Homologous series of organic compounds in aerosols impacted by sugar cane burning in São Paulo State, Brazil

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Sugar cane burning is carried out before manual harvesting to make the process easier and less labour-intensive. It takes place during the dry season, lasting from May to November. São Paulo State is the largest sugar cane producer in Brazil, accounting for 51% of the total production. The planted area in the State was 4.6 million hectares in 2010/2011 (IBGE, 2011). Around 40-50% of this area was burned before manual harvesting.

To evaluate the impact of sugar cane burning emissions on the atmospheric aerosol composition, samples of total suspended particles (TSP) were collected in two agricultural regions of São Paulo State (Araraquara and Ourinhos) using a high-volume sampler at a flow rate of 1140 L min^{-1}. Punches of the filters were solvent-extracted and fractionated into different classes of organic compounds by vacuum flash chromatography. The detailed organic speciation was performed by gas chromatography-mass spectrometry. Polar oxygenated compounds bearing carboxylic or hydroxyl groups were derivatised prior to injection into the chromatograph.

A series of *n*-alkanes were identified in the aerosol samples, ranging from C_{11} to C_{36}. The highest concentrations were observed for the C_{24}-C_{30} homologues. All the samples presented carbon preference indices (the ratio between odd and even carbon number homologues) around 1, which have been described as typical of petrogenic inputs (Alves, 2008). Vascular plants synthesise epicuticular waxes containing odd C number *n*-alkanes, usually in the C_{25} to C_{33} range with C_{29} or C_{31} as dominant homologues. The lack of odd C number predominance in this study could be due to the lesser amount of waxy hydrocarbons in the stems and leaves of the herbaceous biomass crops. The *n*-alkanes derived from plant waxes were calculated by subtraction of the average of the next higher and lower even carbon numbered homologues, taking as zero the negative values. Except for one sample (13/08/2010), in which 33% of the *n*-alkane content was attributable to plant waxes, the waxy fraction of aliphatics in the remaining samples ranged from 4.5 to 7%. The highest concentrations of *n*-alkanes were observed in samples more impacted by emissions from sugar cane burning at nighttime (Figure 1). These concentrations are much higher than those obtained in 24-h samples of PM_{10} in Piracicaba, a city in São Paulo State impacted by the same agricultural activities (Vasconcellos *et al*., 2010).

A discontinuous series of *n*-alkanols (C_{10}-C_{30}) was detected, peaking at C_{18}, C_{28} and C_{30}. Total concentrations ranged from 9.37 to 161 ng m^{-3}. The lowest level of *n*-alkanoic acids (9.66 ng m^{-3}) was obtained during the non-harvest period, while values up to 374 ng m^{-3} were reached in samples strongly impacted by smoke. In the aerosol samples of the harvest season, the homologous series encompassed acids from C_8 to C_{24} with a strong even carbon number predominance, currently associated with vegetative detritus. A series of *n*-di-acids, ranging from propanedioic to hexadecanedioic, were also present in TSP. Malic acid varied from undetectable levels for the non-harvest period to nearly 3300 ng m^{-3} during the dry season.

Taking into account the high concentrations observed for many of the homologous compounds, the exposure to these aerosols by inhalation or skin contact may be of concern due to the hazardous properties of some constituents (e.g. *n*-alkanes > C_{16}).

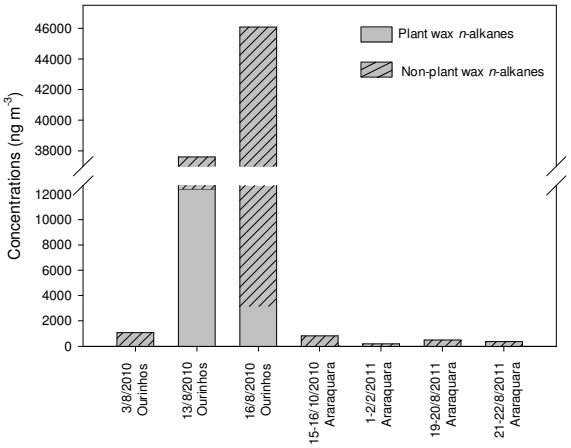

Figure 1. Concentrations of *n*-alkanes in samples from Ourinhos (nighttime samples) and Araraquara (24-h samples).

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