 02 – Nov 04 | 1,522 | 42[i] | AS | APHA | *(6)* |
| Airports (Florida, USA) | Taxiway | 187,700 | A/C | 100 | 0.02 | n.a. | Sept 02 – Nov 04 | 1,522 | 40[i] | AS | APHA | *(6)* |
| Airport of Genova (Italy) | Parking lot | 14,000 | A/C | 100 | 0.002 | n.a. | Nov 05 – Dec 06 | 1,035 | 12 | AS | APAT | *(5)* |
| Austin (TX, USA) | Low traffic density | 526 | A | 100 | n.a. | ~ 9 | Sept 93 – May 95 | 826 | 29 | AS | EPA | *(7)* |
| Le Maris (Paris, France) | Urban streets | < 1,700 | A | 90 | n.a. | n.a. | July 96 – May 97 | 2,250 | 26 | AS | APHA | *(8)* |
| Albaro (Genova, Italy) | Residential area | 2,800 | A | 75 | <0.003 | n.a. | Jan 02– Sep 03 | 1,147 | 12 | AS | APAT | *(9)* |
| London (UK) | Urban roads | n.a. | A | 100 | n.a. | <73 | n.a. | 585 | 10 | GS | APHA | *(10)* |
| Isfahan (Iran) | Urban catchment | 3,600,000 | n.a. | 55 | 0.02 | n.a. | Dec 99 – Mar 01 | 118 | 10 | GS | APHA | *(11)* |
| Yalianfang (Macau, China) | Urban catchment | 140,000 | n.a. | 60 | n.a. | 20 | Aug 05 – Nov 05 | | 5 | AS | APHA | *(12)* |
| Port of Genova (Italy) | Car ferry Terminal | 49,000 | A/C | 100 | <0.005 | n.a. | Feb 06 – Nov 06 | 937 | 5 | AS | APAT | *(13)* |
| Port of La Spezia (Italy) | Container Term. | 9,000 | A | 100 | 0.004 | n.a. | Apr 05 – Jan 06 | 914 | 13 | AS | APAT | *(14)* |
| Port of Savona (Italy) | Breakbulk Term. | 13,000 | A | 100 | 0.002 | n.a. | Sept 06 – June 07 | 954 | 7 | AS | APAT | *(15)* |

[a] Monitored drainage area; [b] A = asphalt, C = concrete, A/C = mixture of asphalt and concrete; [c] Imperviousness on the monitored drainage area; [d] Mean slope of the drainage surface area; [e] Average daily traffic on the number of lanes monitored; [f] Number of rainfall events sampled (snow events not considered); [g] AS = automatic sampler, GS = manual grab sampling; [h] APHA (1992,1998), USEPA (1990), APAT (2003); [i] *(1)* Sansalone and Buchberger 1997; *(2)* Dean at al., 2005; *(3)* Discroll et al., 1990; *(4)* Legret and Pagotto, 1999; *(5)* Gnecco et al., 2008; *(6)* FDOT - Florida Department of Transportation, 2005; *(7)* Barrett et al., 1995; *(8)* Gromarie-Mertz et al., 1999; *(9)* Gnecco et al., 2005; *(10)* Memon and Butler, 2005; *(11)* Taebi and Droste, 2004; *(12)* Huang et al., 2007; *(13)* Gnecco et al., 2007a; *(14)* Gnecco et al., 2006; *(15)* Gnecco et al., 2007b; [i] Number of collected samples.

Table 2. Comparison of Total Suspended Solids (TSS), Zinc (Zn), Copper (Cu) and Lead (Pb) for different land-uses sites. The values are reported as Event Mean Concentration (EMC) values; heavy metal concentration values include both dissolved and particulate-bound fractions.

| **Site** | | **TSS** (mg/l) | | | **Zn** (mg/l) | | | **Cu** (mg/l) | | | **Pb** (mg/l) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Name* | *Land-Use* | *mean* | *median* | *SD* | *mean* | *median* | *SD* | *mean* | *median* | *SD* | *mean* | *median* | *SD* |
| Cincinnati (Ohio, USA) | Highway (I-75) | 122.8 | 126.7 | 49.3 | 1.449 | 0.829 | 1.270 | 0.073 | 0.045 | 0.066 | 0.074 | 0.051 | 0.092 |
| Baton Rouge (Louisiana, USA) | Highway (I-10) | 198.6 | 203.6 | 84.1 | 0.659 | 0.465 | 0.597 | 0.130 | 0.060 | 0.131 | 0.082 | 0.051 | 0.074 |
| Little Rock (Arkansas, USA) | Highway (I-30) | 127.4 | 105.0 | 66.0 | 0.214 | 0.150 | 0.112 | 0.021 | 0.020 | 0.010 | 0.127 | 0.130 | 0.042 |
| Denver (Colorado, USA) | Highway (I-25) | 469.6 | 374.5 | 288.3 | 0.739 | 0.665 | 0.395 | 0.128 | 0.120 | 0.065 | 0.806 | 0.700 | 0.454 |
| Nashville (Tennessee, USA) | Highway (I-40) | 215.2 | 198.0 | 106.4 | 0.283 | 0.250 | 0.121 | 0.070 | 0.070 | 0.046 | 0.501 | 0.500 | 0.305 |
| Loire-Atlantique (France) | Highway (A-11) | 71 | 47 | 61 | 0.356 | 0.254 | 0.288 | 0.045 | 0.033 | 0.027 | 0.058 | 0.043 | 0.044 |
| Airport (Genova, Italy) | Apron Terminal | 27.8 | 18.8 | 25.0 | 0.587 | 0.128 | 1.001 | 0.111 | 0.032 | 0.165 | 0.272 | 0.024 | 0.500 |
| Airports (Florida, USA) | Apron Terminal | 5.8 | 4.9 | 3.0 | 0.066 | 0.045 | 0.043 | 0.023 | 0.018 | 0.013 | 0.005 | 0.004 | 0.003 |
| Airports (Florida, USA) | Taxyway | 33.0 | 23.0 | 30.2 | 0.026 | 0.021 | 0.018 | 0.016 | 0.011 | 0.009 | 0.006 | 0.005 | 0.004 |
| Airport of Genova (Italy) | Parking lot | 36.5 | 23.9 | 25.4 | 0.332 | 0.009 | 0.820 | 0.191 | 0.059 | 0.269 | 0.327 | 0.091 | 0.439 |
| Austin (Texas, USA) | Low traffic density | 142 | 118 | 126 | 0.077 | 0.050 | 0.078 | 0.010 | 0.007 | 0.010 | 0.041 | 0.016 | 0.056 |
| Le Maris (Paris, France) | Urban streets | - | 92.5 | 49 ; 498[1] | - | 0.550 | 0.246 ; 3.839[1] | - | 0.061 | 0.027 ; 0.191[1] | - | 0.133 | 0.071 ; 0.523[1] |
| Albaro (Genova, Italy) | Residential area | 140 | 119 | 115 | 0.081 | 0.084 | 0.033 | 0.019 | 0.001 | 0.020 | 0.013 | 0.012 | 0.006 |
| London (UK) | Urban roads | 551 | 375 | 389 | 0.2649 | 0.2293 | 0.1948 | 0.0441 | 0.0402 | 0.0247 | 0.9597 | 0.9155 | 0.1868 |
| Isfahan (Iran) | Urban catchment | 161 | 123 | 133 | 0.342 | 0.074 | 0.773 | - | - | - | 0.278 | 0.273 | 0.221 |
| Yalianfang (Macau, China) | Urban catchment | 318.6[2] | - | 523.3[2] | 0.055[2] | - | 0.039[2] | 0.005[2] | - | 0.004[2] | 0.003[2] | - | 0.003[2] |
| Port of Genova (Italy) | Car ferry Terminal | 162.9 | 135.6 | 95.8 | 0.763 | 0.517 | 0.872 | 0.157 | 0.086 | 0.160 | 0.270 | 0.042 | 0.464 |
| Port of La Spezia (Italy) | Container Terminal | 170.2 | 110.4 | 139.2 | 3.568 | 2.155 | 5.131 | 0.846 | 0.043 | 1.877 | 0.539 | 0.370 | 0.565 |
| Port of Savona (Italy) | Breakbulk Terminal | 76.2 | 68.2 | 39.1 | 0.284 | 0.002 | 0.431 | 0.091 | 0.023 | 0.184 | 0.038 | 0.011 | 0.072 |

[1] Data indicate the maximum and the minimum concentration values; [2] Data indicate the arithmetic mean and standard deviation of the sample concentration value.

Table 3. Event mean value and standard deviation of the dissolved fraction $f_d$ for zinc (Zn), copper (Cu) and lead (Pb) with respect to each monitored event at the airside site within the Airport of Genova. In the table, the corresponding TSS and pH are indicated.

| Event | TSS | pH | Zn | | Cu | | Pb | |
|---|---|---|---|---|---|---|---|---|
| | *Mean* | *Mean* | *Mean* | *SD* | *Mean* | *SD* | *Mean* | *SD* |
| February 18, 2006 | 36.1 | 7.6 | 0.09 | 0.03 | 0.03 | 0.01 | 0.01 | 0.001 |
| September 14, 2006 | 23.1 | 6.78 | 1.00 | 0.002 | 0.36 | 0.08 | 0.10 | 0.07 |
| September 25, 2006 | 25.9 | 6.90 | 0.99 | 0.01 | 0.30 | 0.15 | 0.15 | 0.08 |
| December 6, 2006 | 13.6 | 7.48 | 0.50 | 0.004 | 0.33 | 0.15 | 0.22 | 0.25 |
| All events | 24.9 | 7.20 | 0.65 | 0.44 | 0.26 | 0.15 | 0.12 | 0.09 |

Table 4. Event mean value and standard deviation of the dissolved fraction $f_d$ for zinc (Zn), copper (Cu) and lead (Pb) with respect to each monitored event at the car ferry site within the Port of Genova. In the table, the corresponding TSS and pH are indicated.

| **Event** | **TSS** | **pH** | **Zn** | | **Cu** | | **Pb** | |
|---|---|---|---|---|---|---|---|---|
| | *Mean* | *Mean* | *Mean* | *SD* | *Mean* | *SD* | *Mean* | *SD* |
| February 18, 2006 | 329.2 | 7.6 | 0.06 | 0.02 | 0.04 | 0.01 | 0.02 | 0.004 |
| October 21, 2006 | 94.7 | 7.0 | 0.35 | 0.02 | 0.19 | 0.04 | 0.03 | 0.04 |
| October 22, 2006 | 135.6 | 7.2 | 0.24 | 0.07 | 0.18 | 0.04 | 0.02 | 0.02 |
| November 16, 2006 | 103.8 | 7.1 | 0.26 | 0.01 | 0.03 | 0.05 | 0.04 | 0.04 |
| All events | 165.8 | 7.2 | 0.23 | 0.12 | 0.11 | 0.09 | 0.03 | 0.01 |