

Sources of organic aerosol: Positive matrix factorization of molecular marker data and comparison of results from different source apportionment models

Manish K. Shrivastava^a, R. Subramanian^c,
Wolfgang F. Rogge^b, Allen L. Robinson^{a,*}

^aDepartment of Mechanical Engineering, Center for Atmospheric Particle Studies, Carnegie Mellon University, Pittsburgh, PA 15213, USA

^bSchool of Engineering, University of California, Merced, CA 95343, USA

^cDepartment of Civil and Environmental Engineering, University of Illinois, Urbana, IL 6180, USA

Received 2 March 2007; received in revised form 8 August 2007; accepted 4 September 2007

Abstract

This paper presents results from positive matrix factorization (PMF) of organic molecular marker data to investigate the sources of organic carbon (OC) in Pittsburgh, Pennsylvania. PMF analysis of 21 different combinations of input species found essentially the same seven factors with distinctive source-class-specific groupings of molecular markers. To link factors with source classes we directly compare PMF factor profiles with actual source profiles. Six of the PMF factors appear related to primary emissions from sources such as motor vehicles, biomass combustion, and food cooking. Each primary factor contributed between 5% and 10% of the annual-average OC with the exception of the cooking related factor which contributed 20% of the OC. However, the contribution of the cooking factor was sensitive to the specific combinations of input species. PMF could not differentiate between gasoline and diesel emissions, but the aggregate contribution of primary emissions from these two source classes is estimated to be less than 10% of the annual-average OC. One factor appears related to secondary organic aerosol based on its substantial contribution to biogenic oxidation products. This secondary factor contributed more than 50% of the summertime average OC. Reasonable agreement was observed between the PMF results and those of a previously published chemical mass balance (CMB) analysis of the same molecular marker dataset. Individual PMF factors are correlated with specific CMB sources, but systematic biases exist between the two estimates. These biases were generally within the uncertainty of the two estimates, but there is also evidence that PMF is not cleanly differentiating between source classes.

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Keywords: Fine particulate matter; Organic carbon; Source apportionment; Receptor modeling

1. Introduction

Organic carbon (OC) is a major component of atmospheric fine particulate matter. OC is directly emitted by sources such as motor vehicles, biomass burning, and meat cooking (primary OC). It is also

*Corresponding author. Tel.: +1 412 268 3657;
fax: +1 412 268 3348.

E-mail address: alr@andrew.cmu.edu (A.L. Robinson).

formed in the atmosphere from low-volatility products of gas-phase reactions (secondary organic aerosol—SOA). The relative importance of the emissions from different source classes and even the primary–secondary split is uncertain.

Individual organic compounds can provide insight into the sources of OC (Schauer et al., 1996). Compounds associated with specific source classes are commonly referred to as molecular markers; examples include hopanes for motor vehicles exhaust and levoglucosan for biomass smoke (Simoneit, 1984, 1999).

Previous source apportionment analyses with molecular markers have used the chemical mass balance (CMB) model (Schauer et al., 1996; Zheng et al., 2002; Subramanian et al., 2007). Advantages of the CMB approach are that it can be performed using a single ambient sample and that it apportions ambient OC directly to source classes. However, CMB requires *a priori* knowledge of source profiles that represent the aggregate emissions from all sources in a given source class. Selecting source profiles is complicated because most profiles are based on a single or a small number of source tests and multiple profiles have been developed for important source classes such as motor vehicles. This creates substantial uncertainty because CMB results can depend strongly on which profiles are included in the model (Robinson et al., 2006c; Subramanian et al., 2006).

Another shortcoming of the CMB approach is that it does not directly estimate the contribution of SOA because source profiles for SOA do not exist. The amount of SOA is estimated indirectly as the difference between the measured ambient OC and the amount of OC apportioned by CMB to primary sources. Some CMB analyses suggest that primary sources contribute the majority of the OC in urban environments (Schauer et al., 1996), but more recent studies indicate that unapportioned OC (presumably SOA) dominates the overall OC mass balance (Subramanian et al., 2007; Zheng et al., 2007). There are other techniques to estimate primary–secondary split (Turpin and Huntzicker, 1995; Zhang et al., 2007), but each has its shortcomings. A number of organic species have been associated with SOA (Fraser et al., 1998; Sheesley et al., 2004; Edney et al., 2005), but these compounds have not been formally incorporated into source apportionment models.

Multivariate factor analysis models such as positive matrix factorization (PMF) offer the

potential to directly infer unknown “source profiles” and “source contributions” from ambient data. PMF has been widely applied to analyze fine particle concentrations using traditional speciation data such as OC, elemental carbon (EC), major ions, and metals; however, many of these species are not source specific, complicating the linking of PMF factors to sources. Molecular markers are highly source-class specific and therefore offer a potentially more definitive link between factors and source classes. Molecular markers for SOA can also be directly included in PMF, potentially providing insight into the primary–secondary split. However, factor analysis techniques have not been previously applied to molecular markers because they require large datasets.

This paper presents results from PMF analysis of ambient molecular marker data to investigate sources of OC in Pittsburgh, Pennsylvania. We consider different combinations of input species to evaluate the variability of the PMF results. Comparisons with source profiles are used to link the PMF factors with actual source classes. We compare the PMF results with previously published source apportionment analyses of the same Pittsburgh dataset, including CMB analysis of molecular marker data (Subramanian et al., 2007), PMF analysis of traditional speciation data (Pekney et al., 2006), SOA estimates based on the EC-tracer method (Polidori et al., 2006), and factor analysis aerosol mass spectrometer (AMS) data (Zhang et al., 2005).

2. Methods

PMF analysis was performed using data collected at the main monitoring station of the Pittsburgh Air Quality Study (PAQS), which was located approximately 6 km east of downtown Pittsburgh in a large urban park (Wittig et al., 2004). We consider 24-h average concentrations measured on 99 days between July 2001 and August 2002. Samples were collected on a 1-in-6 day schedule, with daily samples collected in July 2001 and most of January 2002. Details on the sample collection and analysis are described elsewhere (Subramanian et al., 2004; Pekney et al., 2006; Robinson et al., 2006a).

PMF analysis was performed for many different combinations of input species to identify which species were critical for defining factors. The majority of the PMF models considered different combinations of the 54 molecular markers listed in

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