



Total sugars in atmospheric aerosols: An alternative tracer for biomass burning



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HIGHLIGHTS

- Total sugars may be used as a simple alternative tracer of biomass burning.
- There was a strong correlation between total sugars and levoglucosan in the aerosol.
- The largest identified fraction of the total sugars was from biomass burning.
- On average, ca. 40% of total sugars was present in particles <0.49 μm.

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ABSTRACT

Ambient aerosols were collected in an agro-industrial region of São Paulo State (Brazil) between May 2010 and February 2012 ($n = 87$). The atmosphere of the study region is highly affected by the emissions of gases and particles from sugar and fuel ethanol production, because part of the area planted with sugarcane is still burned before manual harvesting. This work proposes the quantification of total sugars as an alternative chemical tracer of biomass burning, instead of levoglucosan. The quantification of total sugars requires a small area of a filter sample and a simple spectrophotometer, in contrast to the determination of levoglucosan, which is much more complex and time-consuming. Total sugars concentrations in the aerosol ranged from 0.28 to 12.5 μg m⁻³, and (similarly to levoglucosan) the emissions were significantly higher at night and during the sugarcane harvest period, when most agricultural fires occur. The linear correlation between levoglucosan and total sugars ($r = 0.612$) was stronger than between levoglucosan and potassium ($r = 0.379$), which has previously been used as a biomass burning tracer. In the study region, potassium is used in fertilizers, and this, together with substantial soil dust resuspension, makes potassium unsuitable for use as a tracer. On average, ca. 40% of the total sugars was found in particles smaller than 0.49 μm. By including data from previous work, it was possible to identify from 35 to 42% of the total sugars, with biomass burning making the largest contribution. The high solubility in water of these sugars means that determination of their concentrations could also provide important information concerning the hydrophilic properties of atmospheric aerosols.

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1. Introduction

The scientific interest in atmospheric aerosols is frequently due to their potential to affect human health and climate. Direct effects of aerosols on climate result from their ability to reflect, disperse, and absorb solar radiation. Depending on their hygroscopicity, aerosol particles can be more or less efficient as cloud condensation

nuclei, and can therefore indirectly affect rainfall patterns and climate (Monks et al., 2009; Griffin, 2013; Ramanathan et al., 2001).

Particles that are smaller than 10 μm can enter the human lung and can even reach the bloodstream, affecting both lungs and heart. The possible health consequences range from simple irritation of the airways (such as coughing or difficulties in breathing) to premature death in people with heart or lung disease (Griffin, 2013; EPA, 2014). The impact of aerosols on human health and climate depends on their composition and size, which are directly linked to their sources (Hinds, 2005).

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In order to identify the sources of atmospheric aerosols, specific chemical compounds (or ratios between compounds) can be used as tracers (Gonçalves et al., 2014). Polysaccharides (sugars) are among the organic tracers that are present in the atmospheric particulate matter. These polymers are natural hydrophilic carbohydrates that are structural components of the cell walls of higher plants, algae, fungi, and bacteria. They compose at least 75% of the dry weight of the total biomass (BeMiller, 2008).

Sugar sources to the atmosphere are diverse and include direct biogenic emissions, vegetation burning, soil dust resuspension, and bacterial and fungal spores (Yttri et al., 2007; Jia and Fraser, 2011; Fu et al., 2012). In plants, pollen accumulates starch reserves, which are converted into glucose, fructose, and sucrose that can then be released into the atmosphere (Pacini et al., 2006). Sucrose is also often present in soil, which can be resuspended into the atmosphere (Rogge et al., 2007). Arabitol and mannitol are polyols that are used as tracers for fungal spores. Under humid conditions, the spores emit aqueous jets containing polyols, which then dry to produce fine primary particles (Elbert et al., 2007; Bauer et al., 2008).

Many sugars, polyols, and their derivatives are also emitted into the atmosphere during the combustion of vegetation. These sugars can be primary combustion products, formed by direct volatilization from vegetal matter, or may be products of polysaccharide decomposition. They may also be produced by hydrolysis of similar anhydrosugars under acidic atmospheric conditions (Graham et al., 2002). Since these substances are relatively stable in the atmosphere, their quantification in the aerosol enables evaluation of the influence of biomass burning on atmospheric composition (Fraser and Lakshmanan, 2000).

The anhydrosaccharide levoglucosan (1,6-anhydro- β -D-glucopyranose) is used as a molecular marker of biomass burning, as it is the main product of the pyrolysis of cellulose present in plants, and is only formed at temperatures above 300 °C (Simoneit et al., 1999; Urban et al., 2014). Mannosan (1,6-anhydro- β -D-mannopyranose) and galactosan (1,6-anhydro- β -D-galactopyranose) are anhydrosaccharides derived from mannose and galactose, and are emitted at much lower concentrations than levoglucosan (Otto et al., 2006). Factors such as the duration of the burning process, the temperature of the flame, the water content, and the quantity of cellulose and hemicellulose in the vegetation, are critical determinants of the types of anhydrosugars produced during biomass burning (Simoneit, 2002).

Although levoglucosan can be degraded by acid-catalyzed hydrolysis to form β -D-glucose, this compound has a lifetime of approximately 10 days in the atmosphere, allowing it to be used as a tracer for biomass burning on a regional scale (Fraser and Lakshmanan, 2000; Jordan et al., 2006). Hydrated sugars (such as glucose) should have even higher stability, because they are six-membered ring compounds with lower tensional carbon bonds than the five-membered ring levoglucosan (Smith and March, 2007). Hence, it is unlikely that hydrated sugars would be significantly degraded during long-range transport.

Forest burning and the use of fire in agricultural practices emit large quantities of particulate materials and gases to the atmosphere, and both activities are still widespread in Brazil (Oliveira et al., 2011). This work was conducted in an agro-industrial region of São Paulo State, where the economy is based on sugar and fuel ethanol production. To facilitate manual harvesting, farmers set fire to the outer leaves of the sugarcane, and during the experimental phase of this work (2010/2011) about 46,000 km² of sugarcane plantations were burned in São Paulo State alone (IBGE, 2014; UNICA, 2014). There is a State law imposing a phasing out of this practice; however, the solid crushed cane residue is now used as a renewable industrial fuel, so biomass combustion emissions are likely to continue for the foreseeable future.

The emissions of organic compounds are so large in the study region (Campos et al., 2007; Coelho et al., 2008) that the annual wet deposition flux of dissolved organic carbon is similar to that found in Amazonia, where vegetation burning is notoriously intense (Williams et al., 1997). Furthermore, in the study region, the levels of carcinogenic and mutagenic PAHs were found to be above the limit established by the World Health Organization (Urban et al., 2014).

The use of levoglucosan as a molecular tracer for biomass burning has proved to be extremely useful; however, the analytical procedure used to quantify this anhydrosugar is time-consuming because it involves sample extraction, drying, and a derivatization step before analysis using gas chromatography-mass spectrometry (GC-MS). Moreover, the costs associated with the instrumentation are quite high.

Potassium was proposed as a tracer of biomass burning because it is ubiquitous in the cytoplasm of plants (Andreae, 1983). However, there are important limitations in the use of this marker, because soil dust resuspension and fertilizers can be major sources of potassium found in the atmosphere (Urban et al., 2012).

Given the need to find an alternative biomass burning marker, the aim of this work was to evaluate whether measurement of the total concentration of sugars in the aerosol could be a useful tool for that purpose. Total sugars concentrations have been measured quantitatively since 1948, using a procedure known as the “anthrone method”, which is based on a simple spectrophotometric analysis (Morris, 1948).

2. Experimental

2.1. Sampling

Aerosol samples were collected in São Paulo State at the UNESP campuses located in the municipalities of Araraquara and Ourinhos (Fig. 1). The economies of both regions are based on sugarcane production and processing. More detail about the sampling sites can be found in Urban et al. (2012, 2014).

The collection period in Araraquara was from May 2010 to February 2012, with the exception of August 2010, when a field campaign was carried out in Ourinhos. Samples were obtained during daytime (typically from 10:00 to 16:00 local time), nighttime (from 20:00 to 06:00), and 24 h periods. The dry season, corresponding to the sugarcane harvest period, extended from April to November, and the rainy season was from December to March.

Total aerosol samples ($n = 77$) were collected onto Whatman glass fiber filters (25.2 × 20.2 cm) using a high-volume sampler (Model TE-5000, Anchor International, Inc.). Size-resolved samples ($n = 11$) were collected using a six-stage (including backup filter) cascade impactor, as described in Urban et al. (2014), but only the fraction <0.49 μm was available for this study. The filters containing the particulate matter were wrapped in aluminum foil, kept in clean plastic bags, and stored at -22 °C until analysis.

2.2. Total sugars determination

An accurately measured area of between 3.8 and 4.2 cm² of the filter containing the particulate matter was cut into small pieces and placed in a conical flask. The extraction was performed with 1.0 mL of ultrapure water (Milli-Q, Millipore) in an ultrasonic bath (Model T14, Thornton) during 15 min. The extract was centrifuged at 3000 rpm for 10 min to obtain a supernatant containing the soluble species. The extraction procedure was repeated twice and the final solution (3.0 mL) was filtered with a 0.45 μm Millex-PVDF system (Millipore).

The determination of total sugars was performed in duplicate using the anthrone method, as described by Fartas et al. (2009). The

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