Atmospheric Environment 90 (2014) 106–112

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Sugar markers in aerosol particles from an agro-industrial region in Brazil

R.C. Urban [a], C.A. Alves [c], A.G. Allen [b], A.A. Cardoso [b], M.E.C. Queiroz [a], M.L.A.M. Campos [a,*]

[a] Department of Chemistry, University of São Paulo, Ribeirão Preto, SP 14040-901, Brazil
[b] Institute of Chemistry, São Paulo State University, Araraquara, SP 14800-900, Brazil
[c] Centre for Environmental and Marine Studies, University of Aveiro, 3810-193 Aveiro, Portugal

HIGHLIGHTS

- Anhydrosugars in atmospheric aerosol were highly affected by biomass burning.
- Biogenic emissions of sugars were observed mainly during the non-burning period.
- Anhydrosugars may increase the hydrophilic properties of the aerosols.
- A levoglucosan to mannosan ratio is proposed to identify sugar cane smoke particles.

ARTICLE INFO

Article history:
Received 29 October 2013
Received in revised form
12 February 2014
Accepted 18 March 2014
Available online 20 March 2014

Keywords:
Levoglucosan
Sugar cane
Ethanol fuel
Agricultural impact

ABSTRACT

This work aimed to better understand how aerosol particles from sugar cane burning contribute to the chemical composition of the lower troposphere in an agro-industrial region of São Paulo State (Brazil) affected by sugar and ethanol fuel production. During a period of 21 months, we collected 105 samples and quantified 20 saccharides by GC–MS. The average concentrations of levoglucosan (L), mannosan (M), and galactosan (G) for 24-h sampling were 116, 16, and 11 ng m^{-3} respectively. The three anhydrosugars had higher and more variable concentrations in the nighttime and during the sugar cane harvest period, due to more intense biomass burning practices. The calculated L/M ratio, which may serve as a signature for sugar cane smoke particles, was 9 ± 5. Although the total concentrations of the anhydrosugars varied greatly among samples, the relative mass size distributions of the saccharides were reasonably constant. Emissions due to biomass burning were estimated to correspond to 69% (mass) of the sugars quantified in the harvest samples, whereas biogenic emissions corresponded to 10%. In the non-harvest period, these values were 44 and 27%, respectively, indicating that biomass burning is an important source of aerosol to the regional atmosphere during the whole year.

1. Introduction

There is an increasing demand for ethanol fuel due to economic interests and the need to minimize the dependence on oil and diminish the release of greenhouse gases into the atmosphere. Brazil is the world's largest producer of sugar cane, and the second largest producer of ethanol. National production has tripled in the last 20 years, and this trend is likely to be continue over the next decade.

The State of São Paulo alone accounts for over 50% of the total area (96,166 km^2) used for sugar cane plantation in Brazil (IBGE, 2013). To facilitate the manual harvest of the sugar cane, the outer leaves are burnt, leading to large emissions of gases and particulate matter to the atmosphere (Da Rocha et al., 2005). Mechanized harvesting in São Paulo State (which does not require the use of fire) reached about 65% in the 2011/2012 season, and the State goal is to end all manual harvesting by 2017. For this reason, atmospheric emissions in the "sugar cane belt" of São Paulo State are going through intense modifications, with unknown environmental consequences. Another source of biomass burning in the region is that of sugar cane bagasse (the solid crushed cane residue), which returns to the production process as an energy source. The excess bagasse produced by the sugar/alcohol sector is used to generate electricity, or sold to power other types of industry in the

* Corresponding author.
E-mail address: lcampos@ffclrp.usp.br (M.L.A.M. Campos).

http://dx.doi.org/10.1016/j.atmosenv.2014.03.034

region, such as orange processing plants. These activities are likely to be continued for some time in the near future.

Atmospheric aerosols derived from biomass burning are particularly important because of their role in cloud formation, nutrient transport, radiative fluxes, and human health (Allen et al., 2010; Alves, 2005; Artaxo et al., 2005; Monks et al., 2009; Ramanathan et al., 2001; Sena et al., 2013). Saccharides are among the emitted water-soluble organic compounds and can be used as molecular markers (Jia and Fraser, 2011).

Potassium has been proposed as a biomass burning tracer because it is abundant in plants; however, other inputs from the use of fertilizers in agriculture, associated with soil re-suspension, may overwhelm the biomass burning emissions (Andreae, 1983; Urban et al., 2012). The monosaccharide levoglucosan (1,6-anhydro-β-D-glucopyranose), derived from D-glucose units, is the most abundant among the anhydrosugars emitted during the pyrolysis of cellulose. This compound occurs in relatively large quantities in primary fine organic aerosol and only forms at temperatures above 300 °C; therefore, it can serve as a specific biomass burning marker (Simoneit et al., 1999). This sugar significantly correlated with water-soluble organic carbon in smoke particles, indicating that biomass burning can be an important source of organic hydrophilic compounds to the atmospheric aerosol (Urban et al., 2012).

Although the anhydrosaccharides mannosan (1,6-anhydro-β-D-mannopyranose) and galactosan (1,6-anhydro-β-D-galactopyranose) are emitted at much lower concentrations than levoglucosan, they also constitute biomass burning markers – only the burning of hemicelluloses, which contain mannose and galactose units, as well as other carbohydrate monomers, can generate these saccharides (Graham et al., 2002). Anhydrosugars production during biomass burning depends on several factors such as the flame temperature, the process duration, the water content, and the quantity of cellulose and hemicellulose in the vegetation (Otto et al., 2006; Simoneit, 2002).

A previous paper reported that the ratio between levoglucosan and mannosan (L/M) in the particulate material emitted during the burning of various types of wood from Portuguese forests was predominantly smaller than 7 (Gonçalves et al., 2011). The levoglucosan and mannosan concentrations reported for aerosol samples from the Amazon, resulted into an L/M ratio of around 22 (Decesari et al., 2006; Graham et al., 2002; Kundu et al., 2010). These different L/M ratios can support discernment between inputs from different combustion sources.

Some sugars and sugar-alcohols were also identified as good tracers for different types of primary biological aerosol particles such as pollen, fungal spores, vegetative debris, viruses, and bacteria (Fu et al., 2012; Yttri et al., 2007). Since they are highly soluble, these compounds have been the target of several recent scientific studies, due to their probable ability (which is still not well defined) to act as cloud condensation nuclei (Graham et al., 2002; Ekström et al., 2009). Therefore, a better knowledge of the aerosol sugar content, on the molecular level, will contribute not only to the identification of sources, and improvement of the mass balance, but may also help in predicting the formation of cloud condensation nuclei. Particular interest has been given to the study of the chemistry of atmospheric aerosol from the Amazon region (e.g. Martin et al., 2010). More recently, rural regions of the State of São Paulo have also drawn the attention of the scientific community due to the large emission of aerosol and gases to the atmosphere (Allen et al., 2010; Caetano-Silva et al., 2013). However, very little is known about the organic chemical constitution of the aerosol, its radiative forcing and its ability to act as cloud condensation nuclei (CCN).

This manuscript shows data gathered during comprehensive field work in an agro-industrial region of the State of São Paulo impacted by pre-harvesting sugar cane burning. Additionally, this region is of particular interest, because it is undergoing fast changes in the agricultural practices – producers are phasing out biomass burning emissions, but soil re-suspension is likely to increase as a consequence of increasing reliance on harvesting machinery. The presence of sugars in the aerosol is expected to increase the hydrophilic properties of the particles. In this work, we quantified twenty different sugars in the investigated aerosol samples, and used some of these sugars as molecular markers to obtain additional information about the aerosol sources. We aimed to gain better insight into how smoke particles from sugar cane burning contributed to the chemical composition of the lower troposphere in the São Paulo agro-industrial region, to support further studies on particle growth and formation of CCN.

2. Experimental

2.1. Sampling

Aerosol samples ($n = 105$) were collected on the campus of São Paulo State University (UNESP) located on the outskirts of Araraquara (AQA), a city with around 209,000 inhabitants and with the economy based on the production and processing of sugar cane (Fig. 1). From May to July 2010, aerosol sampling was performed during daytime (typically from 10:00 to 16:00 local time) and nighttime (from 20:00 to 06:30 local time). From September 2010 to February 2012, samples were also obtained over 24–h periods (these samples will be identified where appropriate). Three nighttime samples were also collected on the outskirts of Ourinhos (OUR), a town of around 102,000 inhabitants, which is also located in the sugar cane belt of the State of São Paulo (Fig. 1), and were used for a more detailed sugar speciation analysis. Both sites were surrounded by sugar cane and were mostly subjected to emissions from sugar cane production and processing.

Samples were collected using a high-volume sampler (model TE-5000, Anchor International, Inc.), at a flow rate of 1140 L min^{-1}, fitted with glass fiber filters (Whatman, 25.2 × 20.2 cm) – and therefore not baked. Size-resolved samples were collected using a six-stage (including backup filter) cascade impactor, with

Fig. 1. Map showing sampling locations.