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On the water-soluble organic nitrogen concentration and mass size distribution during the fog season in the Po Valley, Italy

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ABSTRACT

The study of organic nitrogen gained importance in recent decades due to its links with acid rain, pollution, and eutrophication. In this study, aerosol and fog water samples collected from two sites in Italy during November 2011 were analyzed to characterize their organic nitrogen content. Organic nitrogen contributed 19–25% of the total soluble nitrogen in the aerosol and around 13% in fog water. The largest water soluble organic nitrogen concentrations in the $PM_{1.2}$ fraction occurred during the diurnal period with mean values of 2.03 and 2.16 μg-N m^{-3} (154 and 145 nmol-N m^{-3}) at Bologna and San Pietro Capofiume (SPC), respectively. The mean PM_{10} WSON concentration during diurnal periods at SPC was 2.30 μg-N m^{-3} (164 nmol-N m^{-3}) while it was 1.34 and 0.82 μg-N m^{-3} (95.7 and 58.5 nmol-N m^{-3}) in the night and fog water samples, respectively. Aerosol mass distribution profiles obtained during fog changed significantly with respect to those estimated in periods without fog periods due to fog scavenging, which proved to be over 80% efficient. Linear correlations suggested secondary processes related to combustion and, to a lesser extent, biomass burning, as plausible sources of WSON. Regarding the inorganic nitrogen fraction, the results showed that ammonium was the largest soluble inorganic nitrogen component in the samples.

1. Introduction

Nitrogen is an essential nutrient for all living organisms and the largest component in the Earth's atmosphere. Diatomic nitrogen molecules in air are nearly chemically inert due to their triple bond (Seinfeld and Pandis, 2006). In the past, studies on inorganic N species received the most attention until Cornell et al. (1995) put forward the potential importance of the organic N fraction. Based on previous studies it can be said that organic N seems to be ubiquitous and exists in gaseous, particulate and aqueous phases (González Benitez et al., 2010; Mace et al., 2003b; Reyes-Rodríguez et al., 2009; Scudlark et al., 1998; Zhang and Anastasio, 2001; Zhang et al., 2008). The role of organic N in acidification of soils and aquatic systems, nutrient enrichment and other atmospheric and particulate processes is not completely understood, but its importance is widely recognized (Cape et al., 2011). It is well known that part of the organic matter found in aerosol samples is soluble in water and its concentration can be substantial (Decesari et al., 2000; Facchini et al., 1999a; Varga et al., 2001). The presence of these compounds may significantly affect the warm rain processes, such as droplet activation, and the chemical and physical properties of hydrometeors in clouds and fogs (Decesari et al., 2003; Facchini et al., 1999b; Frosch et al., 2011; Fuzzi et al., 2002; Gysel et al., 2004; Jacobson et al., 2000; McFiggans et al., 2006).

Organic N constitutes a part of the total organic matter. However, the interest in the water soluble component arises from the assumption that solubility is linked to bioavailability (Peierls and Paerl, 1997; Wedyan et al., 2007). In the case of liquid samples (rain or fog), 'dissolved' or 'soluble' matter is what passes through a filter meanwhile, for aerosol, it means that it is the fraction obtained from the extraction with water. Published reports about the fraction of water soluble organic nitrogen (WSON) with respect to the total amount of nitrogen have shown similar variability in rain as well as in particulate matter. In the case of rainwater the fraction of WSON has a range between 10 and 42% of the total N (Cornell, 2011) while the WSON in particulate matter contributes between the 10 and 39% of the total amount of total soluble nitrogen (TDN) (see Table 3 of Cape et al., 2011). Because fog and cloud droplets are smaller than raindrops, water soluble compounds might be found at higher concentrations than in rain. The mean concentrations of WSON reported by Reyes-Rodríguez et al. (2009) for fog in California and by Zhang and Anastasio (2001) for cloud water in Puerto Rico were 531 μM and 42 μM, respectively. These values are, in general,

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larger than those reported for rain (Cornell, 2011), with the exception of the one published by Zhang et al. (2008) in China.

Analytically, water soluble organic nitrogen is defined as the difference between TDN in a sample (fog/cloud water or the solution extracted from sampled particulates) and the water soluble inorganic nitrogen (WSIN), with WSIN being the nitrogen deriving from all the inorganic species in the solution (ammonium, nitrate, nitrite). This is expressed as WSON = TDN − WSIN.

It is recognized that the water soluble organic carbon (WSOC) is a very complex mixture of organic compounds. Recent developments in mass spectrometry have allowed the examination of a large amount of water soluble organic species in the atmosphere, thus providing their elemental composition. These studies show that a significant fraction of WSOC contains nitrogen and sulfur (LeClair et al., 2010; Mazzoleni et al., 2012). Whereas individual identification of WSON species has been limited to amines, aminoacids, urea and few others, Chen et al. (2010) and Claeys et al. (2012) reported that WSON can be associated with high molecular weight compounds (e.g. humic-like substances, known as HULIS, which include components with strong polar, acidic and chromophoric properties). Apparently, there is a larger set of organic N compounds in the particulate phase. The WSOC:WSON ratio can be used as an indicator of nitrogen bioavailability and for the estimation of the molecular weight of WSON compounds in fog and rain (Michalzik et al., 1997; Zhang and Anastasio, 2001; Zhang et al., 2002).

Dissolved inorganic nitrogen species are commonly determined by ion chromatography. The same technique can be used to quantify some organic nitrogen compounds, as low molecular weight alkyl amines and urea (Facchini et al., 2008; Mace et al., 2003b). Total water soluble nitrogen has been measured by several techniques, e.g. UV photo-oxidation, persulfate digestion and high-temperature oxidation, among others (Cornell et al., 2003). Detailed information about some of the risks and limitations involved in each method can be found in the works of Cape et al. (2011), Mace and Duce (2002), Scudlark et al. (1998) and Yan et al. (2007); although the first ones comment that the high-temperature combustion instruments may be the best option, at least for liquid samples, because of technological and analytical improvements. The main uncertainty in the determination of WSON arises withal from its definition, which is subject to large aggregation of errors.

The main objective of this study was the estimation of the WSON concentrations in aerosol and fog water samples collected in the Po Valley (Italy) during November 2011. The Po Valley is the largest agricultural and industrialized area in Italy and fog episodes are a frequent phenomenon in the region during fall and winter seasons (Fuzzi et al., 1992). In the present paper the major results from this study are presented, including (1) the concentration and relative amounts of WSON in particulate matter and fog water collected and (2) the contribution of amino compounds to the organic N fraction.

2. Experimental methods

2.1. Collection locations and sampling strategy.

The results shown in this study were obtained from atmospheric aerosol and water fog samples collected at the experimental base 'Giorgio Fea' (44.65 N, 11.61 E) in San Pietro Capofiume (SPC) during November (15–30), 2011. The station is located about 30 km northeast from the city of Bologna, in the Po Valley, as shown in Fig. 1 and is classified as a rural background site (Carbone et al., 2010). A second location for sampling during the field campaign (urban background site) was located at the Institute of Atmospheric Sciences and Climate building (44.52 N, 11.34 E) in Bologna (BO), Italy. In this second location only particulate matter was collected.

Aerosol sampling was performed using 5-stage Berner impactors (D_{50} cut offs: 0.050, 0.14, 0.42, 1.2, and 3.5 μm for stages 1, 2, 3, 4 and 5, respectively), with a prestage excluding particles larger than 10 μm at the operation air flow of 80 L per minute. Each Berner stage was

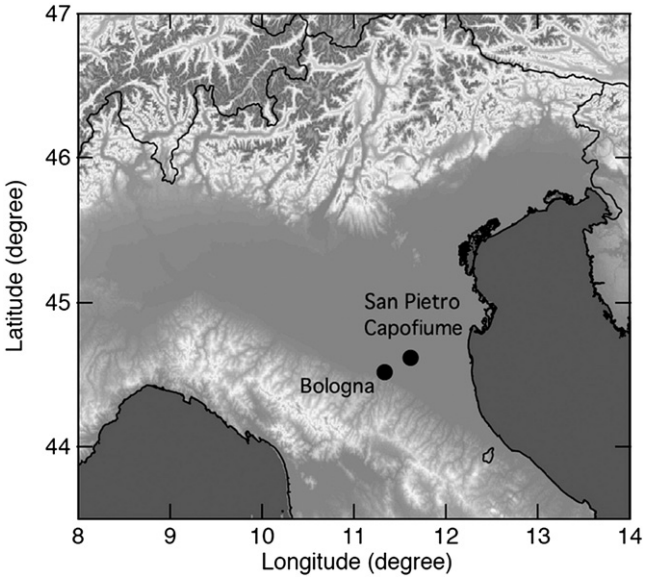

Fig. 1. Geographical location of the sampling sites mentioned in the text.

equipped with Tedlar and aluminum foils in parallel, as described by Matta et al. (2003). Samples were collected in two time periods: day (from 09:00 to 17:00 h, local time) and night (from 17:00 to 09:00 next day). Fog water was collected by means of a custom-made fog water sampler described by Fuzzi et al. (1997). A particulate volume monitor PVM-100 was used to determine the fog liquid water concentration (LWC), with a time resolution of 1 min, which activates the fog collector on the basis of a protocol described by Fuzzi et al. (1997). Whereas the meteorological definition of fog is for a visibility less than 1 km, the definition for fog used here was based on a LWC threshold of 0.08 g m^{-3}, which correspond to about 200 m visibility, according to empirical tests performed during previous field campaigns at the same location. At lower LWC values the sampling efficiency of the fog collector is poor and the amount of fog water in the collected sample is not enough for chemical analysis.

Aerosol samples were labelled as "day" referring to those collected during the diurnal period (as mentioned above), whereas those collected during the nocturnal period were classified according to the presence of fog ("fog") or the absence of it ("night") during the sampling period. According to these definitions, in the present study the aerosol samples labelled as "fog" refer to interstitial particulate matter sampled during fog events.

2.2. Sample analysis

Size-resolved concentrations of WSOC, WSIN, and amines for aerosol samples were determined for the impactor samples after extraction of the Tedlar foils in 10 ml of ultra-pure milli-Q water by sonication for 30 min and their subsequent filtration. Separation and quantification of ammonium, methyl-, dimethyl-, trimethyl-, ethyl-, and diethylammonium ions were performed by ion chromatography (IC) on an IonPac CS16 3 × 250 mm Dionex separation column with gradient MSA elution. Nitrate and nitrite ion chromatographic analyses were done with a similar instrument but equipped with an IonPac AS11 2 × 250 mm Dionex separation column with gradient KOH elution. WSOC was quantified using a TOC thermal combustion analyzer with NDIR detection (a Multi N/C 2100 elemental analyzer by Analytik Jena) as the difference between total dissolved carbon in the water extract and inorganic carbon content (Rinaldi et al., 2007). TDN analysis was performed on the aerosol water extracts using the above instrument operating in N-mode by thermocatalytic oxidation (800 °C in 100% O_2), thus generating NO then detected by