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Organic aerosols in a Brazilian agro-industrial area: Speciation and impact of biomass burning

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ABSTRACT

This work presents the first comprehensive organic characterization of atmospheric aerosols from an agro-industrial region (São Paulo State, Brazil) highly impacted by biomass burning. The organic speciation was performed using different solvents of increasing polarity, enabling the identification and quantification of 172 different organic species by GC–MS. The mass of organic compounds reached 123 μg m^{-3} in an aerosol sample collected during the sugar cane harvest period compared with 0.82 μg m^{-3} in the non-harvest period. The samples most impacted by biomass burning were those with the highest percentages of non-polar compounds (*n*-alkanes; up to 96%). However, in absolute terms, the total mass of polar compounds in such samples was greater than for samples less impacted by this activity. Retene (a marker for biomass combustion) was the most abundant of the 19 polycyclic aromatic hydrocarbons quantified, corresponding to 14%–84%. This work shows that biomass burning was responsible for a benzo(a)pyrene equivalent index value that exceeded the recommendation of the World Health Organization. Principal component analysis indicated that agricultural biomass burning and emissions from crop processing facilities explained 42% of the variance of the data, while 37% was explained by urban emissions, 10% by vehicle emissions, and 10% by biogenic sources. This study provides insights into the emissions of a suite of organic compounds that could participate in anthropic alteration of regional cloud formation and precipitation patterns.

1. Introduction

Intensive biomass burning occurs across vast agricultural areas of São Paulo State, mainly in sugar cane plantations (INPE, 2015). This is due to the need to burn off the outer leaves of the cane to facilitate manual harvesting. The regional emissions of gases and particulate matter increase significantly during the sugar cane harvest period (Allen et al., 2010, 2011), and consequently high concentrations of organic and inorganic species have been found in aerosols and rainwater collected during this period (Campos et al., 2007; Coelho et al., 2008, 2011).

The ethanol/sugar cane industry proposes to end the practice of manual harvesting (which requires the use of fire) in São Paulo State by 2017, based on a voluntary agreement, or by 2021, according to a State law applying to lands with low gradients. In the 2010–2011 period (when the samples used in this work were collected), an area of 46,000 km^2 was burnt in São Paulo State, which is responsible for ca. 50% of Brazilian sugar cane production (IBGE, 2015).

Previous work showed that organic matter makes up approximately 60% of the aerosol emitted during sugar cane burning (Allen et al., 2010). However, little is known about the chemical species that constitute the aerosol organic fraction, mainly due to the great variety of compounds in such matrices (Calvo et al., 2013).

Using levoglucosan, mannosan, and galactosan as chemical tracers of biomass burning in the aerosol, it was possible to establish that agro-industrial activities lead to important emissions of organic compounds to the lower troposphere (Urban et al., 2014). The primary emissions of sugars from biomass burning in the study region were from 2 to 7 times higher than identified biogenic emissions, during both harvest and non-harvest periods (Scaramboni et al., 2015).

Besides the anhydrosugars, other organic tracers have been used to establish relationships between the sources and the chemical characteristics of the atmospheric aerosol. Aliphatic compounds and their homologous series can serve as chemical markers to establish whether the source of atmospheric aerosol is vegetation wax or fossil fuel (Alves et al., 2010, 2014a; Bi et al., 2008; Gonçalves et al., 2010, 2011; Mirante et al., 2013). Polycyclic aromatic hydrocarbons (PAHs) are another important group of chemical markers that can indicate

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incomplete fossil fuel combustion or biomass burning (Alkurdi et al., 2013; Kim et al., 2013).

Phytosterols are ubiquitous constituents of all plants and can be used to infer plant sources. The most abundant sterols in aerosol samples are cholesterol (C_{27}), ergosterol (C_{27}), campesterol (C_{28}), β-sitosterol (C_{29}), and stigmasterol (C_{29}) (Alves, 2008). Cholesterol has a triple origin: it can be derived from cooking emissions (Robinson et al., 2006); from pine, oak, eucalypt, and shrub burning (Alves et al., 2010); and has also been associated with edaphic processes (Puglisi et al., 2003).

Phenolic compounds include methoxyphenols, polyphenols, and alkyl phenols. The most abundant group in atmospheric aerosols is the methoxyphenols, found as lignin thermal degradation products and as semi-volatile components of smoke particles. Therefore, these species can be markers of biomass burning emissions (Kjällstrand and Petersson, 2001). Resin acids, oxy- and hydroxyacids, and aromatic acids are also found in plants and can be useful aerosol markers of biomass burning or direct volatilization from plant matter (Alves et al., 2010; Girisuta, 2007; Graham et al., 2002).

The molecular analysis of organic solvent-extractable compounds associated with carbonaceous aerosols yields discriminating evidence for the assessment of (i) the human impact on the atmospheric environment at a regional level and (ii) the natural background of biogenic emissions to the troposphere. Thus, a detailed organic speciation provides chemical fingerprints that are source-specific and useful for identifying single or multiple contributions in samples of atmospheric aerosols. Moreover, the implementation of consistent interpretative methods applied to organic databases allows detailed comparisons and regional generalizations.

This paper focuses on measurements of the above-mentioned subgroups of organic compounds in aerosols, with the aim of providing the first comprehensive study of the organic composition of aerosol particles from an agro-industrial region of São Paulo State impacted by biomass burning. Several organic markers, diagnostic tools, and statistical methods were used to identify emission sources in order to improve our understanding of how intensive regional agricultural activities can affect the environment and human health.

2. Experimental

2.1. Sampling

Total aerosol samples were collected during 24 h on 15 October 2010, 1 February 2011, 19 August 2011, and 21 August 2011, on the campus of São Paulo State University (UNESP), located on the outskirts of the municipality of Araraquara, within São Paulo State's sugar belt. Three samples were further collected from 20:00 to 06:30 (local time) on 3 August 2010, 13 August 2010, and 16 August 2010, in a rural region near the town of Ourinhos, located at the edge of the sugar cane belt (Fig. 1). The two sites can be considered as an unit because they are predominantly agricultural (with sugar cane cultivation) and have aerosol inputs of similar strength and chemical composition, as shown in other works (Urban et al., 2012, 2014; Caetano-Silva et al., 2013; Scaramboni et al., 2015).

Six samples were collected during the sugar cane harvest period, which extends from April to November (dry season, winter), and one sample was obtained in the non-harvest period (wet season and summer), which lasts from December to March. A field blank was collected during 24 h in Araraquara without switching the aerosol sampler on.

The investigation of samples collected during the harvest period was prioritized because previous work showed that during this period the concentration range of saccharide biomass burning markers was much more variable than for the non-harvest period (Urban et al., 2014). In addition, during the non-harvest period, the aerosol inputs were reduced and the contribution of biomass burning sources was much lower (Scaramboni et al., 2015; Urban et al., 2012).

The populations of Araraquara and Ourinhos are approximately 209,000 and 103,000 inhabitants, respectively. The economies of both municipalities are largely based on sugar cane plantation and processing. Previous work has shown that both sites are highly impacted by biomass burning emissions. Details of the sampling sites and collection procedures can be found in Urban et al. (2012, 2014). Briefly, samples were collected using a high-volume sampler (Model TE-5000, Anchor International, Inc.) placed at 3 m height, fitted with non-baked glass fiber filters (Whatman, 25.2 × 20.2 cm) and operated at a flow rate

Fig. 1. Map of Brazil with a zoom showing the areas planted with sugarcane in São Paulo State.