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Identification of the sources of primary organic aerosols at urban schools: A molecular marker approach

Leigh R. Crilley[a,1], Raeed M. Qadir[b,c], Godwin A. Ayoko[a,*], Jürgen Schnelle-Kreis[b], Gülcin Abbaszade[b], Jürgen Orasche[b], Ralf Zimmermann[b,c], Lidia Morawska[a]

[a] *International Laboratory for Air Quality and Health, Institute of Health and Biomedical Innovation, Queensland University of Technology, Brisbane, QLD 4001, Australia*

[b] *Joint Mass Spectrometry Centre – Comprehensive Molecular Analytics, Helmholtz Zentrum München, Ingolstädter Landstraße 1, D-85764 Neuherberg, Germany*

[c] *Institute of Chemistry, University of Rostock, Dr.-Lorenz-Weg 1, D-18051 Rostock, Germany*

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ABSTRACT

Children are particularly susceptible to air pollution and schools are examples of urban microenvironments that can account for a large portion of children's exposure to airborne particles. Thus this paper aimed to determine the sources of primary airborne particles that children are exposed to at school by analyzing selected organic molecular markers at 11 urban schools in Brisbane, Australia. Positive matrix factorization analysis identified four sources at the schools: vehicle emissions, biomass burning, meat cooking and plant wax emissions accounting for 45%, 29%, 16% and 7%, of the organic carbon respectively. Biomass burning peaked in winter due to prescribed burning of bushland around Brisbane. Overall, the results indicated that both local (traffic) and regional (biomass burning) sources of primary organic aerosols influence the levels of ambient particles that children are exposed at the schools. These results have implications for potential control strategies for mitigating exposure at schools.

1. Introduction

Organic aerosols are frequently the largest component of ambient fine particles in urban atmospheres (Jimenez et al., 2009). These aerosols are a complex mixture of around 10^5 and 10^6 compounds (Goldstein and Galbally, 2007) from a number of primary and secondary sources, where sources that directly emit particles into the atmosphere can be referred to as primary sources. Whereas secondary sources refer to particles formed by reactions in the atmosphere of gaseous species in the atmosphere, such as the photo-oxidation of volatile organic compounds (Seinfeld and Pandis, 2006). In an urban environment primary sources of particles can include vehicle emissions, biomass burning (from both domestic and natural sources), coal combustion, cooking, plant abrasion and paved road dust (see e.g. (Qadir et al., 2013; Schnelle-Kreis et al., 2007; Shrivastava et al., 2007)). For these primary sources there are a number of organic markers that are known to be characteristic of a specific emission source and crucially also have a long lifetime in the atmosphere to enable detection at monitoring stations (Cass, 1998). Examples of some of the more specific organic markers include levoglucosan for biomass burning (Robinson et al., 2006a) and cholesterol for meat cooking (Kleeman et al., 2008). Hopanes are present in fossil fuels, and the different hopanoid compounds are specific to the different types of fossil fuels such as coal, petroleum and lubricating oil ((Schnelle-Kreis et al., 2005) and references therein)). Thus these organic compounds along with others can be used as molecular markers for identifying the contributing sources of primary organics to ambient particles.

A quantitative assessment of the contribution of emission sources is available using positive matrix factorization (PMF), which has been successfully applied previously to organic molecular datasets (Qadir et al., 2013; Schnelle-Kreis et al., 2007; Shrivastava et al., 2007). Assessing the contribution of primary sources is important as there are numerous detrimental health effects associated with exposure to airborne particles (Heal et al., 2012; Rückerl et al., 2011). In particular, children have been shown to be more susceptible to the health effects associated with exposure to airborne particles (Rückerl et al., 2011), and several studies have linked exposure to vehicle emissions to increased risks of

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[*] Corresponding author.
E-mail address: g.ayoko@qut.edu.au (G.A. Ayoko).
[1] Present address: School of Geography, Earth and Environmental Science, University of Birmingham, Birmingham B15 2TT, United Kingdom.

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developing asthma and wheezing (Gehring et al., 2010; Ryan et al., 2009). Children spend a large portion of their day at school. Consequently schools represent a location accounting for a significant fraction of their overall daily exposure. Schools are also unique urban environments that are influenced not only by local and regional sources but also by school-related activities such as drop-off/pick-up traffic, which may result in increased exposure to vehicle emissions. However, there is limited information on children's exposure to vehicle emissions and other sources in the literature (Mejía et al., 2011).

Considering the aforementioned gaps in knowledge, the present study aimed to determine the primary sources of the ambient fine particulate matter present at urban schools by quantifying the levels of selected organic molecular markers. PMF, a receptor model (Paatero and Tapper, 1994), was applied in order to quantitatively determine the contributions of these sources to levels of ambient particles at the schools. This enabled the driving factors to the levels of different primary sources to be investigated and we hypothesized that vehicle emissions will be the main primary source contributing to children's exposure at school and this is reflected in the schools' selection criteria, outlined in the next section.

2. Method

2.1. Sampling sites

The 11 schools selected for this study, which will be referred to as S15 to S25, are in different suburbs in the city of Brisbane, Australia. A map depicting the schools location in Brisbane is given in Figure S1, Supporting Information. This chemical sampling was a part of a larger campaign to study the effect of ultrafine particle from traffic emissions on children's health, known as UPTECH (www.ilaqh.qut.edu.au/Misc/UPTECH%20Home.htm). In this study 25 schools participated but only at the last 11 schools were filters collected for this analysis due to instrument availability. The sampling campaign for the current paper was conducted from November 2011 till August 2012.

The schools that were chosen were not near any other large source of air pollution, other than road traffic and were also not close to any large infrastructure projects. A site close to the middle of the school which gave the best overall representation was chosen to conduct the measurements and sampling at each school. Inlets for the sampling were placed on the top of a trailer, which served to house all of the instruments at the site including an automatic weather station (Monitor Sensors). Data from nearby weather stations was also obtained from the Bureau of Meteorology (BOM) and Queensland Department of Science, Information Technology, Innovation and the Arts (DSITIA) as some of the schools would have been affected by local winds due to schools buildings. Sampling inlets were approximately 3 m off the ground. Traffic counts were taken on the busiest road next to the school, referred to as the main road throughout. In the traffic count, vehicles that were classified as light were cars, motorbikes and scooters. Trucks with 2, 3 and 4 axels were classified as medium vehicle and long articulated trucks classified as heavy vehicles.

2.2. Sampling methodology

The particle size fraction was selected using a low-volume $PM_{2.5}$ cyclone and the required flow rate for the cyclone was maintained using critical orifices. The particles were collected in polycarbonate filter holders on 47 mm, Quartz fiber filters (Whatman) which was pre-treated at 500 °C for 1 h prior to use. The sampling period was from 08:00 until 08:00 the next day, Monday to Friday for one week to give a total of four samples at each school. This sampling regime typically gave sampling volumes of 6 m^3. After sampling each filter was placed in a Petri dish and covered in aluminum foil. The samples were then sealed in a ziplock bag and frozen until analysis. The flow rate for the cyclones was checked at the beginning of each sample and always set to within ±0.1 L per minute of the desired flow rate. Field blanks were collected at each school and all results were field-blank corrected.

2.3. Chemical analysis

The organic composition of the samples was analyzed using In-situ Derivatization Thermal Desorption (IDTD) followed by Gas Chromatography Time-Of-Flight Mass Spectrometry (GC-TOF-MS) (Orasche et al., 2011; Schnelle-Kreis et al., 2011) at the Joint Mass Spectrometry Centre, Helmholtz Zentrum München, Neuherberg, Germany. In brief, filter punches were placed in an injection liner and spiked with internal standards (isotope labeled reference compounds) and 10 µl derivatizing agent N-Methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA). The method allows derivatization using MSTFA reagent of the polar organic fraction of filter samples in-situ on the filter during thermal desorption. Derivatization and desorption of polar organic compounds (e.g. levoglucosan and cholesterol) occurs directly from particulate matter on the filters. Therefore, polar and non-polar compounds are analyzed in one step. An automated sampling robot exchanged the complete GC liners placed in the injector which is automatically closed and opened by a liner exchanging unit (Linex, Atas GL, Netherlands). During thermal desorption (16 min, 300 °C) MSTFA enriched carrier gas was passed through the liner. Desorbed and derivatized molecules were focused at 70 °C on the head of a nearly non-polar capillary column, BPX5, 25 m, 0.22 mm ID, 0.25 µm film (SGE, Australia) which was installed in an Agilent 6890 gas chromatograph (Agilent, USA). After the isothermal run at 70 °C, the temperature was increased to 130 °C within one minute. Then the rate was lowered to 8 $°C\ min^{-1}$ until a temperature of 330 °C was reached followed by an isothermal time of 30 min. The detection of compounds was carried out on a Pegasus III TOFMS (LECO, USA). The data acquisition frequency was 25 spectra per second within a mass-to-charge range of 35–500. The detection limits for the targeted compounds can be found in Tables S1 and S2 (Supporting Information).

Details of the elemental carbon (EC) and organic carbon (OC) analysis can be found in Crilley (2013). Briefly, $PM_{2.5}$ samples were collected concurrently at the same location at each school and were analyzed according to the IMPROVE method on a thermal/optical transmittance carbon analyser (Sunset Laboratories) (Chow et al., 2001).

2.4. Data analysis

Positive Matrix Factorization (PMF) was performed in this study using the EPA PMF v3.0, developed by the U.S EPA (US-EPA and Research Triangle Park N, 2008). A total of 21 organic compounds were used in the initial analysis and these included n-alkanes from C_{20-33}, four hopanes, cholesterol, dehydroabietic acid and its methylester, levoglucosan, mannosan, EC and the OC fraction. Missing values in a certain school site were replaced with the geometric mean at the same site and the uncertainty was set to four times the geometric mean for those values. As about 80% of n-alkanes between C_{18} and C_{21} are typically in the gas phase, therefore these compounds were excluded from the PMF analysis. Species with more than 50% of data below the limit of quantification (LOQ) were also excluded from the inputs. Therefore, some alkanes (C_{20}, C_{21}, C_{26}, C_{28}, C_{32} and C_{33}), dehydroabietic acid and its methylester, and mannosan were excluded from the PMF analyses. In other few cases the values were replaced with half of the LOQ and the uncertainties set to 5/6 of the LOQ. For the other data, the uncertainties are set according to the following equation:

$$u = \left[(\text{error fraction} \times \text{concentration})^2 + (\text{LOQ})^2\right]^{0.5} \tag{1}$$

where error fraction is the percentage of uncertainty, LOQ is the limit of quantification. Overall error fractions were estimated from sampling and analytical errors. Species with low signal to noise ratio ($S/R < 2$), were assigned as weak. One hundred bootstrap runs were performed to assess the uncertainty of the factor loadings and profiles. Changing the Fpeak value did not improve the source profiles or Q value and so base model results ($\text{Fpeak} = 0$) are reported. The PMF solutions are discussed in Section 3.3.

The other data analysis technique employed was one way ANOVA used to compare the concentrations between the seasons and this was performed using SPSS v19.

3. Results and discussion

3.1. General school characteristics

The sampling was conducted over almost a full year and covered both winter and summer, as reflected in the meteorological conditions described in Table 1. Brisbane is a subtropical city with the mean temperatures ranging from 14 to 25 °C (Table 1). October till April is warmer with higher humidity and this period is referred to as summer. May till September is cooler with typically more stable weather and it is referred to as the winter months. A range of traffic conditions were also observed at the schools (Table 2). Some of the schools were on busy arterial roads (S19, S20) while others were in residential areas with low traffic counts (S16, S18, S21). There were also schools alongside roads that service commercial/light industrial areas (S23, S25) and such schools recorded a higher proportion of heavy and medium vehicles (Table 2). Based on the organic compounds detected and their relative abundance, the major contributing sources of primary organic aerosols were determined at the schools and discussed in the next sections.