

Traffic air pollution monitoring based on an air–water pollutants deposition device

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Abstract An air water surface sampler device was developed and used to evaluate the atmosphere deposition due to the urban traffic air pollution in the business center of a mid-sized city. The indicator adopted to assess the cumulative air pollutant deposition in the surface of the device was the electric conductivity that was measured on a regular basis during the experiment. Additionally, a digital camera was used to count the passing traffic in the road of the study site. Water samples were also taken from the device reservoir, and dissolved metal concentrations (copper, iron and zinc) and acidity/alkalinity were determined in the laboratory. The obtained results were compiled and analyzed in order to evaluate the performance of the device and the relation between the atmospheric deposition and the traffic activity under different meteorological conditions. The research successfully proved that the device was able to evaluate the impact of pollutant emissions related to city traffic. It was also proved that electric conductivity can be used as an indicator to evaluate the cumulative deposition of air pollutants from road traffic. A significant correlation (Spearman's rank) between the accumulated traffic and electric conductivity (dry period: $\rho = 0.991626$ and wet period: $\rho = 0.810526$) was observed.

Keywords Air pollution · Monitoring device · Urban pollution · Urban traffic

Introduction

Environmental impact of transport and mobility within urban areas is becoming a major social concern for planners and cities managers. Air quality deterioration is frequently related to traffic emissions, and actually, alternative mobility solutions are considered in order to decrease air pollution. Quantifying the environmental impact of transport and mobility solutions became an important issue assessing those traffic solutions.

Motorized traffic is nowadays recognized as the major contributor to air pollution in urban areas. Efficient transport systems are an important part of the world's economic growth and human life quality. Nevertheless, the traffic is also one of the main negative factors regarding air quality. A series of substances emitted by motor vehicles have been qualified as toxic. Some traditional gases (SO₂, NO_x, CO₂ and CO), HAPs, PM and several metals (Cu, Fe and Zn) are associated with automobile activity (Fenger 1999; Fierro 2000; EMEP/EEA 2013).

This environment problem is being studied using a holistic approach to understand the influence of land use on transportation emissions in urban and suburban areas (Hong and Goodchild 2014; Monzón et al. 2007). Urban transport solutions, behind the inherent efficiency requisites, must be improved to raise the quality of life and the cities environment (Yigitcanlar et al. 2010). In this context, quantifying and monitoring impact of urban transport has become an important issue during decision making and planning for more livable and sustainable cities (Liu et al. 2014; Vanhulsel et al. 2014).

There are many pathways of transport and behaviors of pollutants after its release. One of them is called atmospheric deposition. This deposition is defined as the process by which pollutants are transferred to any terrestrial and

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aquatic surfaces (Valigura et al. 1996; Chu et al. 2007). The deposition of pollutants takes place by two main mechanisms, wet deposition and dry deposition, which together are called bulk deposition or total atmospheric fallout (Park 1995; Chu et al. 2007).

A wide range of emission and deposition of pollutants has been monitored, either in the form of exhaust particulate matter, fluid losses, drips, spills or wear and tear of products until the re-suspension processes resulting from the movement of vehicles (Pitt et al. 2004; Silva and Mendes 2012).

Vehicles burning off gasoline and diesel are responsible for exhaust emissions of CO, NO_x, NMVOC, CH₄, CO₂, N₂O, NH₃, SO_x, exhaust PM, PAHs and POPs, dioxins and furans, and heavy metals contained in the fuel (lead, arsenic, cadmium, copper, chromium, mercury, nickel, selenium and zinc) (EMEP/EEA 2013).

Sulfur dioxide and nitrogen oxides are strong acidic gases. Even in small concentrations, these gases can be responsible for the formation of acid rain. Once in the atmosphere, NO_x and SO₂ are transformed into nitric acid and sulfuric acid and fall back to earth through wet deposition such as rain, snow, fog, cloud water, and dry deposition of acids attached to particles, gases and aerosols. Rain and snow are somewhat naturally acidic due to the combining of carbon dioxide and water vapor in the air, which forms weak carbonic acid (DEC 2012).

Carbon monoxide (CO) results from incomplete combustion of fuel. It is a colorless, odorless and tasteless gas that is slightly lighter than air. Based on atmospheric behavior, once emitted to the atmosphere CO is oxidized to CO₂ (Butterwick et al. 1991).

Metals result mainly from vehicular activities such as tire wear (Zn, Pb, Cr and Ni) and wear of brake linings (Ni, Cr and Pb) (Adekola et al. 2002), wear of studded tires (Fe, Ni, Mo, Cr, Co, Cd, Ti and Cu), corrosion of bushings, brake wires and radiators (Cu, Fe, Ni, Cr and Co), and the various types of de-icing chemicals and friction materials used on road surfaces for slipperiness control especially in temperate climate countries (Adekola et al. 2002).

Pb is commonly found in exhaust emissions from the tailpipe. This metallic element has been used as an additive in gasoline to the present day, particularly in developing countries. Due to the increasing awareness of environmental pollution, the rates of Pb emissions have strongly decreased in Western and Central Europe since the late 1970s (Ruhling and Tyler 1984; Berg and Steinnes 1997; Ballach et al. 2001; Massadeh and Snook 2002). This is why Pb can no longer be taken as an indicator for traffic-induced water pollution in Europe.

Urban streets sediments have limited residence times. The intensity of vehicle activity, together with wind action will determine the transport patterns of deposited particles.

Pitt et al. (2004) concluded that airborne particle concentrations during downwind roadside events were about 10 % greater than during upwind conditions. About 80 % of the particles are in the 0.5–1.0 µm size range. However, about 90 % of the weight of the particles is associated with particle sizes greater than 10 µm. It was also found that the rate of particles re-suspension from street surfaces increases when the streets are dirty (infrequently cleaned) and varied widely for different street and traffic conditions. The re-suspension rates were calculated based upon observed long-term accumulation conditions on street surfaces for many different study area conditions and varied from about 0.30 to 3.6 kg per km of street per day. In a similar study, Cowherd et al. (1977) reported a wind erosion threshold value of about 5.8 m/s. At this wind speed or greater, significant dust and dirt losses from the road surface could result, even in the absence of traffic-induced turbulence.

Dry deposition is the transfer of airborne gases and particles to the earth's surface, including soil, water and vegetation (Seinfeld and Pandis 1997; Odabasi et al. 1999). The removal rate by dry deposition is a function of the physical and chemical properties of the pollutant, meteorological conditions (temperature, wind velocity, atmospheric stability) and surface characteristics (Odabasi et al. 1999).

Direct measurements of dry deposition using surrogate techniques were largely taken in the past (Yi et al. 1997, 2001; Shahin et al. 1999, 2002; Odabasi et al. 1999; Cakan 1999; Franz et al. 1998; Tasdemir 1997; Holsen and Noll 1992). One of these works refers to the use of the air–water surface sampler, AWSS, which is a device used as an approach to measure the dry deposition process in surface water. The main principle was to use water that flows on the surface of a plate with known area to capture dry deposition. In other research, AWSS has been widely used for various purposes. For example, Sakata and Marumoto (2004) used AWSS to measure dry deposition fluxes and deposition velocities of trace metals in Tokyo metropolitan area. Odabasi et al. (1999) used AWSS to measure the dry deposition and air–water exchange of polycyclic aromatic hydrocarbons. And Shahin et al. (2002) compared the use of AWSS and modeling results.

In this work, an air–water surface sampler (AWSS) was used to enable capturing and storing emissions from road traffic. This device acts as a simplification of the process of local deposition from the atmosphere in exposed surfaces. The water surface, on the one hand, acts as an infinite sink for non-volatile species, such as trace metals and highly soluble gases and, on the other hand, does not allow sediments to fly away by wind and/or turbulence. The sampler has a plate that is continuously replenished with water, evenly spread across its surface, and the water flow is poured back into the tank. During the flow in the plate



surface, the water catches and traps the particles that deposit from the air. In the tank, the caught substances have enough time to be dissolved and homogeneously mixed as a result of the continuous circulation. The surface of the sampler is representative of a surface of water in an aquatic environment under low energetic conditions. The parameters used to assess air pollution deposition were pH, EC and dissolved metals such as copper (Cu^{2+}), iron (Fe^{2+}) and zinc (Zn^{2+}).

This research aims to assess the efficiency of a low cost device to measure, in a short-term time scale, the pollutant loads resulting from urban traffic.

The field work takes place at Viana do Castelo (NW Portuguese city) and was carried out during two different periods: the first period from May 29, 2012 to May 31, 2012, and the second one during June 5, 2012 and June 6, 2012. In both periods, the continuous measurements and water samples collection occurred between 8 am until 8 pm.

Materials and methods

In this section, a brief description of the sampling site, monitoring program and procedures, and meteorological data collection are presented. More details are available in Nurusman (2012).

Sampling site location

The experimental work was carried out in Viana do Castelo, Portugal. This city is located in the border of

the estuary of river Lima. Air pollution concentration was taken on the side of the monitored street, next to the sources of pollution from vehicle traffic. The sampler was placed 3.5 m from the edge of the Av. dos Combatentes road and increased 1.2 m from the pavement. Figure 1a, b shows the sampling device position for this study.

Sampling procedure

The field experiment was developed during two periods under different rain conditions: one dry period at the end of May 2012 and one wet period at early June 2012. The traffic data collected allowed the subsequent relation with the atmospheric deposition.

The AWSS was used as a catcher or trap for air pollutants, which are scattered in the atmosphere as a result of urban traffic on Av. dos Combatentes da Grande Guerra. The AWSS unit was placed on the side of the street, free from obstructions and able to interact directly with the activity of vehicles/traffic. The AWSS reservoir was filled with a water volume of 7.5 L and was kept in continuous circulation during the monitoring period. During the night, the sampler was covered and stored in an enclosed space. During the monitoring periods (wet and dry), the volume of water in the reservoir was kept constant by adding water to compensate losses due to evaporation and samples collection. On the wet period, less water was added to the device reservoir.

Measurements of water properties were taken in two stages. The first stage was a field measurement of electric conductivity (EC) using a portable EC meter. These

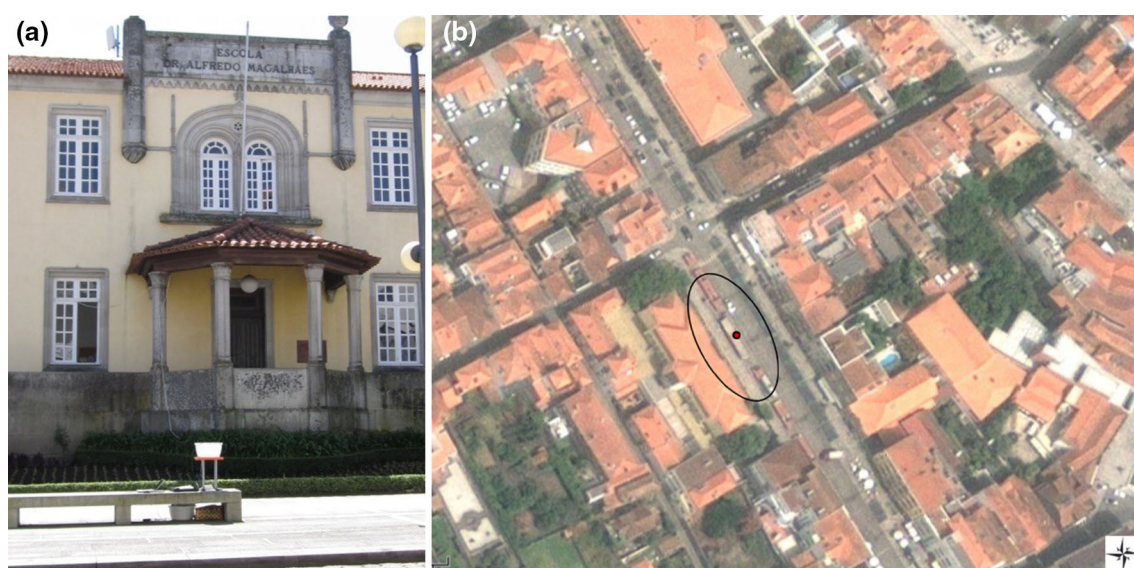


Fig. 1 Air–water surface sampler location: **a** front view, **b** aerial view

measurements were taken periodically, every hour throughout the monitoring periods.

The second stage consisted in the characterization of dissolved metals (Cu, Fe and Zn) from samples collected from the AWSS. The laboratory analyses were carried out at the Hydraulics Laboratory, of the Department of Civil Engineering of the University of Minho. The samples were conditioned in a sterilized bottle and kept in a cooler box. Within less than 48 h, the laboratory characterization was carried out. Characterization included the measurement of pH and of concentrations of dissolved Cu^{2+} , Fe^{2+} and Zn^{2+} .

Traffic counting campaign

Vehicle counts were made in Avenida dos Combatentes da Grande Guerra simultaneously with the AWSS sampling. Using a digital camera, all vehicles and traffic activity were recorded during the working hours (08:00–18:00). In each day, the counting campaign was continuously for 10 h. The vehicles were classified as light or heavy vehicles. The accumulated number of vehicles used for the analysis was obtained from the sum of the equivalent number of vehicles. The conversion to equivalent number of vehicles was

made through the emission factors of PM₁₀ of light and heavy vehicles. According to Silva et al. (2010), the emission factors of PM₁₀ calculated to the city of Viana do Castelo were 0.20997 gr PM₁₀/km and 0.01823 gr PM₁₀/km, for light and heavy vehicles, respectively, and the equivalence factor of heavy vehicles was 11.518.

Air–water surface sampler

The AWSS unit was designed and developed for this study, based on the one proposed by Sakata and Marumoto (2004) and Chu et al. (2007) with some modifications. Some improvements of the sampler were made to measure the wet and dry deposition and to enable the continuous monitoring during sampling periods. The probe of a portable EC meter was used inside the reservoir allowing the continuous monitoring of EC. The cover was removed favoring this way pollutants deposition, the reservoir water level is maintained just 6 cm below the depositional plate reducing the hydraulic head, and consequently the pump power requisites to maintain the closed hydraulic circuit. The probe with automatic temperature compensation guarantees also corrections due to temperature variations. The constant water depth in the reservoir ensures a constant

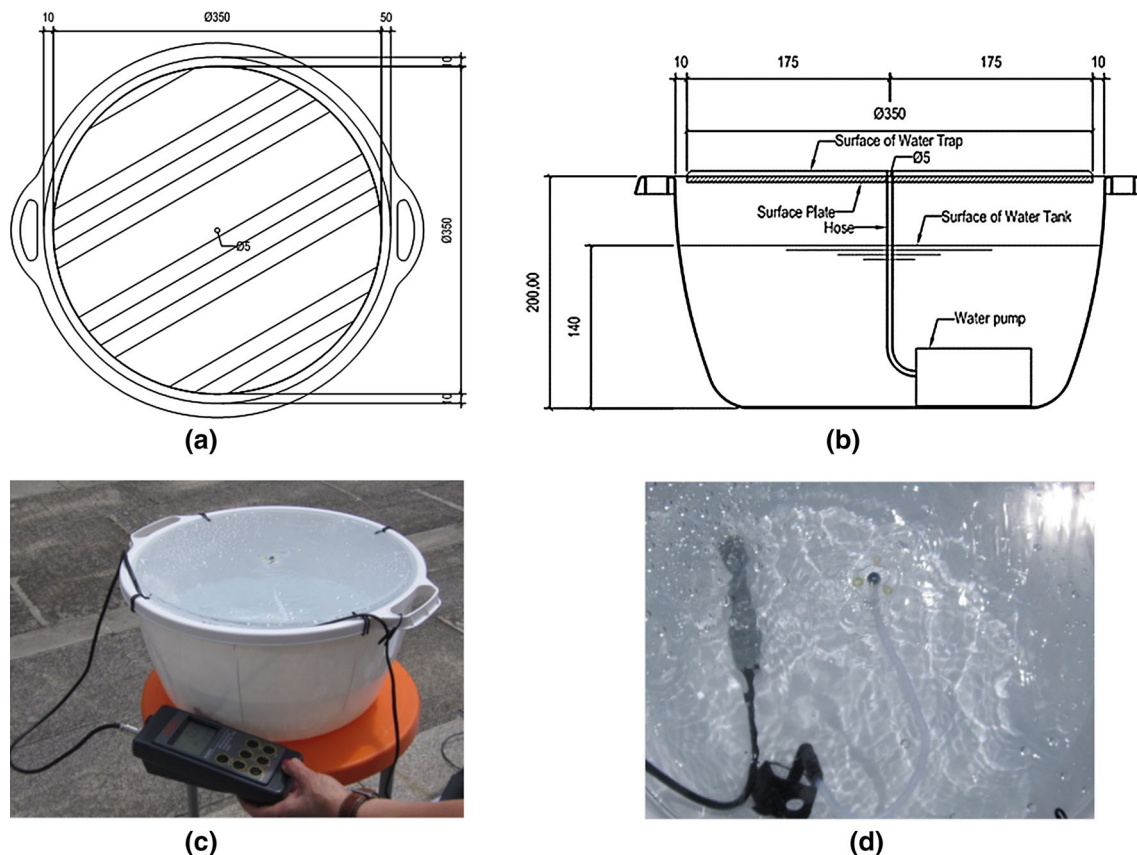


Fig. 2 Air–water surface sampler: **a** top view, **b** front view, **c** EC meter, **d** water spread on the AWSS plate. *Dimensions in mm



debit of pumped water and therefore a constant retention time at the AWSS plate.

This AWSS (Fig. 2a, b, c and d) unit has three principal parts: (1) a bucket with 200 mm of height and top inner diameter of 410 mm. The purpose of this bucket is to serve as the plate holder and water reservoir; (2) a circular plate with 350 mm diameter; (3) a water pump with maximum debit of approximately 30 L/h.

An inlet cap was put on the center hole of the plate, which was intended to even the pressure, so that the water can be easily distributed horizontally in the entire surface of the plate.

The plate was placed horizontally at the top of the bucket. When the AWSS is operating, pumped water enters the AWSS plate from the center hole and flows to its border. It is needed some time to get the water to cover the whole plate. The surface-water depth is 3 mm and has the same height as the top edge of the bucket. The retention time at the plate of AWSS was 2 min and 18 s. This way the water in the plate does not experience saturation. The AWSS reservoir is continuously replenished with water to maintain a constant water volume in the device (Tasdemir 1997; Odabasi et al. 1999; Shahin et al. 2002).

Analysis methods

A field measurement of EC was taken using a portable EC meter (Fig. 2c, d). Laboratory analysis focused on measuring and characterizing several dissolved substances in the collected water samples of the AWSS unit. Analyzed parameters include the acidity (pH), electrical conductivity (EC) and dissolved metals such as copper (Cu^{2+}), iron (Fe^{2+}) and zinc (Zn^{2+}). Several instruments were used (Table 1), and the detailed principles of operation and the characteristics of the analyzers can be found in the web page of Hanna Instruments (www.hannainst.com).

Meteorological data collection

Temperature, wind speed, wind direction and relative humidity were measured at an automatic meteorological station located at Chafé, Viana do Castelo, the nearest meteorological station with available data (about 7 km from the study site). Hourly averages of registered data are processed and are available at the Portuguese Meteorological Agency Services. The instruments used at the automatic meteorological station are listed in Table 1.

Blank test and detection limit

The blank test can be used to determine the water contamination used in the sampling process. Background

Table 1 Measuring methods

Parameters	Method
Temperature and relative humidity	Thermo-hygrometry. Air temperature at 1.5 m height, average from the last 10 min of each hour (°C)
Humidity	Relative humidity at 1.5 m height, average from the last 10 min of each hour (%)
Precipitation	Udometry. Precipitation at 1.5 m height, value accumulated for each hour (mm)
Wind speed and direction	Ultrasonic anemometry 2D. Wind speed (m/s) and direction (°), average from the last 10 min of each hour
EC (electric conductivity) and TDS (total dissolved Solids)	Probe with 4-Ring potentiometric probe EC-TDS-NaCl meter, HI 9835
pH and temperature	Portable pH/ORP Meter HI 7662 stainless steel temperatures probe
Dissolved Cu^{2+} , Fe^{2+} and Zn^{2+}	Photometric analyzer, HI 83 200

water contamination was monitored using operational blanks (unexposed water) which were analyzed together with field samples. In this study, the water contamination is insignificant and can be ignored. The concentrations of the background contamination are 0.063, 0.051 and 0.001 $\mu\text{g m}^{-3}$ for Cu^{2+} , Fe^{2+} and Zn^{2+} , respectively, and 92.5 $\mu\text{S cm}^{-1}$ for electric conductivity. Detection limit was used to determine the lowest concentration value that can be obtained and considered statistically different from a blank. The detection limits of the elements in this study were 0.01, 0.01 and 0.03 mg/L for Fe^{2+} , Cu^{2+} and Zn^{2+} , respectively, and 0.05 $\mu\text{S cm}^{-1}$ for electric conductivity.

Results and discussion

It was expected that the AWSS device effectively capture emissions produced by vehicles on the road, especially metals (Cu^{2+} , Fe^{2+} and Zn^{2+}) since, at this Atlantic coastal city location, the prevailing winds blow from the ocean and no other air emissions are expected at the site.

The obtained results were compiled and analyzed in order to assess the relation between atmospheric deposition, traffic activity and meteorological conditions. The effectiveness of the AWSS in monitoring the occurrence and the exposure level of pollution in urban streets environments were also assessed.



Table 2 Number of vehicles

	08:00 09:00	09:00 10:00	10:00 11:00	11:00 12:00	12:00 13:00	13:00 14:00	14:00 15:00	15:00 16:00	16:00 17:00	17:00 18:00	
<i>Dry period</i>											
Light vehicle	334	310	321	328	339	392 ^a	404 ^a	311	351	438	29-May
Heavy vehicle	14	11	22	16	10	17 ^a	20 ^a	14	13	11	
Total equivalent vehicle	495	437	574	512	454	588 ^a	634 ^a	472	501	565	
Light vehicle	331	311	355	325	391	392 ^a	404 ^a	363	342	459	30-May
Heavy vehicle	14	8	18	16	13	17 ^a	20 ^a	12	15	10	
Total equivalent vehicle	492	403	562	509	541	588 ^a	634 ^a	501	515	574	
Light vehicle	337	294	338	327	365	392	404	252	411	458	31-May
Heavy vehicle	14	11	20	16	12	17	20	22	15	9	
Total equivalent vehicle	498	421	568	511	503	588	643	505	584	562	
<i>Wet period</i>											
Light vehicle	326	328	343	368	386	325	486	400	387	516	05-Jun
Heavy vehicle	10	14	18	26	13	12	22	11	15	10	
Total equivalent vehicle	441	489	550	667	536	463	739	527	560	631	
Light vehicle	349	260	280	278	305	375	426	368	451	586	06-Jun
Heavy vehicle	10	18	16	20	14	9	14	14	5	5	
Total equivalent vehicle	464	467	464	508	466	479	587	529	509	644	

^a Data not available were assumed the same data of 31st May at the same time period

Traffic counting campaign

The hourly recorded number of vehicles in both directions is presented in Table 2. Since it was not possible to record the traffic during the period between 13:00 and 15:00 and considering that the traffic pattern of third day was quite similar to the registered one during the two other days; it was assumed equal values during that period.

The traffic characteristics for both periods were similar. The number of heavy vehicles represents about 4 %, on average, of the number of light vehicles which results from access limitations to this type of vehicles to the business center of the city. The conversion to equivalent number of vehicles was made (11.518), and the accumulated number of vehicles used for the correlation analysis was obtained from the sum of the equivalent number of vehicles. The hourly average total number of vehicles for the dry period was slight lower (531 ± 60) than the one registered during the wet period (536 ± 79). Along the monitoring days, the traffic fluctuations were not remarkable. This traffic results are consistent with the frequency of water sampling collection adopted during the field work.

Meteorological data

The temperature, relative humidity, wind speed and wind direction during the monitoring periods are presented in Table 3.

Besides the rain conditions that distinguish the two analyzed monitoring periods, some differences concerning weather conditions can be inferred from the presented results. The average daily temperature was around 19 °C for all the monitored days except for the last day of the dry period (31st May) that presented an average temperature of 26 °C. For this day, the humidity also presents the lowest value. These conditions favor evaporation which implies on the volume of water that was added in order to maintain the volume in the AWSS device. The average wind speed was situated in the range between 10 and 14 km/h revealing calm conditions in both monitoring periods. However, the prevailing wind direction was from NW quadrant during the dry period and from SW in the wet period.

Field monitoring

Results of electric conductivity and temperature at an hourly basis during the monitoring periods are presented in Table 4.

The hourly EC for the dry period was slight higher (134.8 $\mu\text{S}/\text{cm}$, concentration of the last sample) than the one registered during the wet period (93.9 $\mu\text{S}/\text{cm}$, concentration of the last sample). Along the monitoring days, the cumulative value of EC increases during the dry period; however, slower growth during the wet period was observed.



Table 3 Summary of meteorological data registered

	08:00	09:00	10:00	11:00	12:00	13:00	14:00	15:00	16:00	17:00	18:00	
<i>Dry period</i>												
T- envir. (°C)	15	17	18	19	20	20	20	20	20	19	19	29-May
Humidity (%)	94.0	82.0	73.0	68.0	64.0	64.0	60.0	64.0	73.0	73.0	78.0	
Wind speed (km/h)	3.6		7.2	10.8	10.8	10.8	10.8	10.8	10.8	11.1	11.1	
Wind direction	SE	SE	Variab.	Variab.	SW	W	W	SW	W	W	NW	
T- envir. (°C)	15	16	18	19	19	20	21	22	21	21	21	30-May
Humidity(%)	94.0	88.0	77.0	83.0	83.0	73.0	73.0	68.0	64.0	68.0	68.0	
Wind speed (km/h)	3.2	7.2	10.8	14.4	20.4	18	18	3.6	14.4	14.8	14.8	
Wind direction	Variab.	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	
T- envir. (°C)	18	22	25	28	29	28	28	27	28	29	29	31-May
Humidity (%)	88.0	73.0	61.0	48.0	55.0	51.0	51.0	51.0	45.0	42.0	40.0	
Wind speed (km/h)	3.7	7.4	11.1	9.3	7.4	11.1	11.1	14.8	14.8	14.8	16.7	
Wind direction	Variab.	N	N	Variab.	NW	NW	NW	NW	NW	NW	NW	
<i>Wet period</i>												
T- envir. (°C)	18	20	20	19	21	20	19	19	19	19	18	05-Jun
Humidity (%)	88.0	78.0	73.0	78.0	78.0	83.0	88.0	94.0	94.0	100.0	88.0	
Wind speed (km/h)	7.4	14.8	14.8	14.8	16.7	16.7	18.5	14.8	14.8	14.8	7.4	
Wind direction	W	S	SW	SW	SW	SW	SW	SW	SW	SW	W	
Precipitation	Light drizzle	Light drizzle	Light drizzle	Light drizzle	Rain	Light drizzle	Light drizzle	Light Rain	Rain	Light drizzle	Light drizzle	
T- envir. (°C)	17	17	18	18	20	21	20	20	20	19	17	06-Jun
Humidity (%)	94.0	100.0	94.0	94.0	83.0	73.0	78.0	78.0	78.0	83.0	94.0	
Wind speed (km/h)	5.6	3.7	3.7	7.4	13	13	16.7	18.5	16.7	13	5.6	
Wind direction	N	NW	Variab.	W	SW	SW	SW	SW	SW	SW	N	
Precipitation	Light drizzle	Rain	Rain	Rain	Rain	Rain	Rain	Rain	Rain	Rain	Light drizzle	



Table 4 AWSS field monitoring results

	08:00	09:00	10:00	11:00	12:00	13:00	14:00	15:00	16:00	17:00	18:00	
<i>Dry period</i>												
EC ($\mu\text{S}/\text{cm}$)	92.5	–	92.1	92.3	93.8	96.5	98.9	99.0	100.2	104.3	102.2	29-May
T-sample ($^{\circ}\text{C}$)	18.2	–	18.5	19.9	21.2	21.2	21.4	21.6	23.2	22.2	18.5	
EC ($\mu\text{S}/\text{cm}$)	–	99.4	100.0	104.3	106.2	107.9	109.1	110.8	112.8	112.8	114.8	30-May
T-sample ($^{\circ}\text{C}$)	–	17.4	19.7	20.9	23.2	22.7	22.7	22.5	22.0	20.9	19.3	
EC ($\mu\text{S}/\text{cm}$)	–	112.8	116.5	118.6	119.9	122	125.1	128.2	131.6	132.8	134.8	31-May
T-sample ($^{\circ}\text{C}$)	–	19.0	22.2	26.0	27.2	27.3	27.5	28.0	27.8	25.7	23.2	
<i>Wet period</i>												
EC ($\mu\text{S}/\text{cm}$)	89.6	90.5	91.4	92.5	92.2	91.9	92.2	92.4	91.7	91.1	89.6	05-Jun
T-sample ($^{\circ}\text{C}$)	21.8	19.8	19.3	19.5	19.4	19.3	19.1	19.2	19.2	19.1	21.8	
EC ($\mu\text{S}/\text{cm}$)	93.9	92.2	92.6	92.8	93.5	94.0	94.7	95.1	95.3	95.5	93.9	06-Jun
T-sample ($^{\circ}\text{C}$)	21.0	20.3	20.7	20.3	21.4	20.8	21.3	21.1	20.6	20.4	21.0	

Table 5 AWSS water sample results

Parameters	8:00	10:00	12:00	15:00	17:00	18:00
<i>Dry period</i>						
<i>29-May</i>						
Cu^{2+} ($\mu\text{g}/\text{L}$)	63.0	69.0	20.0	107.0	53.0	86.0
Fe^{2+} ($\mu\text{g}/\text{L}$)	51.0	81.0	67.0	73.0	56.0	71.0
Zn^{2+} (mg/L)	0	0	0	0	0	0
pH	6.6	7.0	7.1	7.2	7.3	7.3
<i>30-May</i>						
Cu^{2+} ($\mu\text{g}/\text{L}$)	–	–	5.0	–	–	144.0
Fe^{2+} ($\mu\text{g}/\text{L}$)	–	–	82.0	–	–	159.0
Zn^{2+} (mg/L)	–	–	0	–	–	0
pH	–	–	7.3	–	–	7.3
<i>31-May</i>						
Cu^{2+} ($\mu\text{g}/\text{L}$)	–	–	42.0	–	–	152.0
Fe^{2+} ($\mu\text{g}/\text{L}$)	–	–	96.0	–	–	114.0
Zn^{2+} (mg/L)	–	–	0	–	–	0
pH	–	–	7.4	–	–	7.5
<i>Wet period</i>						
<i>05-Jun</i>						
Cu^{2+} ($\mu\text{g}/\text{L}$)	–	97.0	–	–	77.0	–
Fe^{2+} ($\mu\text{g}/\text{L}$)	–	9.0	–	–	30.0	–
Zn^{2+} (mg/L)	–	0	–	–	0	–
pH	–	7.3	–	–	7.2	–
<i>06-Jun</i>						
Cu^{2+} ($\mu\text{g}/\text{L}$)	–	39.0	–	–	74.0	–
Fe^{2+} ($\mu\text{g}/\text{L}$)	–	18.0	–	–	17.0	–
Zn^{2+} (mg/L)	–	0	–	–	0	–
pH	–	7.1	–	–	7.0	–

Laboratory sampling characterization

The sampling characterization involved characterizing of dissolved metals (Cu^{2+} , Fe^{2+} and Zn^{2+}) from samples

collected from the AWSS. Table 5 presents the results of the laboratory work.

The concentration of Zn^{2+} during the monitoring period was null or very low. During the dry period, the cumulative concentration of Cu^{2+} and Fe^{2+} increased. As for dry deposition of this two ionic species, by using ASSW indicated that the concentration at the end of the first day was 86 and 71 $\mu\text{g}/\text{L}$, respectively, at the end of the second day was 144.0 and 159.0 $\mu\text{g}/\text{L}$, respectively, and at the end of the third day was 152.0 and 114.0 $\mu\text{g}/\text{L}$.

During the wet period, this did not occur. As for wet deposition the ionic species Cu^{2+} and Fe^{2+} , by using AWSS indicated that the concentration at the end of the first day was 77 and 30 $\mu\text{g}/\text{L}$, respectively, and at the end of the second day was 74.0 and 17.0 $\mu\text{g}/\text{L}$, respectively.

Discussion

Obtained results for correlation between hourly instantaneous EC measurements during the monitoring periods and the accumulated traffic, using hourly data, until the measurement instant at the same periods are shown in Fig. 3a, b. In general, the cumulative value of EC in the AWSS unit increases. A significant correlation (Spearman's rank) between the accumulated traffic and EC (dry period: $\rho = 0.991626$; wet period: $\rho = 0.810526$) was observed. However, and despite fluctuations, the increase of EC in the dry period was more intense than that observed during the wet period. Probably, it was influenced by modification due to pollutants spreading under rain conditions.

Figures 4 and 5 present the obtained correlation between accumulated Cu^{2+} and Fe^{2+} and the accumulated traffic for each period.

The concentration of Zn^{2+} in wet and dry periods was null or very low, below the detection limit value of the



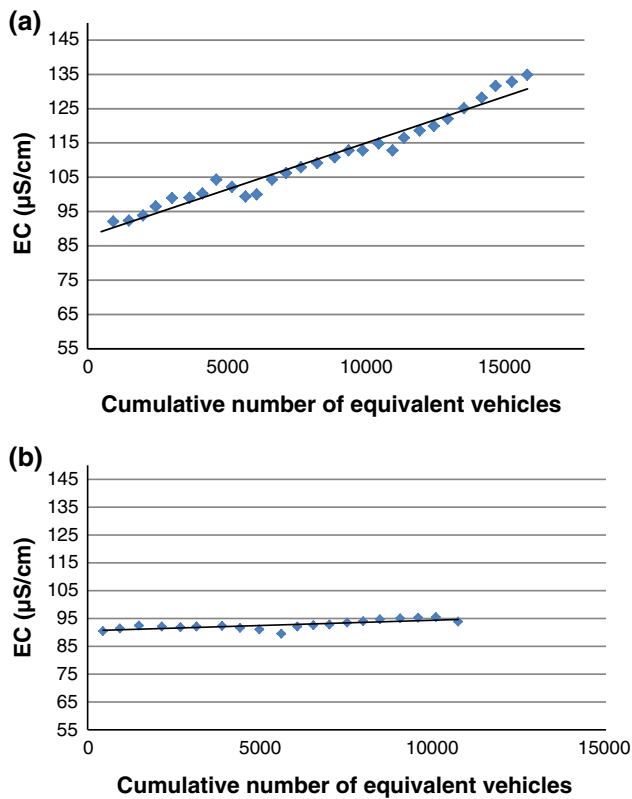


Fig. 3 Cumulative equivalent traffic versus electric conductivity

photometric analyzer (0.03 mg/L). The low concentration of Zn^{2+} in the AWSS may be attributed to the low emission rate and to the subsequent expected low air concentration. The measurement of this pollutant using this method would necessarily require longer sampling periods.

During the dry period, the cumulative concentration of Cu^{2+} and Fe^{2+} increased, despite considerable fluctuation. However, during the wet period, this did not occur, probably due to inhibition of pollutants re-suspension during the wet period.

Spearman's rank correlation was calculated for the concentrations of various elements and the accumulated traffic. A significant correlation (Spearman's rank) between the accumulated traffic and Fe^{2+} ($\rho = 0.700$) was observed, but the Spearman rank for the correlation between the accumulated traffic and Cu^{2+} was low ($\rho = 0.300$). On the other hand, during the wet period, the Spearman rank obtained, for the same correlation, was $\rho = 0.200$ and $\rho = -0.800$, respectively.

Copper appears mainly as a result of brake wear and the mineral filler materials in asphalt road surfaces (Yan et al. 2013). Most iron and copper particles are generated through the direct release of vehicle components rather than in exhaust gas, which deposit in the topsoil near the road edge.

From the obtained laboratory results, it is also notorious a consistent drop in concentrations in the reservoir water

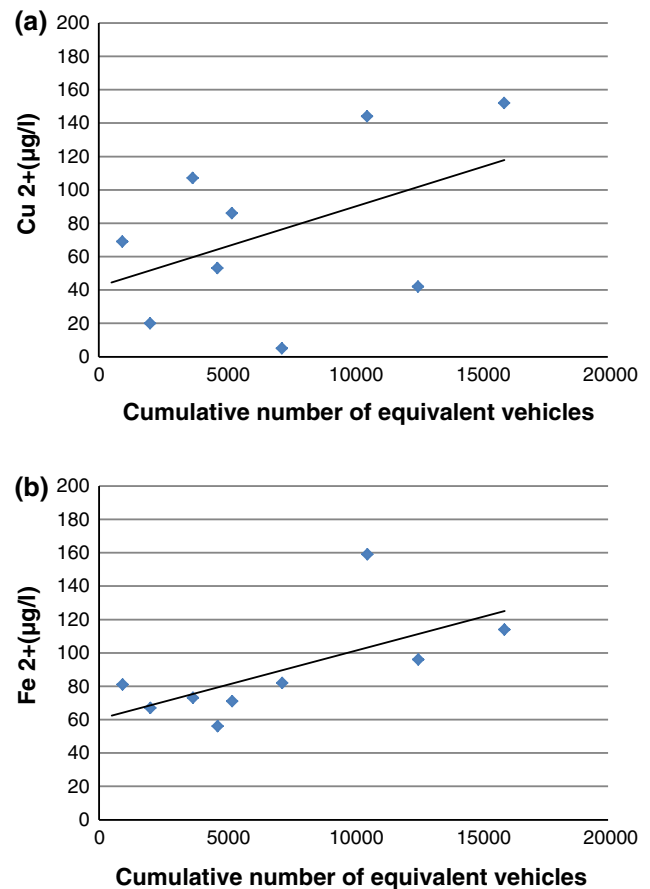


Fig. 4 Cumulative equivalent traffic versus Cu^{2+} and Fe^{2+} , dry period

during the night period. This happens because chemical reactions were not inhibited during night, in this experimental work.

As previously noted, in addition of traffic activity, there were several circumstances that may influence the obtained results. Wind can transport particles, making it impossible to capture them with the sampler, at least as reported by Cowherd et al. (1977), for wind speeds above 5.8 m/s. During the monitoring periods, the average wind speed was 3.07 m/s in the dry period, while on average in the wet period, it was 3.60 m/s. Other natural events can also influence the obtained results, namely the evaporation and water addition during the wet/rain period. These events influence the molarity of the water solution inside the AWSS. The evaporation rate during the dry period was estimated at 0.061 L/h, while additional rain water on the wet period was about 0.011 L/h.

Previous investigations (e.g., Watson et al. 2000; Viskari et al. 1997; Veranth et al. 2003) showed that wind direction (upwind and downwind) has an influence on road traffic-related deposition. During the dry period, the wind



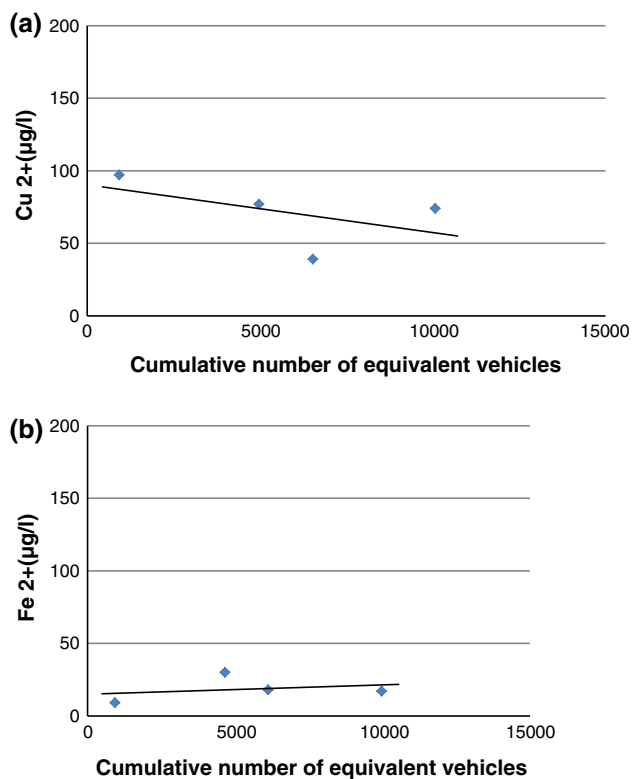


Fig. 5 Cumulative equivalent traffic versus Cu^{2+} and Fe^{2+} , wet period

direction was predominantly lateral from NW and upwind from SW, while in the wet period, the wind direction was upwind from SW.

Traditional methods for urban air quality monitoring are either based on fixed or based on mobile stations that actually measure gaseous emissions concentrations and the mass fraction of particulate matter without chemical speciation (Rakha and Ahn 2004). On the other hand, there are no generally accepted methods to directly measure or estimate dry and wet deposition (Chu et al. 2007). Some attempts to measure deposition were developed for long periods of capture followed by intensive laboratory analyses work. The AWSS method revealed to be efficient for a short-term monitoring period making possible to estimate heavy metals deposition through the EC measurements. It is evident that the correlation of EC and heavy metals concentration can be used since a more comprehensive data base are available and more robust correlations are derived.

Conclusion

Pollutant emissions by vehicles in urban roads are a major environmental concern. Various approaches and many measurements were performed to determine the level of

emissions that can affect humans and the environment. This study aimed to characterize the traffic emission and tracking of several metals, which dispersed through the atmosphere of an urban area by deposition, using an AWSS.

This study is quite important for some reasons. Firstly, the concept of using AWSS is relatively new in air pollution assessment in urban environments. Secondly, this AWSS was developed to capture local deposition, in a small area and was correlated with traffic, which was simultaneously registered.

The AWSS device was specially developed for this research study. It was demonstrated that it is capable of capturing and collecting pollutants resulting from urban traffic. Atmosphere deposition into the water surface is accumulated, and samples can be taken for posterior laboratory analysis. In general, a good Spearman's rank correlation (dry period: $\rho = 0.991626$ and wet period: $\rho = 0.810526$) between atmosphere deposition and accumulated traffic was found. The presence of deposition was indicated by the increase of the EC of the water. This parameter can be used as the main parameter in urban traffic deposition assessment. Several dissolved metals were successfully identified in the AWSS water samples, such as dissolved Cu^{2+} and Fe^{2+} . Meanwhile, the degree of acidity (pH) of the water inside the AWSS was used as a parameter to characterize the nature of the deposit.

The AWSS device results showed the effect of accumulation of deposited pollutants in aquatic environments located near urban roads. With this capability, it can be used as a tool to monitor the deposition of soluble particles.

The particle size plays an important role in air composition and its spatial distribution. The smaller the particles (PM_{2.5} and PM₁₀), the more likely is their origin from the exhausting process. Smaller particles tend to spread over large distances. Larger particles result mainly from abrasion processes, and the deposition of these particles is local (Kleeman et al. 2000; Zechmeister et al. 2005). It must be assumed that the sampling method of this study characterizes mainly larger particles. It cannot take into account particles emitted to increased atmospheric levels, which might be transported and deposited many kilometers away from their release location (Zechmeister et al. 2005). Further studies will be needed (e.g., using longer monitoring periods, analyzing other pollutants or areas with higher traffic flow) to identify the correlation of pollutant deposition with traffic-related sources using the AWSS method.

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