Organic characterization of particulate material from a Brazilian agro-industrial region impacted by biomass burning

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Biomass burning is widely used in Brazil for deforestation and in agricultural practices. Rural areas within São Paulo State emit large quantities of particulate matter to the atmosphere due to extensive biomass burning during sugar cane plantation management. This practice is used to remove the outer leaves of the cane and facilitate manual harvesting.

The objective here was to perform a chemical characterization (including marker compounds) of the atmospheric particulate matter in an agro-industrial region of Brazil impacted by biomass burning (Araraquara and Ourinhos - SP). Ultimately, better knowledge of the chemical composition of these aerosols should improve our understanding of the role played by biomass burning particles in terms of both the regional climate and human health.

Seven samples of ambient total particulate matter (TPM) were collected on glass fiber filters using a high-volume sampler. Samples were extracted using dichloromethane and methanol, fractionated into five different classes by vacuum flash chromatography, and analyzed by GC-MS (Alves *et al*., 2011).

Hydroxy-acids, oxy-acids, and aromatic acids were found at relatively high concentrations, as expected for biomass burning particles (Graham *et al*., 2002). The most abundant acid in the aerosol was glycolic acid (4.3 - 300 ng m^{-3}), which has been described as a product of the hydrolysis of hemicelluloses (Girisuta, 2007).

Among the phenolic compounds, coumaryl-type was the most abundant (60 - 94%), followed by syringyl (5.3 - 37%) and vanillyl (0.87 - 16%). Coumaryl compounds are formed preferentially during the burning of *Gramineae* species (Alves, 2008). The most abundant sterol was *β*-sitosterol (50 - 60%), also characteristic of *Gramineae* burning (Oros *et al*., 2006), followed by cholesterol (4.0 - 33%) and stigmasterol (7.5 - 46%).

The concentrations of polycyclic aromatic hydrocarbons (PAH) ranged from 1.93 to 38.7 ng m^{-3} (average: 19.1 ± 16.1 ng m^{-3}). These values are similar to those reported for other regions where burning is used in sugar cane fields (Vasconcellos *et al.*, 2003).

Retene, a biomass-burning marker, was the most abundant PAH found in the samples (14 – 84%; Figure 1). Benzo[a]pyrene (BaP) concentrations ranged from 0.03 to 2.2 ng m^{-3}. This compound has carcinogenic and mutagenic characteristics, and the World Health Organization recommends a maximum limit concentration of 1 ng m^{-3}. Four out of six samples collected during the harvest period had BaP concentrations (0.94, 0.98, 1.1, and 2.2 ng m^{-3}) either close to or higher than the limit value. Similar observations were made in earlier work by Godoi *et al*. (2004).

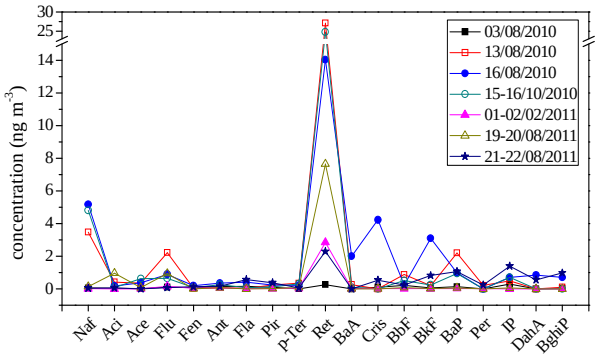

Figure 1. Concentrations of PAHs.

The most polar compounds extracted were alcohols (fraction 4) and sugars and acids (fraction 5). These two fractions corresponded to between 4.0 and 72% of the total measured mass of organic carbon. The lowest percentages of polar compounds (4.0 and 6.8%) were found in the two samples with the strongest influences of biomass burning (collected on 13/08/2010 and 16/08/2010). The percentages of *n*-alkanes in these samples were 95.7 and 92.7%, and the total concentrations of organic compounds were 115 and 123 µg m^{-3} respectively, compared to a range of 0.8 - 2.9 µg m^{-3} for the remaining samples. The highest percentage (72%) of polar compounds was found in a sample collected during the non-harvest period.

In conclusion, although biomass burning made an important contribution to the aerosol loading, the particles concerned were mostly non-polar and therefore might be unable to act effectively as cloud condensation nuclei. The proximity of plantations to urban areas could present a health hazard to the local population due to the emissions of carcinogenic compounds.

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Alves, C. (2008) *An. Acad. Bras. Cienc*. **80**, 21-82.
Alves, C. *et al*. (2011) *Sci. Tot.Environ*. **409**, 1466-1475.
Girisuta, B. (2007) *Levulinic Acid from Lignocellulosic Biomass.* PhD thesis, University of Groningen.
Godoi, A. *et al*. (2004) *J. Chromatogr. A* **1027**, 49-53.
Graham, B. et al. (2002) *J. Geophys. Res.* **107**, 14-1-15
Oros, D.R. *et al*. (2006) *Appl. Geochem.* **21**, 919-940.
Vasconcellos P.C. *et al.* (2003) *Atmos. Environ.* **37**, 3009-3018.