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Chemical characterization of polar organic markers in aerosols in a local area around Bologna, Italy

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HIGHLIGHTS

- The season-dependent occurrence of polar organic markers in air was assessed.
- We investigated urban and suburban area surrounding Bologna, Italy.
- The impact of primary emission sources and secondary processes was evaluated.
- Local emissions from urban, industrial and agricultural activities were identified.
- Photochemical processes showed higher contribution in summer.

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ABSTRACT

The composition and seasonal variations of water-soluble organic compounds, including 18 dicarboxylic acids and 7 sugars, were determined in the atmospheric aerosol in the surroundings of Bologna, Northern Italy, during intensive summer and winter campaigns.

In both seasons the most abundant compound is levoglucosan, as the major by-product from biomass burning. The abundances of dicarboxylic acids exhibit a seasonal pattern with higher winter concentrations (mean total concentrations are 60 ng m^{-3} and 23 ng m^{-3}, in winter and summer, respectively). The distribution profiles and the diagnostic ratios of these markers allowed to estimate the contribution of primary emission sources (power plants, vehicular circulation, biomass burning) associated with secondary constituents from both biogenic and anthropogenic precursors. The distinct seasonal pattern of abundances suggests, overall, the dominant role of secondary formation of particulate organics in summer, and the highest strength of primary emissions in winter.

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1. Introduction

Water-soluble organic compounds (WSOCs), in particular dicarboxylic acids (DCAs) and sugars, are ubiquitous constituents of airborne particulate matter, representing a highly variable fraction (10–80%) of the particulate organics in the atmosphere. WSOCs are relevant chemical markers, since they can be primarily emitted from different combustion sources (e.g. fossil and biomass fuels) or secondarily produced by photochemical oxidation of anthropogenic and biogenic precursors (Dabek-Zlotorzynska et al., 2005; Cheng et al., 2006; Fisseha et al., 2004; Kourtchev et al., 2008; Oliveira et al., 2007; Aggarwal and Kawamura, 2009). In addition, there is evidence that airborne WSOCs affect the global climate, since they alter the hygroscopic properties of particles, changing their ability to act as cloud condensation nuclei, and increasing the atmospheric absorption of solar radiation and atmospheric heating (Ruiz-Jimenez et al., 2012; Gierlus et al., 2012).

The aim of this study is a detailed investigation of the spatial and seasonal variations of selected organic tracers – n-alkanoic dicarboxylic and phthalic acids, hydroxyl carboxylic acids, levoglucosan and saccharides – in a local area surrounding a municipal waste incinerators (MPWI) near to Bologna, an Italian great urban centre. This is a part of the MONITER project developed in Italy by Environmental Protection Agency of Emilia Romagna Region (ARPAER) in order to evaluate the impact of MPWI emissions on the ambient air and to estimate the exposure levels to toxic compounds for a population living in the neighbourhoods (http://www.arpa.emr.it/moniter/). In fact, there is intense social concern about the emissions from MPWI of various atmospheric pollutants, such as heavy metals, toxic organic compounds – persistent, bioaccumulative,

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carcinogenic or endocrine disruptors – and particles (Besombes et al., 2001; Buonanno et al., 2011) and their possible effects on humans, because large population groups live and work close to plants (Hwang et al., 2008; Kim et al., 2011).

In that perspective, it looked important to collect information on the relative strengths of primary emission sources and secondary photochemical processes influencing the air quality in the studied area, which is exposed to MSWI emissions.

2. Materials and methods

2.1. Reagents and standards

Reagents used for the derivatization (BSTFA 1% trimethylchlorosilane and Pyridine) were obtained from Aldrich Chemical Co. (Milan, Italy). Dicarboxylic acid and sugar standards were purchased from Fluka/Aldrich/Sigma (Sigma Aldrich, Srl, Milan, Italy). All standards and reagents were of the highest purity commercially available. All solvents were trace analysis grade (from 99.7%) from Sigma Aldrich (Milan, Italy).

For each dicarboxylic acid and sugar, individual stock standard solutions were prepared in methanol (at 500–1000 μg L^{-1} concentration levels) and diluted serially with water (purified with a Milli-Q system, Millipore, Vimodrone, Milan, Italy) to obtain standard solutions (1.0–30 ng L^{-1} for each compound) for computing the calibration curves.

The derivatizing agents, as well as the individual and composite standard solutions, were stored at 4 °C.

2.2. Sample collection and extraction

The investigated area was close to city of Bologna (~400,000 inhabitants) in Northern Italy, and is characterized by significant agricultural and industrial activities and the presence of main arterial roads. Simulation programmes were used to identify six sampling sites around the incinerator according to the characteristics of the territory, in order to minimize the influence of the other sources and identify the impact associated with MSWI (the site locations are reported in Fig. 1). In particular,

- two maximum impact sites where the incinerator produces the most marked impact in winter (MXW) and in summer (MXS), respectively;
- two control points where the incinerator impact may be considered negligible, i.e., CTW and CTS for winter and summer, respectively;
- two sites corresponding to maximum and minimum of the studied domain, where all the emission sources are estimated to have maximum, MXD, or minimum, MND, impact.

Two sites not influenced by incinerator emission were also included: MGA, which reflects the background atmosphere of the town and CAS representing the rural background away from major anthropogenic sources.

The different locations were simultaneously investigated over 30 days intensive campaigns in summer (June and July 2008) and winter (January and February 2009) in order to maximize small-scale local effects for singling out the variability of primary sources.

The $PM_{2.5}$ samples were collected on a precombusted quartz fibre filter (20 × 25 cm) with an automatic outdoor station consisting of a low-volume sampler (Skypost PM, TCRTECORA Instruments, Corsico, Milan, Italy) operating at a flow rate of 38.3 L min^{-1} for 24 h. After sampling, the procedure outlined in European Standard EN 12341 was applied for equilibration and weighing.

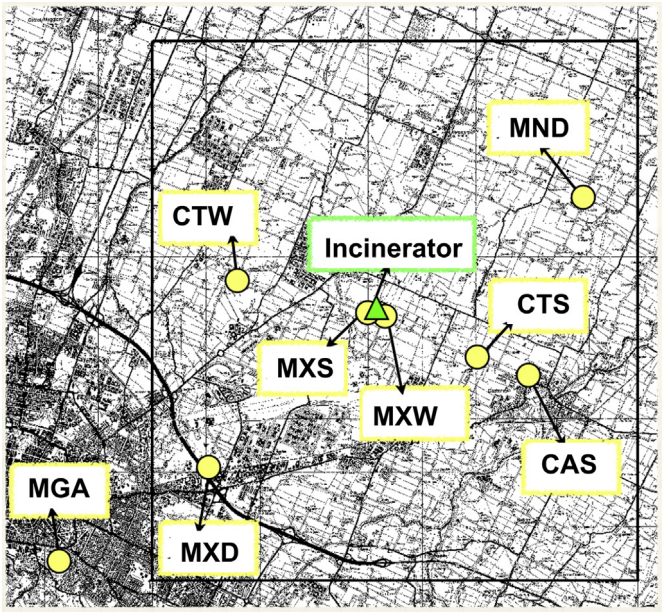

Fig. 1. Location of the sampling sites. Site symbols: MXW: maximum fallout (winter); MXS: maximum fallout (summer); CTW: control point (winter); CTS: control point (summer); MND: minimum of the domain; MXD: maximum of the domain; MGA: urban background; CAS: rural background.

Filter samples were extracted for 30 min in an ultrasonication bath with pure Milli-Q water (3 × 10 mL) and then the extract aliquots were filtered using a glass fibre filter (42.5 mm, GF Grade, Whatman, Maidstone, UK) to remove insoluble particles. The filtrate was then evaporated completely using a stream of high-purity nitrogen.

The Moniter protocol prescribed that each collected PM filter (40 samples for each site for each campaign) was divided into six parts to be delivered to the different laboratories involved in the project for the comprehensive chemical characterization, i.e, EC/OC, metals, inorganic and organic ions, hydrocarbons, PAHs. Consequently, for WSOC analysis the portions corresponding to 6 subsequent days were collected together to represent the air volume of 55.2 m^3 sampled in one day.

2.3. GC–MS instrumental analysis

The analytical procedure has been described elsewhere (Pietrogrande and Bacco, 2011) and briefly summarized in the following. Prior to GC–MS analysis, the filter extract was submitted to a silylation reaction for 70 min at 75 °C: 40 μL of BSTFA plus 1% trimethylchlorosilane (TMCS), 15 μL of pyridine and 40 μL of n-isooctane were added in combination with 5 μL of n-hexadecane, as an injection internal standard (IS, 150 ng injected).

The GC–MS system was a Scientific Focus-GC (Thermo-Fisher Scientific, Milan, Italy) coupled with PolarisQ Ion Trap Mass Spectrometer (Thermo-Fisher Scientific, Milan, Italy). The column used was a DB-5 column (L = 30 m, I.D. = 0.25 mm, df = 0.25 μm film thickness; J&W Scientific, Rancho Cordova, CA, USA). High-purity helium was the carrier gas with a velocity of 1.5 mL min^{-1}.

Temperature programme conditions were optimized for analysis of the wide range of targets: an initial temperature of 75 °C (held for 5 min) was raised to 135 °C at 2 °C min^{-1}, followed by an isothermal hold for 3 min; after that, the temperature was increased to 180 °C at 2 °C min^{-1}, then further raised to 300 °C at 7 °C min^{-1}. All samples were injected in splitless mode (splitless time: 60 s) at the injector temperature of 250 °C.

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