



Dissolved organic and inorganic matter in bulk deposition of a coastal urban area: An integrated approach



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ABSTRACT

Bulk deposition can remove atmospheric organic and inorganic pollutants that may be associated with gaseous, liquid or particulate phases. To the best of our knowledge, few studies have been carried out, which simultaneously analyse the presence of organic and inorganic fractions in rainwater. In the present work, the complementarity of organic and inorganic data was assessed, through crossing data of some organic [DOC (dissolved organic carbon), absorbance at 250 nm (UV_{250nm}), integrated fluorescence] and inorganic [H^+ , NH_4^+ , NO_3^- , non sea salt sulphate ($NSS-SO_4^{2-}$)] parameters measured in bulk deposition in the coastal urban area of Aveiro. The organic and inorganic parameters analysed were positively correlated ($p < 0.001$) except for H^+ , which suggests that a constant fraction of chromophoric dissolved organic matter (CDOM) came from anthropogenic sources. Furthermore, the inverse correlations observed for the organic and inorganic parameters with the precipitation amount suggest that organic and inorganic fractions were incorporated into the rainwater partially by below-cloud scavenging of airborne particulate matter. This is in accordance with the high values of DOC and NO_3^- found in samples associated with marine air masses, which were linked in part to the contribution of local emissions from vehicular traffic. DOC of bulk deposition was the predominant constituent when compared with the constituents H^+ , NH_4^+ , NO_3^- and $NSS-SO_4^{2-}$, and consequently bulk deposition flux was also highest for DOC, highlighting the importance of DOC and of anthropogenic ions being simultaneously removed from the atmosphere by bulk deposition. However, it was verified that the contribution of anthropogenic sources to the DOC of bulk deposition may be different for distinct urban areas. Thus, it is recommended that organic and inorganic fractions of bulk deposition are studied together.

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1. Introduction

During precipitation, rainwater dissolves and scavenges atmospheric gases and aerosols that contain a large array of inorganic and organic materials. Rainwater has been collected and analysed routinely worldwide to determine air quality trends and to understand the effects of atmospheric inorganic chemical substances (e.g. sulphate, nitrate, ammonium) on receiving ecosystems. Many studies have demonstrated the influence of different natural and anthropogenic sources on the inorganic chemical composition of precipitation (Calvo et al., 2010; Zhang et al., 2007a; Zunckel et al., 2003). For example, sea salt aerosol (mainly sodium and chloride) dominates precipitation chemistry in coastal areas (Ceron et al., 2002; Zhang et al., 2007b), wind-borne dust and soil are

important sources of many ions present in rainwater, such as calcium and aluminium (Al-Khashman, 2005; Pulido-Villena et al., 2006), and most of the anthropogenic influences on atmospheric chemistry are due to emissions of nitrogen and sulphur compounds (Al-Momani, 2003; Das et al., 2005). Although several studies have been conducted in relation to the inorganic chemistry of rainwater, less attention has been paid so far to the organic chemistry of rainwater.

With the perception that all rainwater constituents present low concentrations, DOC is a major component of both marine (23 μM) and continental rain (161 μM), with concentrations greater than nitric and sulphuric acids combined (Willey et al., 2000). In rainwater, DOC refers to a plethora of dissolved compounds that are derived from organic materials, and it is composed of 'organic acids', 'organic bases', and neutral compounds (Seitzinger et al., 2003). Willey et al. (2000) reported that organic acids were the largest contributor (40%) to the total rainwater DOC in North Carolina. However, the complexity of rainwater dissolved organic

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matter (DOM) and the large percentage considered uncharacterized (50% of rainwater DOC; Willey et al., 2000) makes DOC a parameter that can be used as a measure of the totality of DOM. The carbon flux in rainwater (0.3 Gt C yr^{-1}) is equal to approximately 6% of the fossil-fuel influx (5.5 Gt C yr^{-1}) to the atmosphere (Willey et al., 2000). As both natural and anthropogenic sources contribute to DOC, it is important to evaluate whether DOC in rainwater has an anthropogenic contribution, and to assess the importance of rainwater as a removal mechanism of anthropogenic DOC.

To the best of our knowledge, few studies have simultaneously analysed organic and inorganic fractions in rainwater (Gioda et al., 2011; Kieber et al., 2002, 2006; Lara et al., 2001; Miller et al., 2008; Mladenov et al., 2012; Mullaugh et al., 2011; Willey et al., 2009, 2006, 2000; Yan and Kim, 2012). Thus, the aim of this study is to contribute to the understanding of the connection between dissolved organic and inorganic matter present in bulk deposition, namely with regard to its anthropogenic component. Thus, the organic parameters, such as DOC content, absorbance at 250 nm ($UV_{250\text{nm}}$), integrated fluorescence [of the three-dimensional surface of excitation–emission matrix (EEM) fluorescence spectrum] were evaluated together with the ionic composition previously associated with anthropogenic sources (NH_4^+ , NO_3^- , non sea salt sulphate: NSS-SO_4^{2-} ; Santos et al., 2011) in bulk deposition collected in the coastal urban area of Aveiro, between September 2008 and September 2009. The complementarity of organic and inorganic data was assessed. The effects of season and of air mass type and source area, determined using back-trajectory analysis, on organic and inorganic composition of bulk deposition were also assessed. It was also essential to determine and evaluate simultaneously the magnitude of the removal of carbon and of anthropogenic ions from the atmosphere by the bulk deposition so as to understand the atmospheric deposition processes.

2. Experimental

2.1. Bulk deposition sampling and sample preparation

Bulk deposition was collected at a sampling station ($40^\circ 38' \text{N}$, $8^\circ 39' \text{W}$) located in the western part of the coastal town of Aveiro, Portugal, between September 2008 and September 2009. The town of Aveiro has an area of 197.6 km^2 and a population of around 78,450 people (“Statistics Portugal”, www.ine.pt). Near the sampling site there is a road that is used daily on a large scale and that may influence the local atmospheric composition and hence the composition of rainwater. The sample collection was carried out 70 cm above the ground, through glass funnels (30 cm diameter) into glass bottles (5 L). The sampling containers were left out open in order to collect the bulk deposition (both wet and dry depositions) on a 24-h basis. Compositional changes may have occurred in the sample collectors during the period of collection, especially in the warm summer months. However, the containers were placed inside PVC opaque tubes, and thus the samples were protected from direct sunlight, in order to minimize changes due to photochemical reactions. Prior to use, all glass materials were immersed for 30 min, in a solution of NaOH (0.1 M), then rinsed with distilled water, followed by another immersion for 24 h in a solution of HNO_3 (4 M), and finally rinsed with ultrapure (Milli-Q) water. During the sampling period the precipitation collected was 417 mm, approximately 50% of the total precipitation that occurred (839 mm), and the samples collected were representative of the sampling period (Santos et al., 2011, 2013). After collection, samples were transported to the laboratory and divided into three aliquots. One aliquot was used for the immediate measurements of pH (Santos et al., 2011). The second aliquot of samples, used to study

the organic fraction, was filtered through hydrophilic PVDF (polyvinylidene fluoride) Millipore membrane filters ($0.45 \mu\text{m}$): one sub-aliquot was stored in glass vials in the dark at 4°C for a maximum of four days for subsequent optical analysis (UV–visible and molecular fluorescence spectroscopy; Santos et al. 2010), while another sub-aliquot of sample was frozen for subsequent analysis of DOC content (Santos et al., 2013). The third aliquot of samples used to study the inorganic fraction was filtered through sterilized nitrocellulose filters (Millipore) of $0.45 \mu\text{m}$ pore size, and frozen until the analysis of ion composition (NH_4^+ , NO_3^- and SO_4^{2-} ; Santos et al., 2011). Details about measurements of measured analytes are presented in Table 1.

2.2. Optical analysis

UV–visible spectra (in the range of 200–600 nm) of samples were recorded on a Shimadzu (Dusseldorf, Germany) Model UV 210PC spectrophotometer using quartz cells of 10 cm path lengths. Ultrapure water was used as reference in order to obtain the baseline.

The molecular fluorescence spectra were obtained using a Fluoromax 3 (JobinYvon–Spex Instruments S.A., Inc, now HORIBA Jobin Yvon Inc, Edison, NJ, USA) with a xenon lamp as the source of radiation. Fluorescence intensity measurements were carried out under thermostated conditions at 20°C and spectra were recorded using 1 cm cells, and 5 nm band passes on both the excitation and the emission monochromators. Excitation–emission matrix (EEM) fluorescence spectra were obtained by concatenating emission spectra measured every 5 nm from 290 to 510 nm using excitation wavelengths (λ_{ex}) from 240 to 400 nm also increasing at 5 nm intervals. Scans were corrected for instrument configuration using factory supplied correction factors (Coble et al., 1993), and data were normalized to a daily-determined water Raman intensity ($275_{\text{ex}}/303_{\text{em}}$, 5 nm bandpasses) and converted to Raman normalized quinine sulphate (QS) equivalents in ppb (Coble et al., 1998). For each sample, a daily blank (Milli-Q water) spectrum was subtracted from each sample spectrum. Replicate scans within 5% agreement in terms of intensity and within bandpass resolution in

Table 1
Analytical methods, method of detection limit (LD), LD and relative standard deviation (RSD) of measurements of measured species.

Species	Method	Method of LD	LD	RSD (%)
DOC	TOC analyser: the concentrations of TC and IC were measured and the DOC concentration was calculated as the difference (TC–IC).	$\text{LD} = 3S_{y/x}/b$	TC: 36 $\mu\text{g/L}$, IC: 112 $\mu\text{g/L}$	<5
NH_4^+	Spectrophotometric: indophenol blue method (citrate method; Hall and Lucas, 1981) and absorbance was measured at 640 nm.	$\text{LD} = 3S_{y/x}/b$	49 $\mu\text{g/L}$	<10
Cl^-	Ion chromatography	$\text{LD} = 3S_{y/x}/b$	0.54 $\mu\text{g/mL}$	<5
NO_3^-	Ion chromatography	$\text{LD} = 3S_{y/x}/b$	0.46 $\mu\text{g/mL}$	<5
SO_4^{2-}	Ion chromatography	$\text{LD} = 3S_{y/x}/b$	0.37 $\mu\text{g/mL}$	<5
NSS-SO_4^{2-}	Calculated from total SO_4^{2-} concentration by subtracting a fraction of 0.103 of Cl^- level (Pio et al., 1991).	–	–	–

TOC is the total organic carbon; TC is the total carbon; and IC is the inorganic carbon. $S_{y/x}$ is the residual standard deviation of the linear regression; b is the sensitivity of the method.

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