Roads as sources of heavy metals in urban areas. The Covões catchment experiment, Coimbra, Portugal

António J. D. Ferreira[1] · Daniel Soares[1] · Luís M. V. Serrano[2,3] · Rory P. D. Walsh[4] · Celia Dias-Ferreira[1] · Carla S. S. Ferreira[1]

Abstract

Purpose This work studies the implications of different traffic patterns for heavy metal and solid pollution generation processes following rainfall events with contrasting antecedent meteorological conditions, at a periurban catchment. The aim is to provide information on the pollution processes and their potential environmental impacts for urban areas.

Materials and methods Seven campaigns were performed covering winter, spring, and summer conditions, for rainfall events with different antecedent conditions. Four types of roads were monitored: low traffic, average traffic, heavy traffic with demanding driving situations (break and turning), and heavy traffic with high vehicle speed (motorway profile). Samples were taken at the beginning, middle and end of the events to measure within event variation in concentration. Analytical standard procedures were used to quantify pH, conductivity, turbidity, total solids, volatile solids, suspended solids, volatile suspended solids and heavy metals (Cd, Cu, Pb and Zn) in the total and dissolved forms (as to infer the particulate fraction), namely copper, zinc, cadmium and lead.

Results and discussion The collected data show a direct relation among the number of vehicles and/or the driving manoeuvres performed by them and the amount of solids and heavy metals present in the wash out overland flow collected. An important fraction of the heavy metals is washed off in the particulate form, which represents an increased problem since the road overland flow is directed to green/brown areas and for the local aquatic ecosystems. Maximum copper values recorded exceed 0.6 mh L^{-1}, zinc exceeds 5 mg L^{-1}, lead 0.1 mg L^{-1} and cadmium 0.01 mg L^{-1}. Values are higher after long dry spells and reduce concentration throughout the rainfall events.

Conclusions An important part of the heavy metals (with relevance for zinc and lead) are washed off in the particulate form, pollutants are typically related to the amount of traffic, and especially to the existence of driving manoeuvres. The summer events show the highest values, due to the accumulation of pollutants during the long dry spells.

✉ António J. D. Ferreira
  aferreira@esac.pt

1 CERNAS, Coimbra Polytechnic Agriculture School, Polytechnic Institute of Coimbra, Bencanta, 3045-601 Coimbra, Portugal

2 School of Technology and Management, Polytechnic Institute of Leiria, Morro do Lena, Alto do Vieiro, ap.4163, 2411-901 Leiria, Portugal

3 ADAI, LAETA Department of Mechanical Engineering, University of Coimbra, Rua Pedro Hispano 12, ap.10131, 3030-289 Coimbra, Portugal

4 Department of Geography, Swansea University, Swansea SA2 8PP, UK

1 Introduction

Traffic emissions are a significant contributor of diffuse pollution loads on urban surfaces and subsequent mobilisation and transport towards the water bodies, aquifers and aquatic ecosystems, posing problems for receiving water quality (Revitt et al. 2014; Shorshani et al. 2015). Part of air pollutants deposits on surfaces by dry and wet processes, becoming available to be entrained by the water runoff during rainfall events (Shorshani et al. 2015).

Traffic pollutants can have distinct sources. They can be emitted by vehicles' engines through internal combustion, by tyre, clutch and brake wear, fuel evaporation, and road wear. Exhaust emissions are composed by carbon dioxide (CO_2), carbon monoxide (CO), nitrogen oxides (NOx/NO and NO2), volatile organic compounds (VOCs), particulate matter (PM), nitrous oxide (N_2O), ammonia (NH_3), persistent organic pollutants (POPs) including polycyclic aromatic hydrocarbons (PAHs), and metals. Nonexhaust emissions are sources of particulate material (PM), which include inorganic species, trace metals and carbonaceous compounds (Shorshani et al. 2015).

Heavy metal ions are ubiquitous in modern industrialised environments and a matter of concern due to their toxicity and persistence that make them particularly hazardous (Burges et al. 2015; Adamcová et al. 2016). Of particular concern are the processes of remobilisation and movement to the soils and into the food chain, thereby reaching humans and causing chronic or acute diseases (Kadi 2009; Brevik and Sauer 2015). Roads can be major sources of heavy metals (Kadi 2009; Pant and Harrison 2013). Kadi (2009) states that roads are an important source of trace metal pollution to nearby agriculture soils, increasing their bio-accessibility. Paved road dust is quoted as a major source of air-born metal to the atmosphere (Kadi 2009; Pant and Harrison 2013), coming mainly from exhaust pipe emissions, tyre wear, brake wear, road dust and surface wear (Pant and Harrison 2013).

Road traffic is a key contributor of Ba, Zn and Pb (Lin et al. 2005), and Perez et al. (2010) found Cu, Sb, Ba, Mn and Zn in Barcelona (Spain).

Even with zero tail pipe emissions, traffic contributes to fine and ultrafine particles through nonexhaust emissions (Kumar et al. 2013). It is estimated that almost 90 % of the total emissions from road traffic will be originated by nonexhaust sources by the end of this decade (Rexeis and Hausberger 2009).

Nonexhaust PM comprises various emissions types that are not derived from the tail pipe of a vehicle, including particles generated by brake and tyre wear, road surface abrasion, wear and tear/corrosion of other vehicle components such as the clutch, and resuspension of road surface dusts (Pant and Harrison 2013). Nonexhaust emissions are characterised by their inherent toxicity including the tendency to act as carriers of heavy metals and carcinogenic components (Hjortenkrans et al. 2007; Johansson et al. 2009). They have potential acute and chronic human health implications (Crosby et al. 2014).

Nonexhaust emissions are typically characterised by trace metals (e.g. Cu, Zn, Ba, Sb, Mn), known to vary with fleet composition, with heavy duty vehicles being reported as having higher emissions (Grieshop et al. 2006; Mancilla and Mendoza 2012). The profile of trace metal concentrations in nonexhaust PM is found to be unique for every region and varies with traffic volume and pattern, vehicle fleet characteristics, driving patterns and the climate and geology setting for the region (Omstedt et al. 2005; Duong and Lee 2011). Sources of nonexhaust emissions present a wide variability given the diversity of tyre and break or road surface types and composition, many times manufacturer dependent, making it very difficult to relate source profiles to fleet composition (Pant and Harrison 2013).

No clear linear relationship can be found between nonexhaust emissions and traffic characteristics, but several authors establish a relation with increase vehicle speed (Hussein et al. 2008; Mathissen et al. 2011).

Nonexhaust emissions are equivalent or even greater than exhaust emissions, especially when rainfall rates are low and the wash-off of the road is reduced (Amato et al. 2010b).

Emissions from traffic represent a substantial fraction of primary PM within urban areas (Charron et al. 2007). Albeit control regulations led to a significant reduction in exhaust emissions, currently nonexhaust emissions from road vehicles are persistent. Querol et al. (2004) showed that exhaust and nonexhaust sources contributed approximately with equal amounts to total traffic emissions at several European cities. Quantification of nonexhaust particles and attribution to specific sources is difficult. Thorpe and Harrison (2008) stated that the quantification depends upon the use of chemical tracers, which are seldom characterised.

Brake wear particle properties are difficult to characterise due to the wide variations in brake lining formulations (Thorpe and Harrison 2008). Garg et al. (2000), Sanders et al. (2003) and Iijima et al. (2007) performed dynamometer tests on different brake lining materials considered to account for the majority of the formulations used, respectively, in the USA, Sweden and Japan. Nevertheless, there is limited information on the presence of specific organic tracers because of the refractory nature of brake linings, and attention has been directed to identify metals (Sanders et al. 2003; Blau and Meyer 2003; von Uexküll et al. 2005; Iijima et al. 2007).

Tyre wear is an important contributor of PM10 emissions, Thorpe and Harrison (2008) estimated in several thousands of tons the annual losses of rubber from tyres in Europe. Tyres contain a vast range of both organic and inorganic constituents. Nevertheless, many of the pollutants are not specific only for tyres and can stem from other sources. For instance, zinc can be found in tyre wear particles and in other emission sources (Thorpe and Harrison 2008). In regions with long dry spells, such as the Mediterranean, road dust resuspension is a major source causing PM10 exceedances. The chemical composition of dust varies seasonally and among sites (Amato et al. 2014).

Before the abandonment of lead gasoline, this was the main source of lead pollution, and although lead gasoline is no longer used for a few decades, soils still act as lead pollution reservoirs (Kadi 2009).

Pant and Harrison (2013) present a comprehensive description of nonexhaust sources of airborne particles. Tyre tread

contains natural rubber copolymers and Zinc (Zn) that is added to tyres in the vulcanisation process. Car tyres in the EU contain almost 1 % zinc oxide (Milani et al. 2004; Councell et al. 2004) with rubber representing around 47 %, metals 16.5 % and carbon black 21.5 % (Milani et al. 2004).

Zinc concentration is about 15 times higher in tyres compared to brakes while concentrations of heavy metals such as copper and barium were higher for break materials (Apeagyei et al. 2011). Nevertheless, Lough et al. (2005) found that zinc can be emitted from break wear, motor oil and other sources, and are therefore common in areas with high volumes of traffic, undergoing start-stop manoeuvres (Crosby et al. 2014). Road surface and the type of tyres also plays important roles in tyre emissions (Pant and Harrison 2013).

Iijima et al. (2007) reported that cars can emit around 44 g car^{-1} year^{-1} of brake dust, while Sanders et al. (2003) identified high concentrations of Fe, Ba and Cu in brake lining wear. Hjortenkrans et al. (2007) stated that Cu, Zn and Sb were present in brake wear emissions, and Amato et al. (2010b) found Fe, Cu, Cr and Zr as resultants of brake wear.

Brake pads have different composition based on the manufacturer and the brand, particularly in what concerns Cu and Sb (Hjortenkrans et al. 2007). Crosby et al. (2014) found high levels of Cu related with pedestrian crossings, junctions and traffic lights, with high concentrations of stopping-points in London, showing reduced concentrations in the direction of traffic flow. The authors ascribe Zn and Cu potential deposition to brake linings and tyre wear.

Road surface wear consists of primarily coarse-sized particles derived from different sources, mainly from traffic, industrial emissions and mineralogical dust. Its composition shows spatial and temporal variation (Pant and Harrison 2013). The amount of particulate matter accumulated on an urban surface is influenced by surface texture depth. Gunawardana et al. (2012) found that for a residential area with a surface texture depth of 0.76–0.92 mm produced on average 0.81–1.79 g m^{-2} of solids loading, which increased to 1.75–2.22 g m^{-2} for a commercial area with a surface texture depth of 0.63–1.11 mm.

The amount of resuspended road dust particles is related with vehicle movement (i.e. traffic speed), street maintenance, season and related meteorological parameters. In the UK, wind seems to have a strong influence in resuspension of pollutants from heavy duty traffic, whereas precipitation was found to have no influence on the amount of resuspension (Thorpe et al. 2007). Nevertheless, in Sweden, road wetness is an important factor in the amount of resuspension (Omstedt et al. 2005), although this appears to be related to road sanding and the use of studded tyres.

Pavement type is also relevant for road dust emissions. Granite-based pavements emit more PM than quartzite pavements (Gustafsson et al. 2009).

Particular matter emissions from vehicles are determined by the engine type, age and maintenance, containing small amounts of trace metals (Peltier et al. 2011). Emissions from diesel and gasoline vehicles are different in their composition as diesel engines emit both a greater mass of PM and a larger number of ultrafine particles (UFPs) compared to gasoline vehicles (Rose et al. 2006). Gasoline engines are known to release a higher fraction of organic carbon (OC) while diesel engines emit more elemental carbon (EC) (Ntziachristos et al. 2007). Emissions of ultrafine and fine particles from heavy duty diesel vehicles (HDDVs) are one order of magnitude higher than LDGVs (low duty gasoline vehicles) (Pant and Harrison 2013).

Metals are emitted from various exhaust-related sources including fuel and lubricant combustion, particulate filters, engine corrosion and catalytic converters (Lough et al. 2005; Pulles et al. 2012; Sysalova et al. 2012; Varrica et al. 2012) although many come from nonexhaust sources (Pant and Harrison 2013). Ni and V were reported to be present in emissions due to oil combustion (Pey et al. 2010). Br, Ba, Sb and V were reported in emissions from gasoline and liquefied petroleum gas (LPG) engines compared to diesel engines in Hong Kong (Cheng et al. 2010). Ba, Cd, Zn, Sb and V were reported to be strongly associated with diesel fuel whereas Cu, Mn and Sr were found associated with gasoline (Lin et al. 2005).

Metal concentrations from diesel and gasoline vehicles can vary over two orders of magnitude (Pulles et al. 2012). Nevertheless, the levels of trace elements emitted from the exhaust is quite low, reason why several authors attributed metals to different sources, making source attribution very difficult unless detailed information on local source particle composition is available (Pant and Harrison 2013). Table 1 presents a comprehensive analysis of heavy metal sources.

This paper discusses the processes of heavy metal transfer from different road types to surrounding soils and water bodies, during rainfall events. The assessment of total and dissolved heavy metal allows inferring the amount of heavy metals exported in the particulate form, therefore providing a further insight on the generation and transfer processes.

2 Materials and methods

2.1 Case study characterisation

The Ribeira dos Covões catchment (40° 13′ N and 8° 27′ W), close to Coimbra city centre, the main city in central Portugal (Fig. 1), has an area of 6.2 km^2, an elongated form and a south to north direction. The main watercourse is perennial, supplied by several springs, while the smaller tributaries are ephemeral. The area has a moist Mediterranean climate, with a mean annual temperature of 15 °C and rainfall of 892 mm (between years 1941 and 2000), with dry summers and wet winters

Table 1 Sources of heavy metals from traffic

Study	Metal								
	Zn	Cu	Pb	Ba	Fe	Sb	Cr	Cd	Ni
Amato et al. (2010b)		Break wear			Break wear		Break wear		
Apeagyei et al. (2011)	Tyre wear	Break wear		Break wear					
Crosby et al. (2014)	Tyre and break	Stop points			Break wear				
Han et al. (2007)	Traffic	Traffic	Traffic						Traffic
Hjortenkrans et al. (2007)	Break wear	Break wear				Break wear			
Kadi (2009)			Gasoline (historic)						
Keuken et al. (2010)	Tyre ware	Break wear							
Lough et al. (2005)	Tyre and break, motor oil								
Milani et al. (2004)	Tyre wear								
Pant and Harrison (2013)	Tyre wear								
Sanders et al. (2003)		Break wear		Break wear	Break wear				
Sansalone and Buchberger (1997)	Break and tyre wear	Break and tyre wear	Break, oil and additives, combustion		Tyre and vehicle structure		Tyre wear	Tyre wear	Break wear
Wei and Yang (2010)	Traffic	Traffic	Traffic				Traffic		Traffic

(Ferreira et al. 2015, 2016a). The geology comprises Jurassic dolomitic and marl-limestone in the east, and Cretaceous and Tertiary sandstones, conglomerates and mudstones in the west (Tavares et al. 2012). There are also some Pliocene-Quaternary sandy-conglomerate and alluvial deposits. Soils are generally deep (>3 m) and classified as Cambisols and Podzols according to the FAO system (Tavares et al. 2012). The highest point is 205 m. The average slope is 8° but with few steep slopes of 47° (Ferreira et al. 2015).

Recent land use change in the catchment has been studied in detail by Tavares et al. (2012) and Ferreira et al. (2016b). The former rural catchment (until 1958) has undergone first discontinuous urbanisation (1973–1993), followed by urban consolidation (since 1993). The population of the catchment increased from around 2500 in 1958 to 8000 inhabitants in 2011. Agricultural area fell from 48 % in 1958 to 4 % in 2009, involving mainly decreases in olive groves and arable land. Considerable woodland cover increased from 46 to 66 % over the same period, changing also from *Quercus suber* and mixed woodland to large commercial plantation of pine and eucalyptus (Tavares et al. 2012; Ferreira et al. 2016c). Early urbanisation was mainly associated with buildings along major roads and concentrated settlement in the old hamlets that possessed a medieval urban structure, typically in ridges. This was replaced during the 1973–1993 period, by a great increase in the number of residential buildings, mostly detached houses surrounded by gardens and delimited by walls, and later construction of apartment's blocks. The area also contains educational and health facilities, including a central hospital. There are also some small industrial facilities, and an enterprise park is under construction in the upper part of the catchment. Numerous new roads were built, especially from 1973 onwards, including a recent major road, with motorway profile, the main road between Lisbon and Porto without toll (the IC2, former National Road number 1). The total urban areas have increased from 6 % in 1958 to 30 % in 2009. The catchment therefore contains areas of contrasting urbanisation types: some well-defined urban cores, but also a discontinuous arrangement of buildings and infrastructures, with population density ranging from <25 inhabitants km^{-2} in low-density areas to over 9900 inhabitants km^{-2} (Tavares et al. 2012).

Within the urban areas, separate drainage systems transport wastewater into a treatment plant located outside study site, and the storm water (including roofs, streets and concrete paved areas runoff) is piped downstream to the main river and some of its tributaries downslope. When urban buildings and derelict urban land are surrounded by agriculture fields, however, storm water just dissipates in these areas. Despite the urban drainage system, as a result of the proximity of some urban centres to water courses and their location in downslope areas, a flood event occurred in 2005. It is unclear if this flood resulted from urbanisation or extreme rainfall events. According to older local residents, only a few significant flood events were reported some 50 and 80 years ago.

Fig. 1 Study area location and characterisation

To provide information on the impact of traffic on heavy metal contamination transfer to the aquatic ecosystems through washing off by overland flow during rainfall events, six sites were sampled. The first three sites were then pooled, since they were collected in the same area of the IC2 (that has a motorway profile within the catchment). An average of more than 26,000 cars circulates daily in this road at full speed (typically more than 100 km h^{-1} for cars and in between 60 and 80 km h^{-1} for trucks, without making use of breaks or clutch. P4 represents a road with little movement (less than 50 cars per day). P5 has almost 6000 cars circulating daily. Being at a junction, some of the cars use breaks, clutch and steering wheel, which is expected to enhance the deposition of materials from the degradation of brakes and tyres. Finally, P6 records the circulation of 850 vehicles daily, without any major driving manoeuvres (Table 2).

2.2 Sampling

Sampling sites selection was made after a detailed survey of the entire catchment to find the best places representative of different traffic patterns, the accessibility and the existence of collection points. Four roads were selected. The IC2 (a motorway profile road) was sampled in three neighbour places, to cover the entire motorway profile. The details are given in Table 2 and in photos of Fig. 2.

Point 1, assembles three sampling points in the motorway bridge close to the catchment outlet.

Point 4 (P4) is located on a municipal road of local access, at Bordalo village. This site is characterised by a reduced number of vehicles. Located on County Road 572, the Central street crosses the medium area of the catchment and is the local access to an hospital and a basic school, to which cars access by reducing speed of stop and then turning at a junction (P5). This connects the top of Santa Clara parish to the Covões hospital and has a medium to high traffic intensity. Point 6 is located on the road that accesses the basic school Inês de Castro (Fig. 2).

A sampling device was designed to collect three samples allowing to monitor overland flow throughout the rainfall events. The first sampler had a container with 5 l that was blocked when full, so that the subsequent sample filled in a 35 l container that when filled in was blocked and the subsequent sample filled in a 70-l container. This way, we were able to sample a first sample with the first wash, and then two more for the rainfall event duration.

2.3 Analytical methods

pH and conductivity were determined right after collection using a portable metre (HATCH Test Kit). After reaching the laboratory (typically less than 0.5 h after sampling), turbidity

Table 2 Road characterisation

	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
Name	IC2					
Point ID	P1			P4	P5	P6
Slope angle (%)	7	5	2	0	2	10
Average number of vehicles per day	26,284	26,284	26,284	45	5782	850
Contribution area (m^2)	1496	308	1353	155	1250	364
Road width	20 m	20 m	20 m	5 m	10 m	12 m
Land use around sampling points	Forest/urban	Forest/urban	Forest/urban	Forest	Urban	Forest
Pavement age (years)	4	4	4	4	30	9
Pavement type	Draining bituminous concrete 35/50	Draining bituminous concrete 35/50	Draining bituminous concrete 35/50	Bituminous concrete 35/50	N/D	N/D

was measured, using a single beam spectrophotometer (HACH DR 2000). Sediments were evaluated in accordance with Method B 2540 (APHA 1998), based on sample evaporation at 103–105 °C to constant weight. Suspended sediments were determined previously through sample filtration, using filters with porosity <0.2 μm, and a vacuum pump. Volatile solids were determined after sample ignition in a muffle at 550 °C. For solids analysis, ceramic capsules resistant to high temperatures were placed in muffle for 1 h at approximately 550 °C to ensure the elimination of organic residues. The total solids present in the samples were determined by the gravimetric 2540B standard methods (APHA 1998).

The samples for determination of heavy metals were preserved with nitric acid (pH < 2), to inactivate the microorganisms present in the sample, and frozen for later analysis.

The determination of heavy metals in samples was performed by atomic absorption spectrophotometry (Perkin Elmer AA300), using method B 3111-Standard Methods (APHA 1998). Before the spectrophotometer analysis, samples were digested with nitric acid according with E 3030 Standard Method (APHA 1998). All samples were analysed in duplicate to confirm results, and results were repeated when values differ more than 10 %.

2.4 Statistic methods

In line with the paper objectives, statistic methods were kept simple, as we aim to prove the temporal distribution of road

runoff concentrations throughout the rainfall events; the values presented in Fig. 4 are the actual values as they occurred during the rainfall events. The box graphics present the average, the quartiles and the extreme values recorded. The significance of differences between road sites for each chemical parameters was explored by applying Kruskal-Wallis statistical tests ($p < 0.05$). Nonparametric comparison tests were used given the nonnormal data distribution. In the case of significant differences between sites, further analysis was applied with the least significant difference (LSD) post hoc test. Significant differences were identifies at $p < 0.05$. Statistical data analysis was performed using IBM SPSS Statistics 22 software.

3 Results

3.1 Meteorological characterisation

The sampling campaigns cover a wide range of meteorological conditions, during the spring, summer, autumn and winter of 2013, ranging from 0.2 mm events to 14.6 mm per day, which represents a normal rainy day during the wet season. During the summer, some events succeed to long dry spells (37 days), while for some campaigns, the dry spell was almost inexistent. Table 3 also presents the amount of rain 2 days, 1 week, 2 weeks and 1 month before each campaign. As expected, there are major differences on the amount of rainfall, the length of the
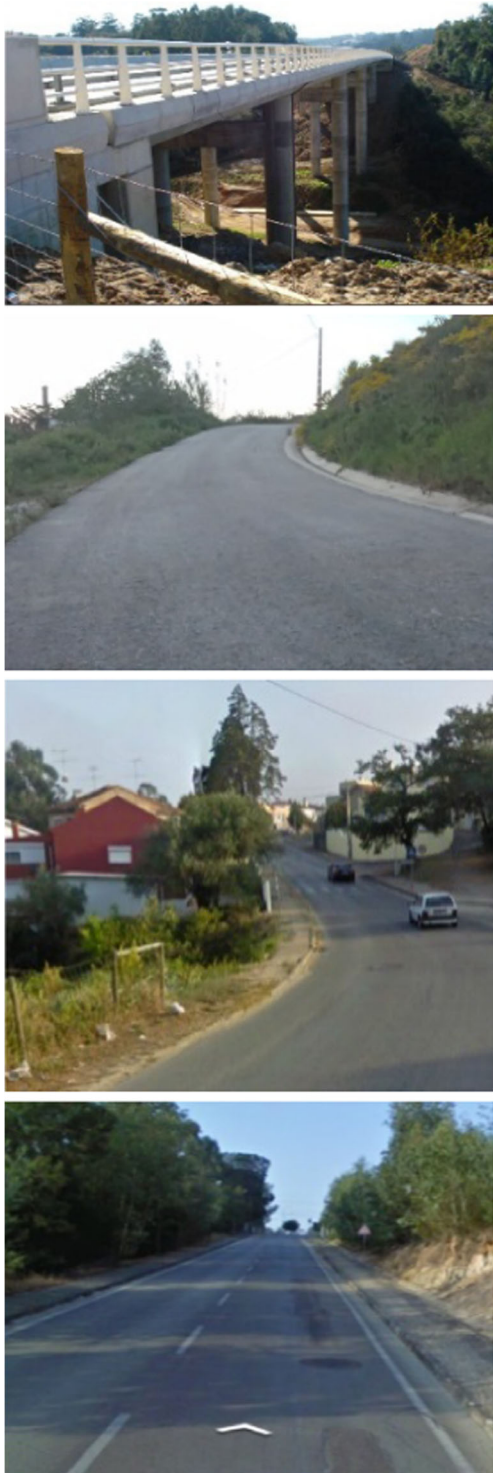
Fig. 2 Sampling sites (*left to right*): IC2 bypass, connecting Coimbra to Condeixa (P1); low traffic road located at Bordalo (P4); central street located at Póvoa de São Martinho do Bispo (P5); Ines de Castro street (P6)

antecedent dry spell and the amount of rain fallen previously for the different sampling campaigns throughout the year.

3.2 pH, conductivity, turbidity and solids

In what concerns the chemical outcomes, the different parameters present significant differences between the four road types monitored. The sites with more traffic present the highest pH values (Fig. 3a).

Road overland flow conductivity also shows the highest values for the sampling points with more traffic, and a wider dispersion throughout the sampling campaigns that have different length antecedent dry spells (Fig. 3b). Turbidity (Fig. 3c) presents a distinct distribution, with average values inferior to 50 mg L^{-1} for the motorway and above 200 mg L^{-1} for the junction (P5). The entire range of solids sampled showed a more uniform distribution between sampling points. The higher values for the motorway site differ from the turbidity results mainly because there is little input of tyre abrasion. The most driving demanding site P5, where abrasion is expected to be higher, presented the highest values for total solids (Fig. 3d), volatile solids (Fig. 3e), total suspended solids (Fig. 3f), and total suspended volatile solids (Fig. 3g).

Comparison between the various Fig. 3 graphics shows that the suspended solids represent the highest percentage of total solids captured, and that the volatile fraction is about half of total suspended solids.

3.3 Heavy metals

The box includes the average in the middle, the 25 % at the bottom and 75 % on top, and the segments indicate the maximum and minimum values monitored. Values are presented for the total amount and for the dissolved fraction, which allows to infer the percentage of particulate matter flushed by road overland flow. Some of the samples of total copper had concentrations above 0.5 mg L^{-1}, for the sampling sites with more traffic (Fig. 4a). Most of the material washed was particulate, since dissolved copper represented about one third of total copper (Fig. 4b). For sites with higher volumes of traffic, the maximum values recorded in the dissolved form represented between 20 and 25 % of the highest values of total copper measured. For the sites with less traffic, this percentage increased to around 50 %, although the concentrations were significantly lower ($p < 0.05$). The comparison of the average values shows a more explicit trend, with dissolved forms representing 40 to 60 % of total copper, while in the motorway, it represented 35 % and in the more demanding driving site, it represented less than 20 % of total copper.

Zinc values are presented in Fig. 4c (total) and in Fig. 4d (dissolved). Here, the percentage of dissolved zinc is substantially lower than total zinc, reason why the dissolved forms contribute only marginally to the total amount of zinc, a clear indicator of its vehicle origin, since most of the zinc is exported in the particulate form.

Table 3 Rainfall during and before the sampling campaigns

Campaigns	Total rainfall (mm)	Previous dry spell (days)	Rainfall previous to the rainfall event			
			2 days before (mm)	1 week before (mm)	2 weeks before (mm)	1 month before (mm)
8 May 2013	7.2	5	0	0.8	2	19.2
16 May 2013	14.6	6	0	7.2	9.2	11.2
6 June 2013	8.2	6	0	0.2	4.6	38.4
28 July 2013	0.2	37	0	0	0	0
3 September 2013	7.4	37	0	0	0	0
17 December 2013	4.4	5	0	0.2	3.2	5.2
31 December 2013	8.2	2	5	100.4	152.2	155.6

Cadmium values are typically less than 0.015 mg L^{-1}, presenting the highest values at the sites with highest traffic and/or where driving is more demanding, which results in higher degradation of the car components (Fig. 4e for the total cadmium; Fig. 4f for dissolved forms). The concentration values are significantly lower ($p < 0.05$) than for the other measured heavy metals, and the percentage of the dissolved component is dominant.

Lead is dominated by the particulate fraction, as can be inferred by the comparison between total lead (Fig. 4g) and dissolved lead (Fig. 4g). Although tetraethyl lead was phased out from mid-1970s as an addictive to gasoline, in Portugal, it was completely banned in 1999 and worldwide in 2000. Nevertheless, more than one and half decades, lead still appears on road wash out, although the dissolved fraction represents only a small percentage of the total amount, implying that most of it comes from car components.

3.4 Event distribution

Figure 5a presents the values for conductivity during the seven sampling campaigns performed, including a range of events from very wet, winter and spring events to others following extreme dry spells of more than 1 month in length. Details on the rainfall events sampled can be found in Table 3. Three samples were collected, at the beginning, middle and end of the rainfall events. Results showed higher conductivity values for the summer events, following extreme long and dry spells that decrease sharply throughout the event duration. In these cases, the events were not big enough to collect three samples. With the exception of the extreme dry events, values seldom exceeded 400 µS L^{-1}. The heavy traffic road with motorway profile presented the highest values.

For turbidity, the heavy traffic with demanding driving location presented very high values for the rainfall events occurring during the period. Surprisingly, the highest values did not occur during the first samples, but at the middle of the event, which may imply that some substances need a good wash to be released and become detectable. The highest values for all the sampling sites occurred during the summer events, following long dry spells, as expected. At the wet winter events, the low traffic site values are higher than expected, which may result from contamination from overland flow coming from surrounding areas and due to soil saturation entering the road system (Fig. 5b).

The total amount of solids presented higher values for the summer events, after long dry spells, with a sharp decrease in concentrations throughout the event. This implies that deposition is a key process in the transfer of traffic to the road pavement from where they are washed by overland flow. The comparison with the total volatile sediments (Fig. 5d) shows that most of the solids were organic in origin. They represent almost the entire amount of total sediments during the wet period events. They are typically a high percentage of total solids, although in some cases, suspended solids had a dominant role in total sediments. Values for the E5 extremely dry event show very high values for the heavy traffic, driving demanding area (Fig. 5e), most of it of organic origin given its volatile characteristic (Fig. 5f), which witnesses the provenance from car oil and tyres. Typically, the values for both the suspended solids and volatile suspended solids showed an increase following long dry spells and concentrations decreased throughout the rainfall event. The sampling sites with the highest values were those with heavy driving demanding traffic. The low traffic site appears to have an additional source that only becomes apparent following dry spells or under very wet conditions.

Copper presented higher values at the sampling sites with more traffic, seemed to build up storage during the summer long dry spells, was transported mainly in the particulate form (Fig. 5g, h), and decreased sharply throughout the event. The decrease of concentrations along the rainfall event was more evident in the
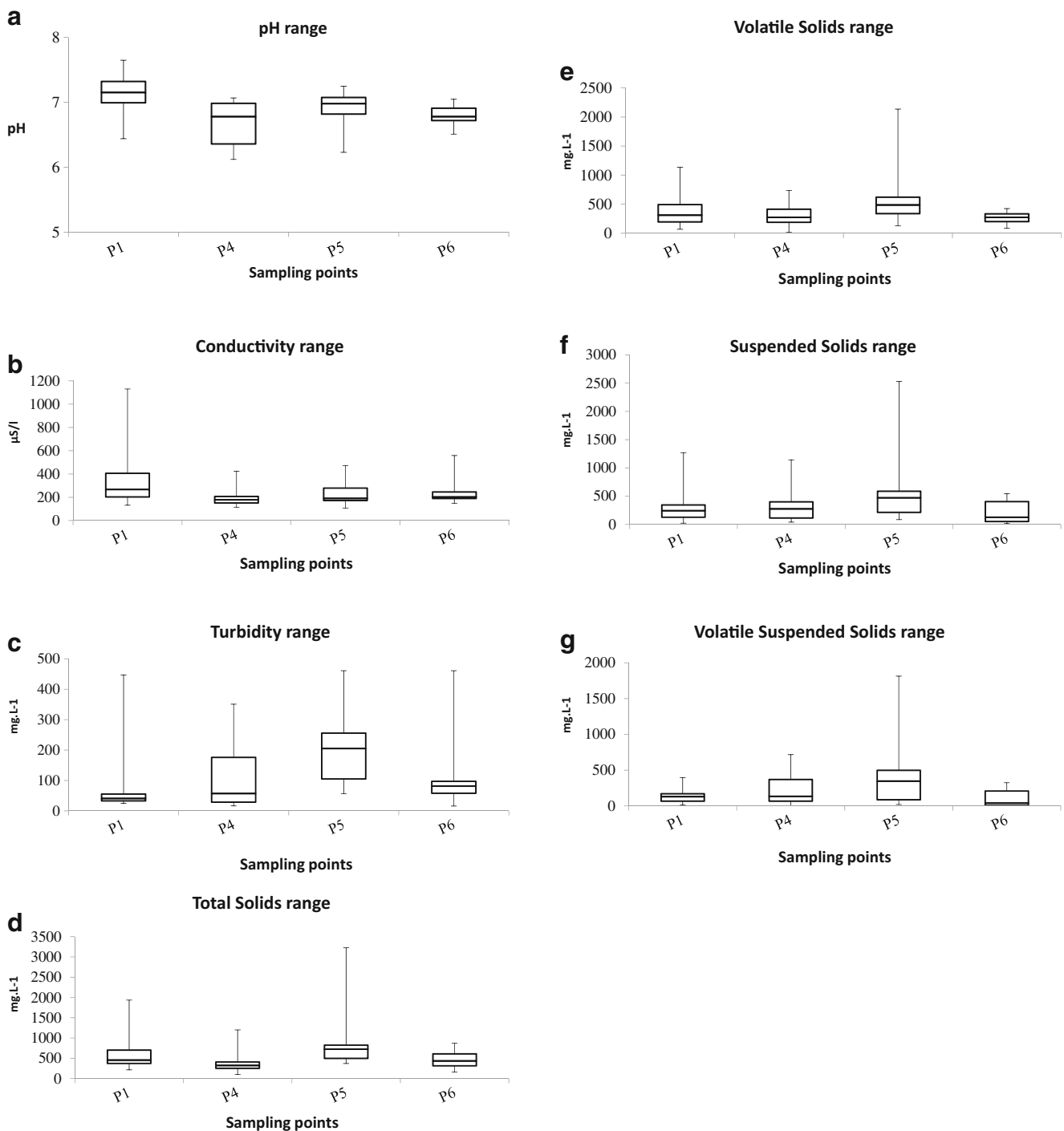
Fig. 3 Distribution of pH, conductivity, turbidity and solids range for the recorded events

dissolved form. The total copper, which witnesses the response of particulate forms, presented a more even distribution and sometimes increased throughout the rainfall event, which may be linked to the processes of transport of particulate matter.

In what concerns zinc, it is typically exported from roads in particulate form. Dissolved forms account for only a minor

percentage and are only evident during the dry period, as a result of accumulation during the long dry spells. Zinc concentrations were higher at the road with motorway profile (Fig. 5i, j).

Cadmium presented the lowest concentrations monitored (Fig. 5k, l), with most of this ion being mobilised in particulate form, especially during the wet periods.
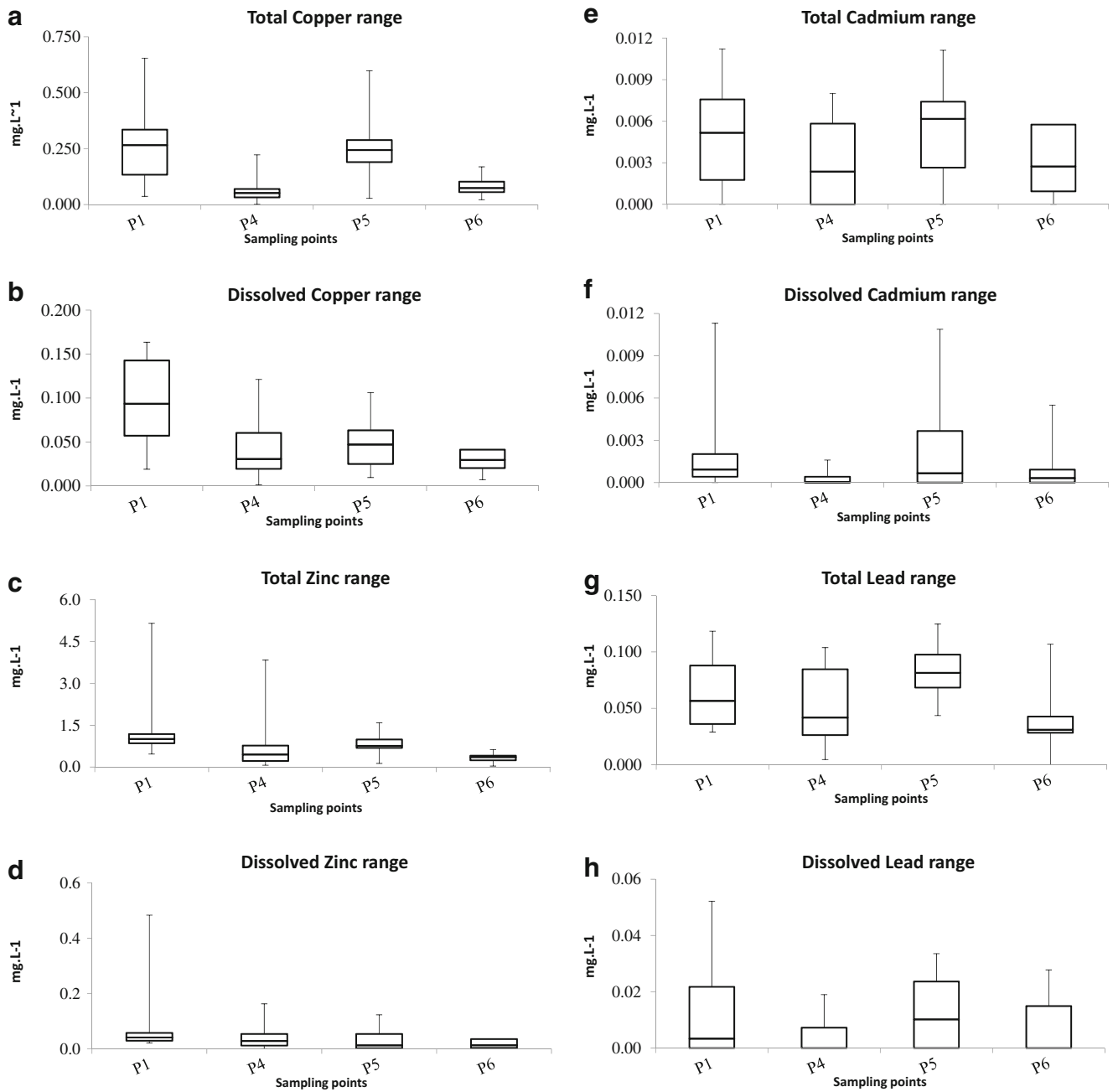
Fig. 4 Distribution of heavy metals range for the recorded events

During the summer events, dissolved forms in some cases accounted for almost the totality of cadmium exports.

The sites with heaviest traffic showed the highest cadmium concentrations.

Despite the ban from gasoline, lead is still present, and the Fig. 5m, n shows an intriguing distribution. It looks as if during the wet periods, the concentrations of lead were mainly exported in particulate form, while during the summer dry period events, it is exported partly in the dissolved format.

4 Discussion

The problem of heavy metal contamination in urban areas is a pressing issue, in face of the recent trend of renature the cities, and increase their overall resilience and food security by expanding the green infrastructure and promoting urban agriculture (e.g. Ferreira et al. 2013). This is overall important since even in a self-sustainable and renaturing philosophy, there is a tendency to use local urban sources of water and potential soil fertilisers from waste to close the mass loops and

a

Event distribution of Conductivity

b

Event distribution of Turbidity

c

Event distribution of Total Solids
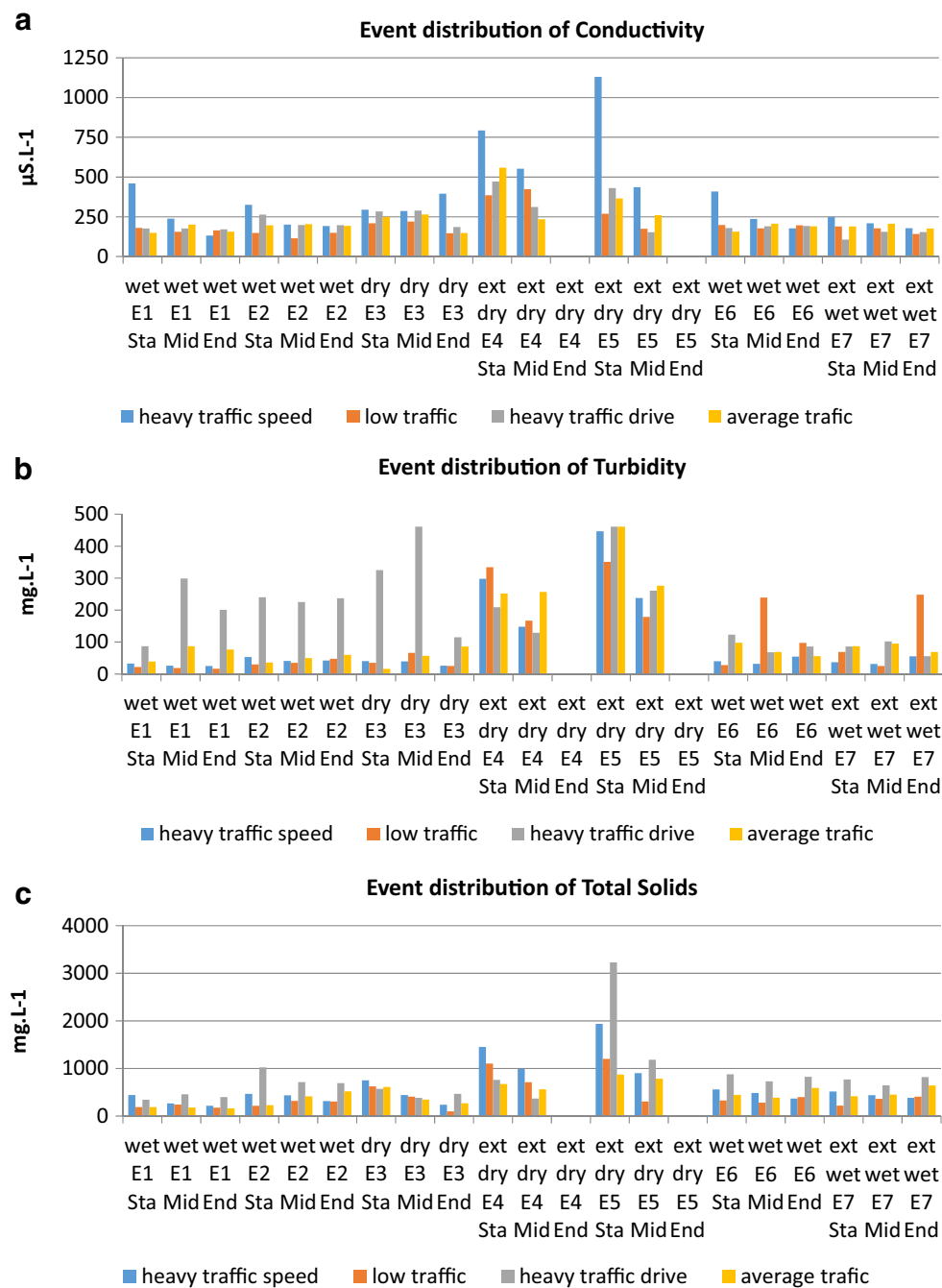
Fig. 5 Pollutant distribution for the monitored rainfall events

reduce the disruption of the natural cycles and the energy consumption, towards a lower carbon economy. These may nevertheless be hindered by the impact of pollution in the environment and human health, especially if pollutants such as the heavy metals get into the food production and processing systems (see for instance Roy and Mcdonald 2015).

In this context, particular attention has to be paid to the sources of heavy metal pollution and especially in the transmission to the water and soils, which may represent a risk to human and ecosystem health (e.g. Brunekreef and Forsberg 2005), if it gets into the food chains. Transition metals, such as Cu, Zn, Fe, Ni, Cr and Mn, are likely related to toxicity. Schwarze et al. (2007) state that coarse particles can induce inflammatory effects, while Perez et al. (2009) found that cardiovascular and cerebrovascular mortality are linked to increased levels of particulate air pollution.

Cars are often considered one of the main sources of heavy metals in urban environments (Thorpe and Harrison 2008;

d

Event distribution of Total Volatile Solids

■ heavy traffic speed　■ low traffic　■ heavy traffic drive　■ average trafic

e

Event distribution of Suspended Solids

■ heavy traffic speed　■ low traffic　■ heavy traffic drive　■ average trafic

f

Event distribution of Volatile Suspended Solids

■ heavy traffic speed　■ low traffic　■ heavy traffic drive　■ average traffic
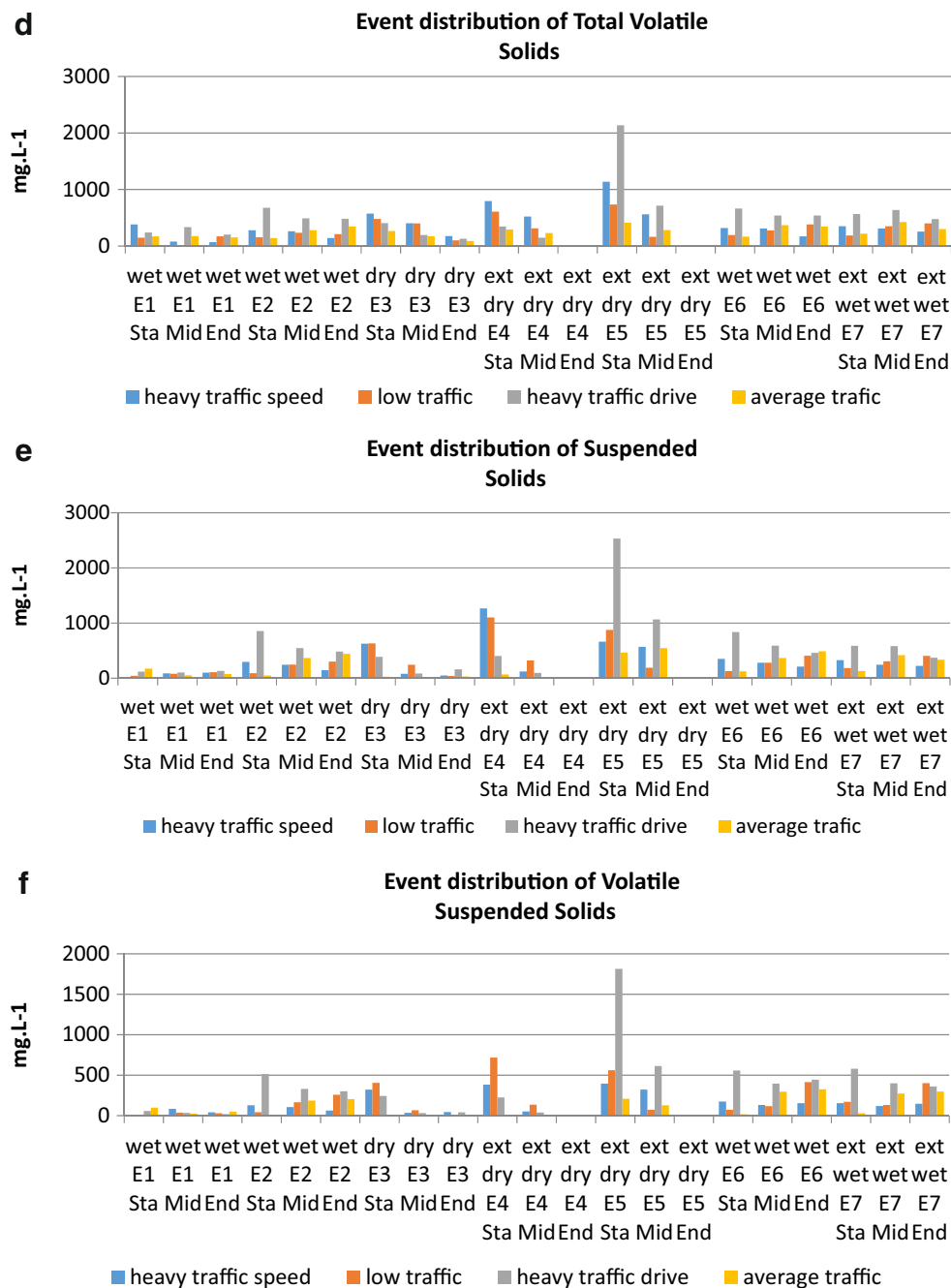
Fig. 5 continued.

Lundy et al. 2012), particularly at locations heavily influenced by traffic through both direct deposition and subsequent resuspension processes. In this context, traffic is a major contributor to diffuse pollutant in many urban and suburban environments (Revitt et al. 2014).

Overland flow quality from roads, like all diffuse urban runoff chemical composition, is expected to be highly variable (Freni et al. 2008) and varies with factors such as surface type, storm intensity and frequency and the antecedent conditions (Greenstein et al. 2004). Road wash-off of surface

accumulated pollutants is expected to increase significantly the diffuse pollution that may exceed the thresholds established by the EU Water Framework Directive (Revitt et al. 2014).

The results presented in this paper show unequivocally that the driving mode, together with the number of cars passing by a given location has a significant impact on the amount of heavy metals deposited and then washed-off during rainfall events, in line with the findings of Revitt et al. (2014).

g

Event distribution of Total Copper

h

Event distribution of Dissolved Copper

i

Event distribution of Total Zinc
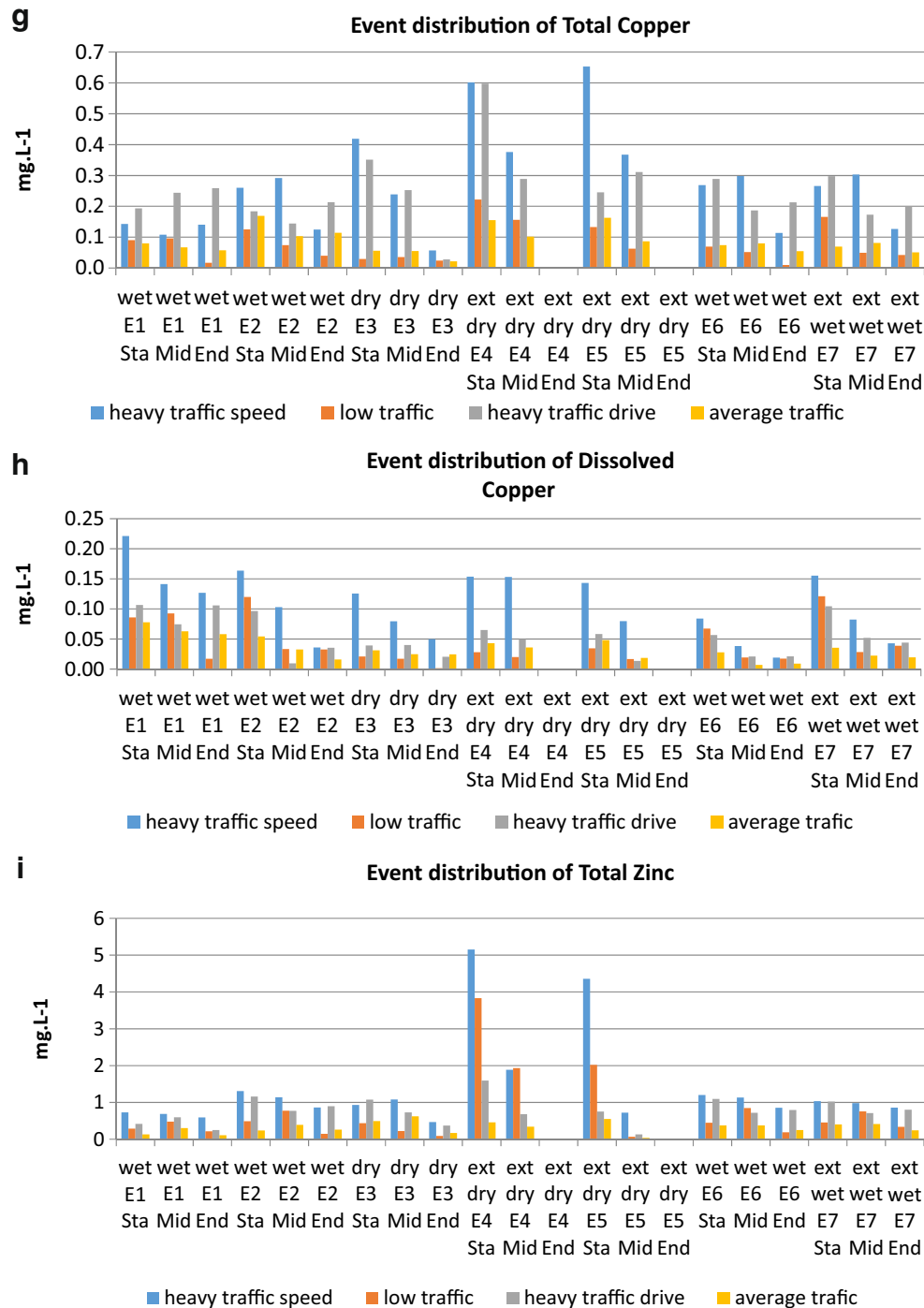
Fig. 5 continued.

4.1 pH, turbidity and solids

pH presents the highest values at places with more traffic and/ or with traffic abrasion (i.e. the motorway and the junction sites), as a result of the amount of cations released.

Turbidity, being influenced by particulate matter, presents the higher values in the areas where steering manoeuvres are more frequent and smaller where cars drive at full speed with little

steering or brake use. Total solids present similar distribution. The comparison with the total volatile sediments shows that most of the solids were organic in origin. They represent almost the entire amount of total sediments during the wet period events, which imply a provenance from oil-based products, such as engine lubricants or gasoline/diesel and other car components, such as tyres. Some of the solids reaching the sampler were dragged by water, while most solids get there suspended in overland flow.

j

Event distribution of Dissolved Zinc

■ heavy traffic speed　■ low traffic　■ heavy traffic drive　■ average trafic

k

Event distribution of Total Cadmium

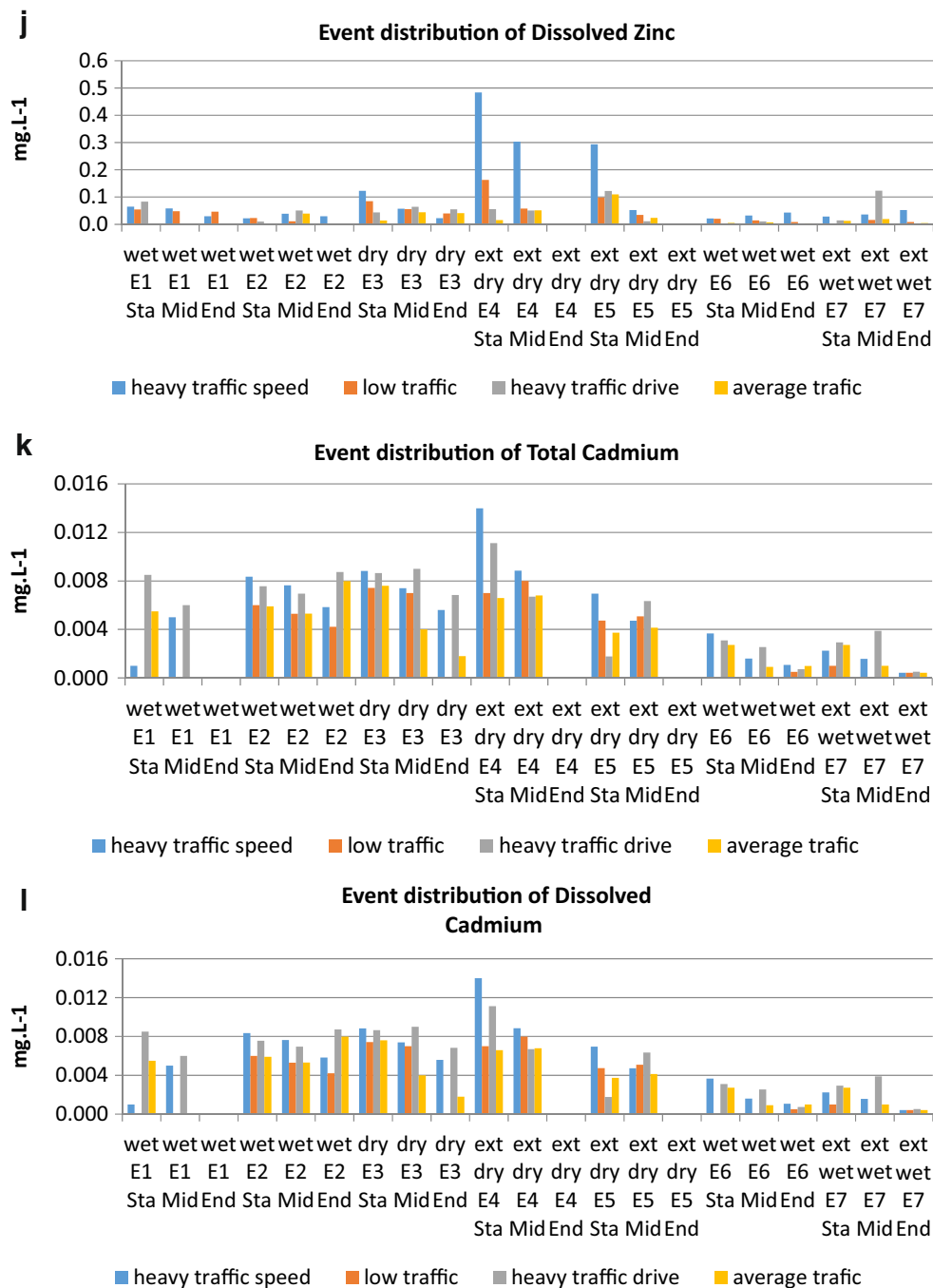■ heavy traffic speed　■ low traffic　■ heavy traffic drive　■ average trafic

l

Event distribution of Dissolved Cadmium

■ heavy traffic speed　■ low traffic　■ heavy traffic drive　■ average trafic

Fig. 5 continued.

4.2 Heavy metals

The results show that a substantial part of the heavy metals washed off from roads to nearby soils and aquatic ecosystems are in the particulate form. These are produced by friction or abrasion within braking systems and between tyres and surface materials. The quantities released may cover several orders of magnitude, influenced by the mode of use (Thorpe and Harrison 2008). The results presented show that the concentrations of heavy metals washed away vary with the traffic conditions and with the antecedent conditions, namely with the length of the previous dry spells; therefore, the highest peaks are found following the first autumn rainfall events. Heavy metals can be originated from bitumen and asphalt. In fact, Sorme (2003) reported concentrations of 13 mg kg^{-1} of copper, 52 mg kg^{-1} of zinc, 0.09 mg kg^{-1} of cadmium and 24 mg kg^{-1} of lead, which implies that some of the values ascribed to a second source can be originated in the
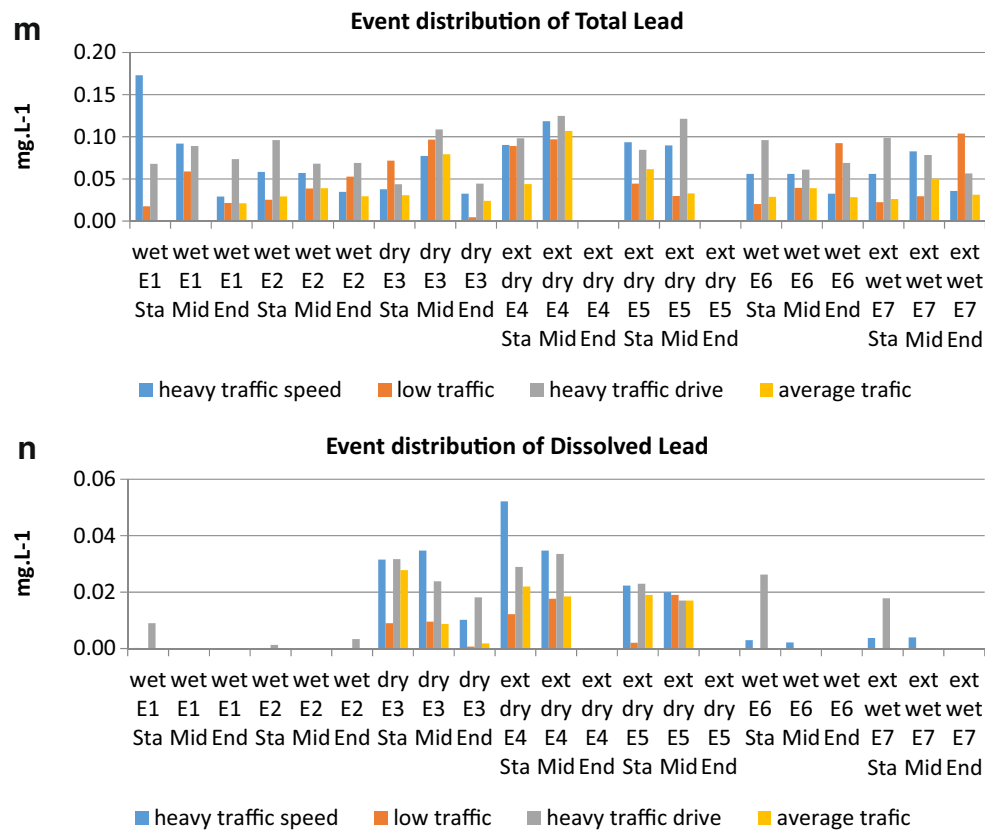
Fig. 5 continued.

type of pavement. This is the case for zinc. In fact, although the sites with more traffic show the highest values of metals, particularly in the particulate form, with some sampling sites present more than 1 mg L^{-1} in average, the high values of the low traffic sampling site seemed to indicate the existence of an additional source that is also dependent on the accumulation time. This is consistent with the concentrations of heavy metals in soils near highways, reported by Trujillo-González et al. (2016), although these authors have found higher concentrations in commercial areas, probably as result of a larger number of driving actions.

Another factor that may influence the export of sediments and heavy metals is the rainfall event size and intensity. In this respect, all the monitored events are similar in size and intensity. Nevertheless, the samples taken at the middle and end of the events show consistently lower concentrations than those collected at the begging of the events. At the beginning of the event, the amount of material available to be washed off is higher and decreases throughout the rainfall event.

Soonthornnonda et al. (2008) predicted that metals are likely to be removed from a surface in the order Pb > Ag > Zn > Cu > Ni > Hg > Cd. This partly explains the sequence found in our study: Zn > Cu > Pb > Cd, meaning that removal rates are also affected by source availability. In fact, lead, omnipresent

up until 2000, and that can be find in more industrialised areas and near long-term heavy traffic sites (see Dias-Ferreira et al. 2016), may not be so easily available at low traffic locations, or where the new roads were built after the 2000 lead ban as a gasoline addictive. In addition, the fact that since from early times was used in construction (house paints) and pluming, makes it a pervasive element. The results indicate a double source of lead, with the export during the wet seasons coming from the traffic (break wear, motor oil) and the concentrations during the dry season being partly the result of atmospheric deposition. The concentrations found in this study are consistent with these reported by Lundy et al. (2012), ranging from 0.01 to 0.44 mg L^{-1} in average.

The cadmium concentrations found are within comparable range to those found by Lundy et al. (2012). These authors found values lower than 0.005 mg L^{-1} for cadmium, in average, which matches the values found at the Ribeira dos Covões catchment, where the highest values can reach twice that value, but the average values are within the 0.002–0.006 mg L^{-1} range. The maximum values are nevertheless significantly lower than those found by Shorshani et al. (2015), a pattern extended to all studied heavy metals and can be ascribed to a lesser polluted environment, since the data was collected in the vicinity of Paris. The results are

consistent with its main source, namely from tyre wear degradation (Sansalone and Buchberger 1997).

Zinc is also within the range found by Lundy et al. (2012), for suburban roads that in average are within the 0.02–1.9 mg L^{-1}. At Ribeira dos Covões catchment, the average values for zinc are around 1 mg L^{-1}, although for some samples, it may exceed 5 mg L^{-1}.

Lundy et al. (2012) found copper concentrations in runoff ranging from 0.01 to 0.12 mg L^{-1}, which are in range with the sampling sites with lower traffic (P4 and P6) but are significantly lower than those measured at the heavy traffic sampling sites, which can exceed 0.2 mg L^{-1} in average.

One of the more important aspects in what concerns health impacts is the impacts of heavy metals and metalloids in particulate form, sourced by vehicle-wear particles (brakes, tyres, rotor, discs and catalysts) as a result of abrasion and resuspension processes, given their high potential health burden (Amato et al. 2010a). The results show that this is particularly worrying for copper and lead, but especially for zinc, where more than 80 % of the exports are on particulate form.

Several solutions have been proposed, especially to reduce the resuspended by traffic-generated turbulence (Amato et al. 2010a), although sweeping, water flushing and use of chemical suppressants will have an overall negligible impact on the health impact, since the overland flow that washes off the pollutants will end up at the urban soils and at the aquatic ecosystems.

Nevertheless, little is known on the potential fade of those pollutants and the best way to treat them, despite the work of Amato et al. (2010a). Improved information about the chemical composition and the rates of emission is important to implement source-oriented mitigation measures, health studies and to model source contributions.

5 Conclusions

A major issue in what concerns the threats to human and ecosystem health in urban areas is the presence of heavy metals, and the related processes that govern their source, transport and fate or uptake by the vegetation. Traffic is wildly acknowledged as a major source of pollutants, namely heavy metals in urban environments, especially when the wash off overland flow is diverted to local soils or to the local aquatic ecosystems.

This study brings some light on the role of roads and traffic on the pollution generation and transport, namely in what concerns heavy metals. Results show that a significant part of heavy metals, especially zinc and lead are washed off from roads in the particulate form, which may represent an additional problem for heavy metal impacts management in urban areas.

Concentrations are higher at the sites with more traffic and especially when the vehicles have to perform driving manoeuvres, such as break and turn. This increases the abrasion of tyres and breaks and is responsible for higher concentrations of solids and heavy metals.

The highest concentrations were recorded during the summer rainfall events, which occur following long dry spells of more than 1 month.

The samples collected along the rainfall events show a decrease in concentrations throughout the rainfall events, with the samples collected at the beginning of the event showing higher values than those collected at the middle or the end of the events, which witnesses the reduction of material storage at the road surfaces.

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