First measurements of source apportionment of organic aerosols in the Southern Hemisphere

Leigh R. Crilley, Godwin A. Ayoko*, Lidia Morawska

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

ARTICLE INFO

ABSTRACT

An Aerodyne Aerosol Mass Spectrometer was deployed at five urban schools to examine spatial and temporal variability of organic aerosols (OA) and positive matrix factorization (PMF) used for the first time in the Southern Hemisphere to apportion the sources of the OA across an urban area. The sources identified included hydrocarbon-like OA (HOA), biomass burning OA (BBOA) and oxygenated OA (OOA). At all sites, the main source was OOA, which accounted for 62–73% of the total OA mass and was generally more oxidized compared to those reported in the Northern Hemisphere. This suggests that there are differences in aging processes or regional sources in the two hemispheres. Unlike HOA and BBOA, OOA demonstrated instructive temporal variations but not spatial variation across the urban area. Application of cluster analysis to the PMF-derived sources offered a simple and effective method for qualitative comparison of PMF sources that can be used in other studies.

1. Introduction

In an urban environment, OA have been frequently shown to be the largest component of ambient particles in the non-refractory PM_1 (mass concentration of particles with a diameter less than 1 μm) (Jimenez et al., 2009 and references therein). One analytical instrument for quantitative measurements of the chemical composition of OA with a high temporal resolution is the Aerodyne Aerosol Mass Spectrometer (AMS) (Canagaratna et al., 2007). One technique, which has been successfully applied to the OA mass spectra from AMS datasets, is positive matrix factorization (PMF) (Lanz et al., 2007; Ulbrich et al., 2009). PMF is a quantitative technique that requires no prior knowledge of the sources before analysis. The application of PMF has allowed for the variability in the OA to be extracted resulting in the apportionment of distinct OA factors to better model the source contributions (Lanz et al., 2007).

In many urban datasets, the two main components that are extracted by PMF are hydrocarbon-like OA (HOA), and oxygenated OA (OOA) (Lanz et al., 2007; Ulbrich et al., 2009; Zhang et al., 2005a). HOA has been shown to be correlated with primary tracers such as CO and NO_x and is considered representative of primary emissions (Ulbrich et al., 2009; Zhang et al., 2005a). The

OOA component is representative of secondary OA and can be further broken down into two subsets based upon the degree of volatility and oxidation (Lanz et al., 2007). These sub components are known as semi-volatile OOA (SV-OOA) and low-volatility OOA (LV-OOA) (Lanz et al., 2007; Ulbrich et al., 2009). SV-OOA is less oxidized and hence freshly formed OOA while the LV-OOA is more aged and oxidized OOA, and are usually derived from regional sources. However, there is a continuum of oxidation levels between fresh OOA and the more aged OOA and when this is considered with the dynamic nature of OA there can be substantial variability in the mass spectra of the factors.

Thus the OA in an urban environment is highly complex and originates from a number of local and regional sources. Many of the studies investigating the source apportionment of OA were conducted based at one site within a city (See e.g. (Brown et al., 2012; Hersey et al., 2011; Huang et al., 2010). Therefore, conducting measurements at a number of locations around one urban area for extended periods would give more accurate representation of the OA and the spatial and temporal variation in the source profiles for that urban area. There has been limited research on the spectral variability of PMF-derived source factors of OA from multiple sites within one urban environment. Studies that have used an AMS at multiple sites have been mobile measurements conducted on road and focused on vehicle emissions (Canagaratna et al., 2004) or with limited time at a particular site (Mohr et al., 2011). Mohr et al. (2011) found that though the chemical composition of PM_1
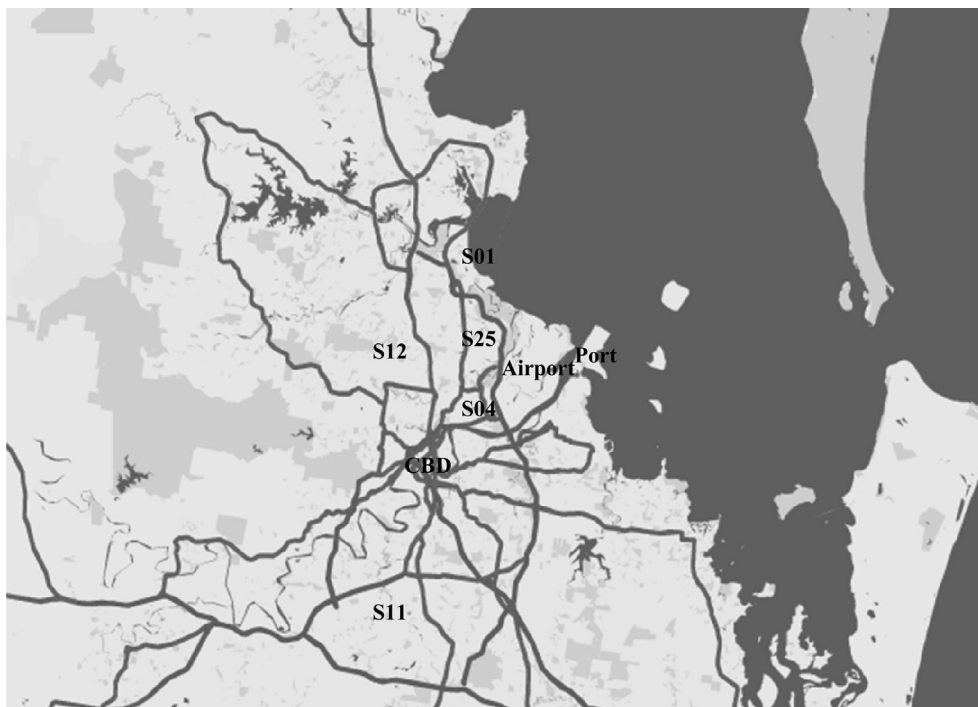
Fig. 1. Map of Brisbane city indicating the locations of sites and potential sources. Light shaded areas represent bushland, dark shaded areas the ocean/lakes and major roads are shown. CBD indicates central business district.

around Zurich in winter had a uniform distribution, by sampling at multiple sites the contribution of local sources could be distinguished. To date research has predominantly been carried out in North America and Europe (See (Ng et al., 2010), with measurements required in the Southern Hemisphere to improve the understanding of the global budget of secondary OA (Spracklen et al., 2011).

Considering the aforementioned gaps in knowledge, the aim of the current study was the source apportionment of OA at five locations around the subtropical city of Brisbane, Australia. Thus the source apportionment of the OA in an urban environment using PMF was performed, for the first time to the author's knowledge in the Southern Hemisphere. The similarities of the mass spectra for the PMF derived factors were compared using cluster analysis to quantitatively analyze the variability in the source profiles between the sites. Conditional probability function is as far as we know, applied for the first time to PMF- derived factors from AMS OA data to analyze the direction of the main contributions of sources, and their relationship with the local sources in this study.

2. Method

2.1. Sampling sites and methodology

Brisbane is a subtropical city with a rapidly growing population and as such the contribution of vehicle emissions and other anthropogenic sources to air pollution is increasing. An Aerodyne compact Time-Of-Flight Aerosol Mass Spectrometer (TOF-AMS) (Canagaratna et al., 2007; Drewnick et al., 2005) was deployed at five schools in different suburbs in the metropolitan Brisbane area, which are referred to as S01, S04, S11, S12 and S25. This study was a part of a larger project at these schools designed to study the effect of ultrafine particles from traffic emissions on children's health (www.ilaqh.qut.edu.au/Misc/UPTECH%20Home.htm). Twenty-five schools participated in this project, however measurements with

the TOF-AMS was conducted at only five schools due to various logistical reasons, and their locations are shown in Fig. 1. The schools selected were not near any other large source of air pollution including large infrastructure projects except traffic emissions. Measurements at S01 and S04 were conducted during summer whereas for S11, S12 and S25 it was performed in winter. As Brisbane is a subtropical city, the variation between the seasons is limited with winter typically drier than the summer months.

Detailed description of the sampling method, meteorology, TOF-AMS operation and the schools are given in Crilley et al. (2013). Briefly, the TOF-AMS was housed in a vacant classroom within the school and sampled for 2–3 weeks at each site with a 5 min interval. The TOF-AMS was calibrated for ion efficiency according to the standard protocols (Drewnick et al., 2005; Jayne et al., 2000; Jimenez et al., 2003). In addition to the TOF-AMS, a NO$_x$, and CO gas analyzer (Ecotech, Knoxfield, Australia) and an automatic weather station (Monitor Sensor, Caboolture, Australia) were also deployed at the schools. These instruments were housed within a trailer at a site within the school grounds reflecting the best overall exposure to the pollutants present. The trailer site was located between 50 and 150 m from the classroom with the TOF-AMS. The sampling heights for the TOF-AMS varied between 1.5 and 2 m at the sites and the gas analyzers were 3 m at all sites.

2.2. Data analysis

2.2.1. PMF analysis

The TOF-AMS data was processed and analyzed using Squirrel v1.51 in IGOR Pro v6.22. Squirrel was used to generate the organic and error matrices in the *m/z* range 13–300 for subsequent PMF analysis. PMF analysis was applied to the organic fraction data at each location using PMF2 developed by Paatero and Tapper (1994) and the PMF evaluation tool (PET) for IGOR Pro as described in Ulbrich et al. (2009). Pre-treatment of the data prior to PMF analysis as set out in Zhang et al. (2011) was applied to the organic data from