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Determination of soluble ultra-trace metals and metalloids in rainwater and atmospheric deposition fluxes: A 2-year survey and assessment

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Abstract

The present work investigates the relationships between composition of rainwater and dry deposition fluxes by trace metals and metalloids. A modification in automatic "wet-only" and "dry-only" samplers was applied, which allowed the collection and conservation of samples separately. ICP-MS technique was used for the determination of analytes in samples. A sequential acid treatment with nitric, hydrofluoric and finally perchloric acids was used to measure the total contents of metals and metalloids in coarse particles. Concentrations of soluble elements in rainwater were measured directly in filtered samples. Variation between periods of heavy and light rains was assessed. Almost all of the metals and metalloids studied in dry deposition showed important decreases in concentrations (40-92%) during periods of heavy rainfall. Most of these metals and metalloids presented their highest levels (25-40%) in heavy rainfall periods in rainwater samples. Sources were identified in both types of samples

collected using a new chemometric tool (SPCA). Urban traffic, surrounding contaminated soils and local anthropogenic sources were identified for rainwater samples. Natural and contaminated soils and general anthropogenic emissions were the sources identified for dry deposition fluxes.

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1. Introduction

The chemical composition of atmospheric precipitation is closely related with the degree of air pollution in urban, industrial and rural ecosystems. It is well known that due to the dynamic nature of the atmosphere, metals in particle form can be deposited in areas far away from their original sources (Andreae and Rosenfeld, 2008). Trace metals in precipitation can also accumulate in surface water and soil, where they can cause harmful effects on aquatic life, forest ecosystems and plants (Barrie et al., 1987; Fernández and Rossini, 2006).

The elimination of particles in the atmosphere can occur by: 1) aerosols can fall to the earth surface when particles are coarse, as dry deposition; 2) wet precipitation as rain or snow can remove coarse and fine particles, as wet deposition.

In terms of wet deposition, it is accepted that there are two major wet scavenging processes: in-cloud scavenging and below-cloud scavenging (Slinn 1974; Charlson et al., 1983; Colin et al., 1987). Scavenging processes are determined by such particulate properties as particle size, gas solubility and the characteristics of precipitation. Other factors such as particle availability and vertical distribution could determine the relative significance of different removal processes during a single event (Lim et al., 1991). Besides, the potential capacity of dissolve toxic metals from atmospheric particulate matter was also studied employing speciation

schemes (Fernández et al., 2000; Fernández and Ternero, 2004b). Similar studies demonstrate the importance of the soluble and mobile fraction regarding the total metal content (Davis et al., 2001; Joshi and Balasubramanian, 2010).

Acid rain has harmful effects on aquatic organisms, mainly because it favors the solution of trace metals, increasing their bioavailability (Baez et al., 2007). Anthropogenic emissions of particles and gases come from mainly the industrial combustion of fossil fuels and agriculture (Galloway et al., 1982).

Recently, a lot of information about the composition of precipitations has been gathered in America, Central and Northern Europe (Arsene et al., 2007; Celle-Jeanton et al., 2009) and other parts of the world, as China (Wei Hong et al., 2005), Japan (Hou et al., 2005), India (Momin et al., 2005), etc. In Spain, several authors have studied the chemistry of atmospheric precipitation (Alastuey et al., 1999; Encinas et al., 2004). Furthermore, the papers pertaining to rainwater and dry deposition composition are scarce when compared to those referring to Total Suspended Particles (TSP) (Fernández et al., 2004a).

Therefore, the aim and novelty of this work is to study the relationship between atmospheric pollutants in wet deposition and in dry deposition samples in an urban location, covering a long period of more than two years; additionally other objective is to investigate the relationship between pollutants in periods of heavy rainfall and periods of light rainfall. Finally, concentrations measured will allow identifying sources of atmospheric pollutants using a recent novel chemometric tool on both types of samples.

2. Experimental

2.1. Instrumentation for analytical determinations

Determination of heavy metals (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Ag, Cd, Tl and Pb), light, alkali and alkaline-earth metals (Be, Al, Sr, Cs and Ba), actinides (Th and U) and

metalloids and nonmetals (B, As and Se and Sb) was carried out by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), and a X7 SERIES ICP-MS (Thermo Elemental, Pierce Biotechnology, Rockford, IL, USA) was used. ICP-MS is often used for the determination of environmental samples.

Their operating conditions (Montoya et al., 2001) were optimized daily to give the highest sensitivity and S/N ratio. The complete determination of heavy metals and metalloids by ICP-MS was carried out according to the 200.8 US EPA Method (USEPA, 1994) with some modifications relating to the tuning and mass calibration solution. There were some analytes where the number of samples over the detection limits were very low, <15%, (Ti, Fe, Ag, Sn, Hg, Tl, Cs, Be, Si, Se, Th and U) and they were excluded from statistical analysis, indicating only an informative value.

2.2. Methodology for chemical analysis

The chemical composition determined in rainwater samples was obtained by analyzing concentrations of metals and metalloids. The general parameters pH, electrical conductivity (EC) and redox potential (E) were measured in situ during the collection of samples from the automatic sampler. Experimental pH values were converted to H^+ concentrations for their statistical treatment.

In addition, the concentration of rainwater solutes was calculated from a method based on the measurement of the pH-value and the electrical conductivity (Krämer et al 1996).

Composition of soluble pollutants in rainwater was determined on direct samples only after vacuum filtration. The chemical composition determined in dust samples was obtained by acid treatment. For this, coarse particles were acid digested in two stages. Particles were digested with a mixture of 5.0:2.5 ml $HF:HNO_3$ in a Teflon reactor (Savillex, Minnesota, USA; 60 ml) at 105°C in an oven over night. Later, 2.5 ml $HClO_4$ was added to the residue and this was

dried and then re-dissolved with 2.5 ml HNO_3 and a volume of 50 ml with ultrapure water (Montoya et al., 2011) was made up.

Acids and standard solutions for metals were taken from VRW (Darmstadt, Germany). Ultrapure water came from Waters-Millipore (Milli-Q grade, model Milli-Q Plus). Standard solutions for pH, EC and E_{exp} came from Crison® as well as the corresponding laboratory instruments.

Additional care was taken in handling the samples to avoid contamination problems. Consequently, all reagents, materials and samples were handled within a vertical laminar airflow cabinet (Indelab, model IDL-48 V) that ensured air cleanliness standards of class 100 according to Federal standard 209E, and it was located in an isolated dark room for analytical weighing known as the balance room.

2.3. Measurement site and sampling

In this paper, the results corresponding to over two years of sampling and analysis of rainwater and atmospheric deposition loads are presented. Samples were simultaneously collected in an urban-trafficked site close to the navigable Guadalquivir River (Andalusia, Spain). This study was undertaken in the city of Sevilla (38°12′–36°51′ N, 4°39′–6°32′ W, 141.3 km^2), a city 60 km from the sea and only 8 m above sea level, the capital of Andalusia, in South West Spain. The collector was installed at 4 meters over the floor into the University Campus of Reina Mercedes.

Sevilla is characterized by high temperatures and low wind speeds. Prevalent air currents come from the southwest–northeast direction. All this data is averaged from the 1971–2000 period (AEMET, 2012). The majority of rain episodes and Saharan inputs enter into the region of Andalusia through this valley from a westerly direction, mainly from the southwest.

Important episodes of 'heat wave' occur frequently in summer coming from Sahara and Sahel deserts.

Rainwater samples (wet deposition) and bulk depositions fluxes (dry deposition) were collected with a TISCH ENVIRONMENTAL 78 100 APS (Tisch Environmental Inc., South Miami Ave. Cleves, Ohio. USA) automatic wet-only and dry-only sampler. This type of sampler is designed to collect atmospheric depositions in two separate buckets of 15 litres (Fig. 1): one of these, the rainfall bucket ("Wet" bucket), opens only during episodes of rain, detected by an electronic sensor, and the other, the dust fall bucket ("Dry" bucket) is always open during dry periods. This allows the collection of both wet deposition (rainwater) and dry deposition (dust depositions) separately. All samples were collected during a period of over 2 years, from September 2006 to January 2009.

Samples of rainwater were collected dairy during each rain episode and accumulated later for a period of a week according to the recommendations of the OSPAR (OSPAR, 2007; European Community, 1998) and Barcelona Conventions (European Community, 1977; MAGRAMA, 2012a) for the coastal zones protection. Samples of dust depositions were collected every 28 days, once per month, according to the Federal methods of the USA (USEPA, 2008) and Regional laws of Spain (BOJA, 2006). This resulted in a total of 67 dairy samples collected and 39 weekly values accumulated for rainwater and a total of 22 samples collected of bulk samples, which are presented in this study. Also, for relationships with 22 monthly samples of dry deposition fluxes, 20 monthly values were accumulated for rainwater samples.

According to these conventions, dry deposition fluxes were expressed as mg m^{-2} day^{-1} (dividing total monthly depositions by 28 days). Additionally to the weekly period – expressed as L m^{-2} week^{-1} – rainwater samples were also averaged over monthly periods to give an objective relationship with dry depositions, expressing it as L m^{-2} day^{-1}, not by month. For metal and metalloid, concentrations in dry deposition fluxes and in rainwater were expressed

as $\mu g\ m^{-2}\ day^{-1}$. Additionally concentrations of analytes in rainwater samples were also expressed as $\mu g\ L^{-1}\ week^{-1}$ referring to a concentration in an aqueous basis for comparison with other world results.

2.4. Design of the modifications on the sampling engine

To ensure the optimal preservation of samples during dairy rain events, some modifications were carried out to the automatic collector (Fig. 1):

Firstly, a small-fridge was protected from the sun under the sampler. The rainwater was collected in bottles made of low density polyethylene (LDPE) with a 0.5-L capacity stored inside the small-fridge. The fridge power was adjusted to achieve a temperature between 3 and 5ºC.

Secondly, a stainless steel funnel with a collection area of 0.063 m^2 was inserted into the "Wet" bucket to collect rain drops and to channel rainwater into the small-fridge. The surface of funnel and all tubes were Teflon-coated, thus avoiding the contact between rainwater and the surface of the steel funnel, so as to prevent cross-contamination.

Thirdly, a waste system was coupled to the sampling train to prevent the rain overflowing into the small-fridge during extreme rainfall events. All connections between different parts of the sampling train were made with Teflon tubes. The modified automatic sampler is shown in Fig. 3.

2.5. Sample pretreatment of rainwater and bulk deposition

Rain drops wash atmospheric particles of different sizes (coarse and fine particles, see Fernández et al., 2004a) during their fall; these particles contain metals and metalloids that are dissolved, together dissolved gases, determining part of the composition of rainwater. After

each rain event, these particles are removed through filtering samples in the laboratory. Vacuum filtration was done with 47 mm $\varnothing$ ultrapure quartz filters Whatman QM/A (Middlesex, UK), which have 0.45 mm film thickness and a particle retention for 0.3 µm of 99.95% -determined according to ASTM (American Society for Testing and Materials) D 2896-91-. The mean concentration of suspended solids in rainwater was extremely low, 57.0 mg L^{-1}. After the in situ determinations and vacuum filtration, samples were divided in three portions for determinations by ICP-MS. For each replicate, an aliquot of concentrated Nitric acid (Suprapur quality, from Merck; Darmstadt, Germany) was added to 10 mL of the filtered sample until a concentration of 1% was achieved.

In the case of bulk particles (only coarse particles) collected into the "Dry" bucket, the complete samples were carefully transferred from the bucket to vials using dry and clean nylon pencils. Vials were previously dried and weighed before the transfer and sealed hermetically after. The treatment of coarse particles was done in the balance room monitored at 50±5% R.H and 20±1ºC.

After transfer coarse particles in each open vial were placed into a 96 L desiccator for a 48-h period continuously under 5% R.H. Conditions of low humidity inside the desiccator were achieved with a combination of Silica-gel and Phosphorus pentoxide, and using an indoor air extractor. After drying treatment vials were then weighed to a precision of 0.1 mg on an analytical balance (Sartorius LA 130 S-F). The bulk deposition concentration was expressed in mass of particles by surface area and day (mg m^{-2} day^{-1}).

2.6. Multivariate statistical technique (SPCA, Sequential Principal Component Analysis)

On the basis of the results, basic and multivariate statistical analyses were applied to the analytical and meteorological data. The SPCA tool is a PCA technique modified by Fernández et al., 2004a. The SPCA method consists in identifying and characterizing outliers that appear

before their elimination (Montoya-Mayor et al., 2011). The STATISTICA version 7 (2004) software package (StatSoft) was used. The SPCA was performed with a Varimax rotation, extracting the factors or principal components (PCs). This explains more than 5–10% of the total variance of the data set, and together accounts for more than 65–80% of the accumulated variance.

2.7. Method performance and quality controls

The performance of the method was tested. The accuracy of the spectroscopic determinations was established by an international Certified Reference Materials (CRM). Experimental concentrations were obtained from 18 replicates over 6 days. Quality Control samples were applied according to the EPA protocol (section 9.0 of EPA 200.8:1994). CRM-TMDW (Charleston, South Carolina, United States) is certified for trace metals in drinking water and it was used to determine the accuracy of the US EPA method for rainwater by ICP-MS. Recoveries (R) were calculated dividing the mean value of the determined element by the certified value (Wood 1999). The obtained results are shown in Table 1. As we can see, the method presented optimum trueness, with values into the AOAC (AOAC, 2010) range.

Limits of detection were calculated from the standard deviation, obtained from the calibration curves. Limits of detection are quite low, therefore allowing the analysis of very low levels of metals and metalloids in rainwater. The LOD for the elements are lower than 0.46 µg L^{-1}, and the LOQ are lower than 1.54 µg L^{-1}.

Linearity in the calibration range was calculated as $100*(1-s_b/b)$ (Cuadros, 1996), *b* being the slope of the calibration curve and s_b its standard deviation. The ICP-MS calibration curves were linear for all elements analyzed, obtaining values higher than 95.0%.

3. Results and Discussion

In this study, the results from metals and metalloids were obtained for the 67 individual rainwater samples and 22 monthly samples of depositions fluxes collected during the 2006-08 period. In addition, physicochemical parameters were studied in rainwater samples. As above mentioned, the 67 dairy data of rainwater were cumulated into 39 weekly concentrations and 20 monthly concentrations.

3.1. Concentrations of soluble pollutants in rainwater and bulk depositions

Values obtained for metals and metalloids analyzed in rainwater and dust depositions are shown in Table 2. These resulted in some being below the detection limit (LOD) in rainwater. Fe and Mn concentrations obtained in samples of particles were similar than those obtained in a desert area of Israel (Herut et al., 2000). Mn and Zn concentrations were also similar than those reported in the polluted zone of the NY-NJ harbor (Yi et al., 2006). Zn, Pb, Cu and Ni levels in particles were obtained on the same order of magnitude than in France (Chester et al., 1996). Regarding other heavy metals, similar concentrations were measured in Jordan for Pb, Cu and Cd (Al-Momani 2003), in Turkey for Cr (Demircioglu et al., 2011) and in Israel for Cd and Pb (Herut et al., 2000). Regarding rainwater levels, Fe, Zn and Cu concentrations obtained in Sevilla were similar than obtained in a suburban area of Japan (Hou et al., 2005). Also Zn and Cd levels were of the same order than those found in Paris (Garnaud et al., 1999). Regarding other heavy metals, Ni concentrations found in Sevilla were similar than those obtained in a rural area in México (Baez et al., 2007) and also in Turkey for Ni and Cr (Kaya and Tuncel, 1997).

Observing the values of ratio bulk/rainwater, it can see considerable differences between the two types of samples. For example, the more concentrated elements in dust depositions were Al, Fe and Ti (ratio of 56, 26 and 32-fold), probably coming from earth crustal

resuspended coarse particles. Other elements resulted also more concentrated – but much most moderately – than in rainwater, such as Cr and Pb (ratio~4-fold) and Mn and Co (ratio ~2-fold), indicating anthropogenic (industrial – Cr – and traffic – Pb –) pollutants deposited in natural soils (Mn, Co) along the time. The rest of metals and metalloids – mainly toxic and anthropogenic – have higher values in rainwater than in coarse particles: The analytes B, Tl, Zn and Ba have considerable ratios around 43, 32 and 15 respectively (see Table 2). The elements Ag, Be, U, Cd, Sr and Ni have ratios between 10.6 and 5.1, and the other, Cs, Th, Sb, As, Mo and Cu, have ratios between 3.2 and 1.4. This indicates that toxic metals, such as Cd, Ni, Mo, Cu, and metalloids, As, were deposited in soils and plants most from rainwater than from coarse particles. So we can assume that the majority of toxic elements – anthropogenic – were most bioavailable than natural elements (most present in dry deposition fluxes); therefore toxic elements are best removed by rain than by dry deposition to ground.

Regarding physicochemical parameters in rainwater – pH 6.5 (4.0-7.8), EC 19.6 (2.3-147) μS cm^{-1} and E 328 mV (224-442) – they were agreed with the usual values in normal rain events and with non-acidic conditions and non-oxidizing-reducing waters.

3.2. Relationship between wet precipitation and levels of dry deposition fluxes

Generally, when wet precipitation was abundant, the dry deposition was low, and vice versa. To make this comparison, weekly rainwater values were grouped monthly and averaged by day (MWP, L m^{-2} day^{-1}). Besides, concentration of coarse particles deposition fluxes were expressed also as mg m^{-2} day^{-1} (MDD). We can observe this relationship in Fig. 2 when correlations between monthly values of wet and dry atmospheric precipitation were represented for the 2006-2008 period: When it rain, pollutants in the atmosphere (gases and particulate matter) are incorporated into the rainwater, and they are later deposited on the ground as wet precipitation. In contrast, when rainfall was scarce or null, pollutants were

slowly deposited on the ground as dry deposition of coarse particles, increasing their levels (arrows).

These results were agreed with the normal behavior in the atmosphere. These relationships, negative correlations, were observed in the autumn-winter and winter-spring periods: seasonal variation of rainfall showed two main periods of abundant rain events (Fig. 2), the period autumn-winter (October-February) and the period winter-spring (March-May). The rainiest month was March 2008, followed by October 2006, November 2006 and April 2007 and December 2008. On the other hand, the highest monthly dry deposition corresponds to August 2007, September 2007, May 2007, September 2006, November 2007 and October 2008. So, after these inverse relations between wet and dry depositions were assessed, the next step is to study how many the rain episodes can influence in metals and metalloids concentrations of both types of samples, particles and water.

3.3. Comparison between the highest and the lowest values of rainfall

A comparison was made between the events of heavy rain – high intensities – and periods of light rain – low intensities –, in order to study the differences on scavenging rates of pollutants in coarse particles of dry depositions. After rain events, these differences on particles are reflected on characteristics of rainwater samples collected. Fig. 3 shows variations in the percentage between periods of light and heavy rainfall for physicochemical parameters measured in rainwater, as well as for wet precipitation (MWP, L m^{-2} day^{-1}) and dry deposition (MDD, mg m^{-2} day^{-1}) values. Most of physicochemical parameters determined in rainwater excepting the redox potential presented the highest values in periods of light rainfall (< 11 L m^{-2}), showing the lowest values during periods of heavy rainfall (> 23 L m^{-2}). This fact is another consequence of differences between both types of episodes, which needs to be studied regarding analytes determined.

With the aim of study this comparison on metals and metalloids, first, monthly rainwater episodes and dust deposition samples were arranged from highest to lowest values of rainfall (L m^{-2}). Then, rainwater and particle samples assigned to episodes of heavy rainfall-EHRs (higher than 0.75 percentile of rainfall, 23 L m^{-2}) were grouped and those assigned to episodes of light rainfall-ELRs (lower than 0.25 percentile of rainfall, 11 L m^{-2}) were grouped also.

After classification, the difference of the concentrations studied between heavy and light rain events was expressed as percentage regarding EHR and ELR. The percentage regarding ELRs and EHRs (*%$_{LH}$*) was calculated as:

$$\%_{LH} = \frac{C_{ELR} - C_{EHR}}{C_{ELR}} \times 100 \, ; \quad (C_{EHR} < C_{ELR} \, ; \%_{LH} > 0)$$

or,

$$\%_{LH} = \frac{C_{ELR} - C_{EHR}}{C_{EHR}} \times 100 \, ; \quad (C_{EHR} > C_{ELR} \, ; \%_{LH} < 0)$$

Where,

C_{EHR}, is de concentration of pollutant averaged for all dry-wet samples collected in

EHRs,

C_{ELR}, is de concentration of pollutant averaged for all dry-wet samples collected in

ELRs.

Thus we can know the percentage of increment or decrement of a pollutant regarding EHRs and ELRs. In the case of samples of dry deposition fluxes, when this percentage is positive, concentration of pollutant in dry depositions in ELRs is higher than in EHRs, indicating a better scavenging rate in EHRs. However when this percentage is negative, concentration is higher in EHRs, indicating a better scavenging rate in ELRs. In the case of rainwater samples, when this percentage is positive, concentration of pollutant in rainwater in ELRs is higher than in EHRs, indicating a better scavenging rate in ELRs. However when this

percentage is negative, concentration is higher in EHRs, indicating a better scavenging rate in EHRs.

As can be seen in Table 2, $\%_{LH}$ percentages in dry depositions were positive in most metals and metalloids studied, resulting negative only for Zn, Pb, Sb, Ba, Mo and Cu. Boron was the metalloid that had the greatest percentage, meaning that particles of dry depositions in EHRs have 92% less concentration of boron than particles deposited in ELRs, indicating that B was the element best removed from the atmosphere by heavy rain events. B is followed by Tl, Th, U, Al, Cs, Be, Ti with percentages higher than 40%, and also by Cr, Mn, Sr, Co, As, Fe and Ni with percentages between 25 and 37%.

Regarding results in rainwater samples, it was also found that metals and metalloids with positive percentages in dry deposition fluxes have negative percentages in rainwater, as the expected result. This means that pollutants with negative percentages have higher concentration in rainwater felled during EHRs than those felled during ELRs, confirming that EHRs increase the scavenging rates from these elements in coarse particles and increase their levels in rainwater samples. Results in both types of samples demonstrated the scavenging process of washout in EHRs, which highlight the transport process from coarse particles in the air to rainwater system before the falling down the soil. The elements nickel and arsenic (25-30%) and especially chromium (37%) should be highlighted for their toxicities.

3.4. Sequential Principal Component Analysis (SPCA)

In this section, the differences among the precipitation data were studied using *SPCA*. This was done in order to study the sources of pollutants in rainwater and in bulk depositions. In addition, Sequential Principal Component Analysis characterizes outliers of the system.

Rainwater

According to the SPCA procedure mentioned earlier, Table 3 shows the results corresponding to the Sequential PCA for rainwater samples. SPCA1 to SPCA6 include outliers, whereas SPCA7 is the final SPCA. Outliers have been interpreted and characterized before their elimination.

Results obtained in SPCA1 showed one interfering case, se04. This case corresponds to an episode with high concentrations of variables (H^+, B, Zn, Cd, Al and Cu) originating from urban traffic sources. In addition, this sample was characterized by its extremely low pH value (4.0) as an acid rain episode. PC1 (only one case) accounts for 27.2% of the variance of all cases; consequently, this proves that the first PCA – SPCA1 – is not valid to explain the variance and main sources of 67 samples. Therefore, according to the present methodology of SPCA, it is necessary to remove the outliers and repeat the PCA sequentially until no more outliers appear.

After removing se04 and repeating SPCA, the outlier se34 (March 2007) appears in SPCA2 corresponding to the highest values of atmospheric pressure and evapotranspiration with southern winds of low speed, so, an anticyclonic period prior to spring rains. SPCA3 shows the case se62 (November 2007) corresponding to a dry period of more than 20 days with high wind speed and characterized by As and Ba (traffic emissions, Fernández and Ternero, 2004b). In SPCA4, the group Mo, redox potential and Sb (se91, October 2008) was originated mainly from emissions of intense traffic. In SPCA5, se47 (May 2007) was characterized by the highest values of rainfall, 85 L m^{-2}, and a low value for electrical conductivity, 7.7 µS cm^{-1}. The variables grouped V, rainfall-PP and Cu showed a mixed origin from both anthropogenic and natural sources. Finally, in SPCA6, se20 (November 2007) was characterized by Cr and high wind speeds (4.1 m s^{-1}), showing a mixed origin, from foundries, soil or traffic.

Once all outliers were explained and removed, the last PCA – SPCA7 – could not reveal the presence of any interfering PC and 7 significant PCs explain up to 67.4% of the total variance in SPCA7 (Table 3).

PC1 is formed by EC and Ba related to the traffic of the city (Fernández and Ternero, 2004b). Most of representative cases corresponded to April 2008, in days with winds coming from southern directions, with moderate and high wind speeds. PC2 is formed by V, Cu and Zn, related with soils polluted by a fertilizer factory of the city, confirmed by previous studies (Fernández 2001). PC3 and PC4 are represented by soils and also traffic emissions (Pb and Ba). The Ba^{2+}–Sr^{2+} pair is frequently attributed to a terrestrial source, although Ba^{2+} together Cu and Pb is also attributed to vehicle traffic (Fernández and Ternero, 2004b). So, we can relate these PCs with the resuspended contaminated soils from the trafficked city. Samples of this group correspond to the summer-autumn period, characterized by high temperatures.

PC5, PC6 and PC7 are formed by elements characterized by anthropogenic activities. The metals Cd, Cu, Ni and Zn are related to emission from foundries (Fernández and Ternero, 2004b). Mo comes from the making and use of alloys in the nearest the great national city's shipyard and the plane factory of the industrial zone of the Port of Sevilla, with more than 25 enterprises conducting industrial activities.

Dust depositions

When we realized SPCA for dry deposition, we found 2 PCs that explained 89.3% of the variance. These PCs are very different to those from rainwater and no outliers appear. In SPCA for dust depositions there are only 2 PCs, while in SPCA for rainwater samples many different PCs appeared. As a consequence, there is no diversification of sources in coarse particle depositions, as shown in Table 4.

PC1 is formed by Fe, Ti, Co, V, Al, Mn, Ni, As, B, Sr and Ba. Some elements such as As or Ni may have an anthropogenic origin, but most of the elements have a predominantly terrigenous origin, like Fe, Ti, Al, Mn, Sr and Ba. So we can relate this PC to the influence of soils in dry deposition. In contrast, PC2 is represented by Sb, Cd, Mo, Cr, Zn, Cu, Pb and As. Moreover, PC2 has elements that mainly have an anthropogenic origin.

In dry depositions we found a very basic division of the variables studied; just a terrigenous PC and one anthropogenic PC, where the terrigenous PC is much more important. It must be taken into consideration that the bulk depositions were collected every 28 days. This is a long period of time with different weather conditions and emissions from different sources. Therefore, all these factors contribute to a mixture of pollutants, not occurring the diversification of sources of emission.

4. Conclusions

For sampling, the modification and optimization of the original automatic sampler has allowed the optimal conservation of rainwater samples. Differences between periods of heavy and light rainfall were much more severe for metals and metalloids in dry deposition than in wet deposition. Dry deposition presented higher values for B (92%), Tl (49%), Th (44%) and U (41%) in periods of light rainfall than in periods of heavy rainfall. On the other hand, almost all of these metals and metalloids presented their highest values in rainy periods for rainwater samples, such as Cr (-90%), Co (-75%) and Cs (-72%). This way it was calculated the contribution of the rainwater to the scavenging of atmospheric coarse particles. Similar studies it would be interesting in the future for suspended particles, PM_{10}, $PM_{2.5}$ or ultrafine particles.

The use of the advanced chemometric tools Sequential Principal Component Analysis (SPCA) have been very useful for the interpretation of the results in the complex environmental system studied. Thus, it has identified the mixture of a traffic source (25.6 % of the variance),

followed by contaminated soil (18.1 %) and anthropogenic sources (16.4 %) such as metallurgy and port activity. The terrestrial source is also present (6.9%), along with the combustion source (4.0 %). The chemometric study on dry depositions has shown no diversified sources as a result of the long period of sampling. Two principal components were only obtained: soils (69.3 % of the variance) and anthropogenic sources (20.0 %), however the two sources were good discriminated. Therefore anthropogenic pollutants contained in coarse particles probably could cause contamination in soils and plants in the city. This fact is another future objective to develop studies in rural and coastal sites where many crops constitute important economic activities for human consumption.

Acknowledgments

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Table 1
Recovery, linearity and sensitivity for the ICP-MS method

Analyte	Concentration obtained±SD (µg L⁻¹)	CRM concentration ±SD (µg L⁻¹)	Recovery (%)	Linearity (%)	LOD (µg L⁻¹)	LOQ (µg L⁻¹)
Be	20 ±0.10	19.2 ± 0.20	96.0	99.1	0.035	0.117
Al	120 ± 0.60	120.6 ± 1.33	100.5	97.4	0.409	1.363
Cr	20 ± 0.10	19.3 ± 0.09	96.5	97.8	0.042	0.140
Mn	40 ± 0.20	38.5 ± 0.45	96.3	98.7	0.035	0.117
Fe	100 ± 0.50	113.1 ± 2.38	113.1	95.7	2.872	9.573
Co	25 ± 0.13	24.6 ± 0.23	98.4	98.8	0.040	0.133
Ni	60 ± 0.30	53.8 ± 0.59	89.7	98.1	0.126	0.420
Cu	20 ± 0.10	18.5 ± 0.20	92.5	98.2	0.071	0.237
As	80 ± 0.40	80.6 ± 0.16	100.8	98.1	0.125	0.417
Se	10 ± 0.05	9.5 ± 0.19	95.0	98.2	0.463	1.543
Sr	250 ± 1.25	264 ± 1.85	105.6	99.4	0.035	0.117
Mo	100 ± 0.50	96.8 ± 1.07	96.8	99.3	0.062	0.207
Ag	2 ± 0.01	2 ± 0.03	100.0	99.5	0.052	0.173
Cd	10 ± 0.05	10.3 ± 0.17	103.0	99.4	0.053	0.177
Sb	10 ± 0.05	10.4 ± 0.07	104.0	98.1	0.048	0.160
Ba	50 ± 0.25	50 ± 0.04	100.0	99.5	0.083	0.277
Tl	10 ± 0.05	10 ± 0.01	100.0	99.5	0.045	0.150
Pb	40 ± 0.20	36.2 ± 0.29	90.5	99.1	0.135	0.450
U	10 ± 0.05	10.1 ± 0.18	101.0	99.8	0.053	0.177

SD standard deviation, CRM certified reference material

Table 2

Metal and metalloid concentrations in 22 monthly samples of bulk particles and 39 weekly samples of rainwater. Percentage $\%_{LH}$ of variation between ELR and HER periods for bulk particles and rainwater

Analyte	Bulk (B)[*] ($\mu g\ m^{-2}\ day^{-1}$)	Rainwater (R)[*] ($\mu g\ m^{-2}\ day^{-1}$)	B/R-R/B (Ratio>1)	Rainwater ($\mu g\ L^{-1}\ week^{-1}$)[**]	$\%_{LH}$ in dry deposition	$\%_{LH}$ in Rainwater
Al	1705 (1042-4666)	30.5 (≤LOD-853)	56	2.4 (≤LOD-67)	40	-30
Fe	939 (505-2352)	18.3 (≤LOD-36.5)	26	≤2.87	28	---
Ti	173 (101-503)	2.3 (≤LOD-5.5)	32	≤0.43	40	-67
Mn	29 (17-64)	14.0 (≤LOD-320)	2.1	1.1 (≤LOD -25)	37	-45
Zn	20 (8-75)	306 (≤LOD-3131)	15	24.0 (≤LOD-246)	-38	59
Ba	10 (4-52)	153 (10.5-5116)	15	12.0 (0.825-402)	-27	31
Cr	9 (4-22)	2.6 (≤LOD-776)	3.5	0.2 (≤LOD-61)	37	-90
Cu	9 (7-15)	12.7 (≤LOD-407)	1.4	1.0 (≤LOD-32)	-11	23
Sr	7 (5-23)	43.3 (3.5-2800)	6.2	3.4 (0.277-220)	37	-45
Pb	6 (4-15)	1.8 (≤LOD-42.0)	3.4	≤0.14 (≤LOD-3.3)	-35	93
Ni	2 (1-4)	10.2 (≤LOD-331)	5.1	0.8 (≤LOD-26)	25	-65
B	0.8 (0.4-32)	34.4 (≤LOD-1044)	43	2.7 (≤LOD-82)	92	-56
Co	0.7 (0.4-2)	0.51 (≤LOD-99.3)	1.4	≤0.04 (≤LOD-7.8)	31	-75
As	0.6 (0.3-1)	1.6 (≤LOD-127)	2.8	≤0.13 (≤LOD-10)	30	99
Mo	0.5 (0.3-1)	0.76 (≤LOD-649)	1.5	≤0.06 (≤LOD-51)	-16	98
Sb	0.4 (0.3-0.9)	1.2 (≤LOD-35.6)	2.9	0.09 (≤LOD-2.8)	-28	74
Th	0.3 (0.2-1)	0.89 (≤LOD-1.9)	3.0	≤0.07 (≤LOD-0.15)	44	---
Cs	0.2 (0.08-0.4)	0.64 (≤LOD-54.7)	3.2	≤0.05 (≤LOD-4.3)	40	-72
U	0.1 (0.06-0.3)	0.64 (≤LOD-1.3)	6.4	≤0.05 (≤LOD-0.1)	41	---
Cd	0.1 (0.05-0.2)	0.64 (≤LOD-14.0)	6.4	≤0.05 (≤LOD-1.1)	0.2	-64
Ag	0.06 (0.04-0.09)	0.64 (≤LOD-12.7)	11	≤0.05 (≤LOD-1.0)	12	---
Be	0.05 (0.03-0.1)	0.51 (≤LOD-3.8)	10	≤0.04 (≤LOD-0.3)	40	---
Tl	0.02 (0.01-0.06)	0.64 (≤LOD-1.3)	32	≤0.05 (≤LOD-0.1)	49	---

[*]: Medians and minimum-maximum in brackets
[**]: Rainfall expressed as $\mu g\ L^{-1}\ week^{-1}$ according the international conventions
---: Not calculated because mean concentration was ≤LOD in rainwater

Table 3
Sequential PC Analysis (SPCA) of seven iterations for rainwater (19 variables x 67 cases)

SPCAn	PCn	Variance (%)/ Cumulative variance (%)	Sign	Variables	Cases	Source
SPCA1	PC1	27.2 / 79.1	+	H$^+$, B, Zn, Cd, Al, Cu	*se04*	Acid rain
SPCA2	PC1	27.5 / 76.6	+	Co, Cu, Mn, V, Al, B, EC	*se34*	High conc.
SPCA3	PC6	5.3 / 80.2	+	As / Ba	*se62*	Traffic
SPCA4	PC6	5.3 / 78.0	-	Mo / E, Sb	*se91*	Traffic
SPCA5	PC8	4.3 / 77.6	+	V, PP, Cu	*se47*	Industrial-Plastics?
SPCA6	PC11	3.3 / 78.4	+	Cr	*se20*	Unidentified
SPCA7	PC1	25.6 / 25.6	+	EC/ Ba	*se82, se 62 / se86 / se 83, se81, se60*	Traffic
	PC2	10.4 / 36.1	+	V / EC, Cu / Zn	*se80, se81 / se45, se87, se85, se47, se88 / se74, se50, se84 / se89*	Contaminated soil
	PC3	8.1 / 44.2	+	Pb, Sr, / Ba / Cu	*se60, se55 / se61 / se62, se58, se57 / se80*	Soil-traffic
	PC4	6.9 / 51.1	+	Mn, Al / Ba, B / Zn	*se80, se90 / se95 / se18, se26 / se20, se75, se62, se08*	
	PC5	6.3 / 57.4	+	Cd, Zn / Co, B	*se33 / se06, se80 / se47 / se50, se22, se09*	
	PC6	5.6 / 62.9	-	Mo, As / Sr, Cu	*se65 / se92 / se 74, se55, se77, se67 / se35*	Anthropogenic: Metallurgy and Port Activity
	PC7	4.5 / 67.4	-	Ni / Cr, Cu / Zn	*se10 / se80, se41, se43 / se38, se44, se35, se55, se07*	

Variables are in decreasing order of loading above 0.5. Underlining indicates variables with the highest loading between PCs.
Bold indicates cases with high scores (outliers).
EC electrical conductivity, E redox potential, PP total rainfall
SPCA1 to SPCA6 outliers, SPCA7 final PC analysis

Table 4
PC Analysis for soils (13 variables x 18 cases)

| PCA	Variance (%)/ Cumulative variance (%)	Sign	Variables	Cases	Source/Interpretation
PC1	51.1 / 51.1	+	$PhtalO^-$, NH_4^+, K^+ >> Cl^-, AcO^-, PO_4^{3-}, Na^+ >> Mg^{2+}, $OxalO^-$	$SSL_{10}12 > SSL_{10}29 \sim SSL_{10}47$	Components that increased with SSL/10% amendment
PC2	21.3 / 72.4	-	NO_2^-, Ca^{2+}, SO_4^{2-}	$NC12, NC29, NC47$	Components that increased with liming
PC3	10.2 / 82.6	+	NO_3^- >>> $FormO^-$, Mg^{2+}	$Ncal47 > Ncal29 > Ncal12$	Components that decreased with liming
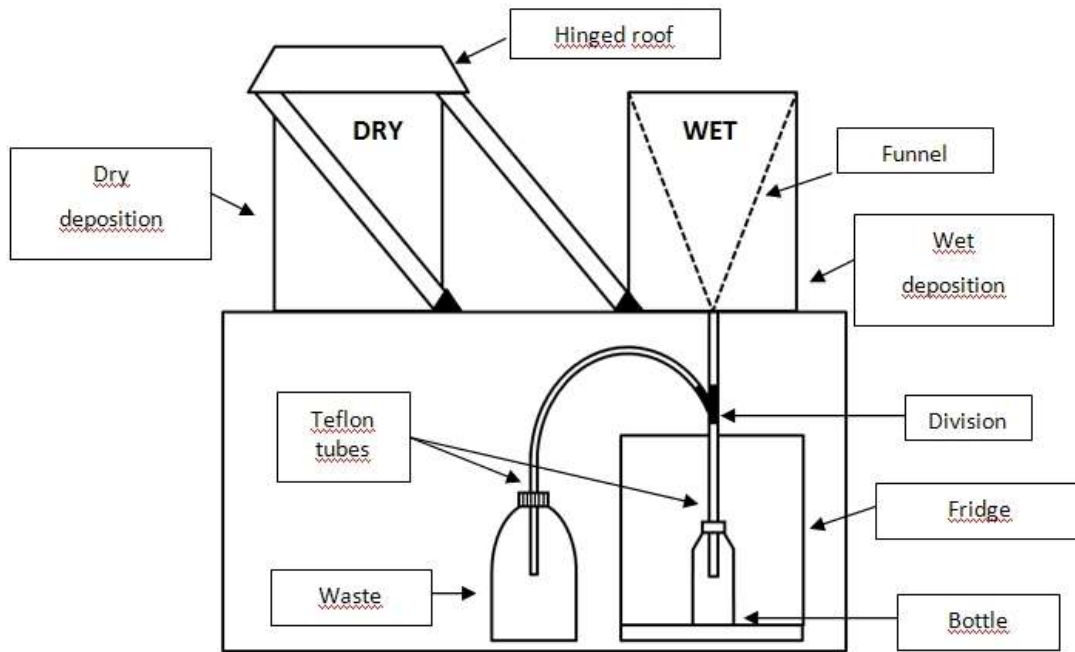
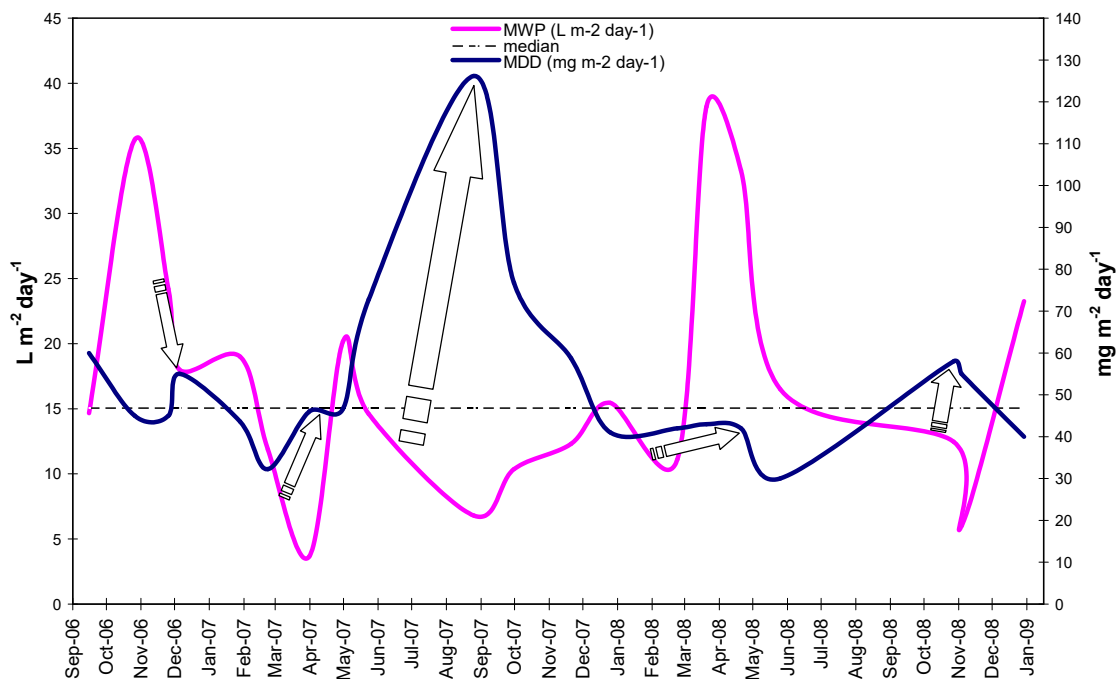Fig. 1 Modifications made to the automatic sampler TISCH ENVIRONMENTAL 78 100 APS

Fig. 2 Graphical correlation between monthly wet precipitation (MWP, L m^{-2} day^{-1}) and monthly dry deposition (MDD, mg m^{-2} day^{-1})
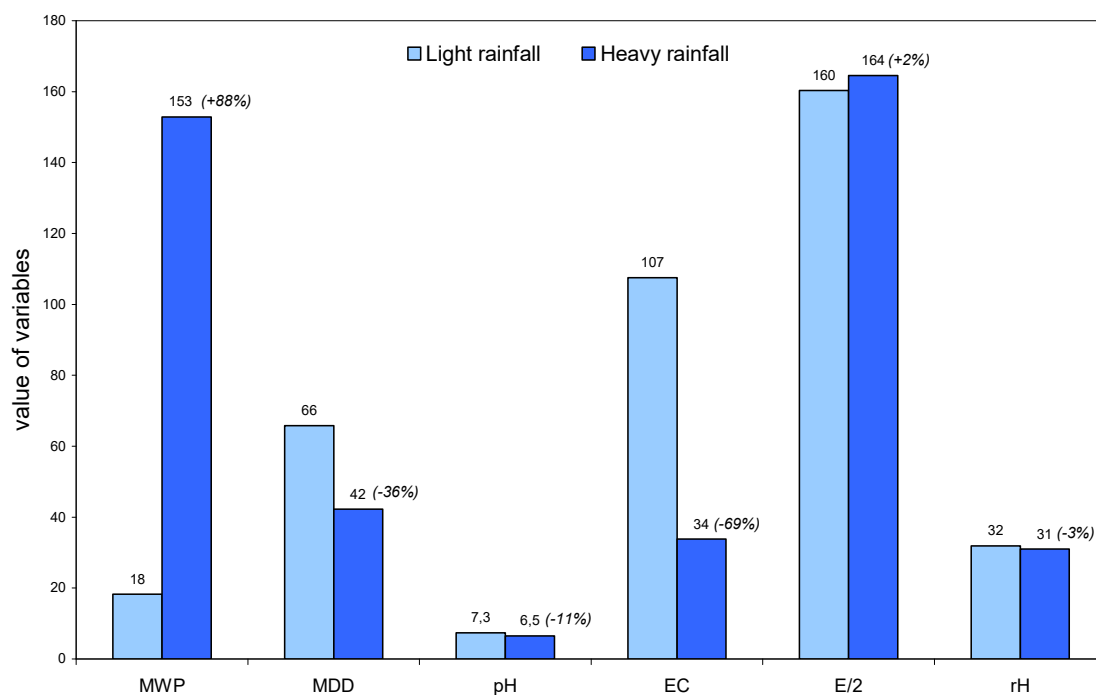
Fig. 3 Percentage variation of physicochemical parameters in rainwater and variation for wet precipitation (MWP, L m^{-2} day^{-1}) and dry precipitation (MDD, mg m^{-2} day^{-1}) values