Atmospheric Environment 82 (2014) 238–249

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Sensitivity of a Chemical Mass Balance model to different molecular marker traffic source profiles

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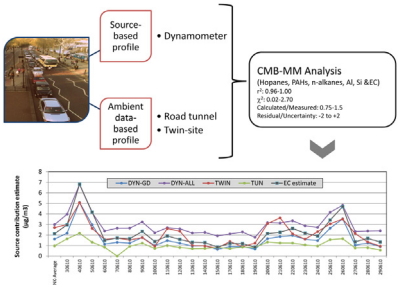
HIGHLIGHTS

- Traffic profiles for organic molecular markers are selected.
- Profiles derive from dynamometer, tunnel and twin site studies.
- The sensitivity of the CMB model to different traffic profiles is evaluated.
- Overall, the twin site profile gives the best result.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 June 2013
Received in revised form
1 October 2013
Accepted 1 October 2013

Keywords:
Receptor models
CMB
Source profile
Traffic emissions
Particulate matter

ABSTRACT

Use of the Chemical Mass Balance (CMB) model for aerosol source apportionment requires the input of source profiles of chemical constituents. Such profiles derived from studies in North America are relatively abundant, but are very scarce from European studies. In particular, there is a lack of data from European road vehicles. This study reports results from a comparison of road traffic source profiles derived from (1) US dynamometer studies of individual vehicles with (2) a traffic profile derived from measurements in a road tunnel in France and (3) new data derived from a twin-site study in London in which concentrations at an urban background site are subtracted from those measured at a busy roadside to derive a traffic increment profile. The dynamometer data are input as a diesel exhaust, gasoline exhaust and smoking engine profile, or alternatively as just a diesel exhaust and gasoline exhaust profile. Running the CMB model with the various traffic profiles together with profiles for other sources of organic carbon gives variable estimates of the contribution of traffic to organic carbon and to $PM_{2.5}$ concentrations. These are tested in two ways. Firstly, unassigned organic carbon in the output from the CMB model, assumed to be secondary organic carbon, is compared to secondary organic carbon estimated independently using the elemental carbon tracer method. Secondly, the estimated traffic contribution to organic carbon and $PM_{2.5}$ is compared with an estimate derived simply from the measured elemental carbon concentrations, and the effect on aerosol mass closure is investigated. In both cases the CMB model results correlate well with the independent measures, but there are marked differences according to the traffic source profile employed. As a general observation, it appears that the use of dynamometer data with inclusion of a smoking engine profile has a tendency to over-estimate traffic emissions at some sites whereas the tunnel profile shows a tendency to under-estimate. Overall, the traffic profile derived from the twin-site

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1352-2310/$ – see front matter
http://dx.doi.org/10.1016/j.atmosenv.2013.10.005

study gives probably the best overall estimate, but the quality of fit with independent estimates of secondary organic carbon and traffic particle mass depends upon the site and dataset for which the test is conducted.

1. Introduction

Road traffic is one of the key urban air pollution sources, and in the last few decades a significant amount of research has been undertaken in order to understand the emission characteristics as well as processes that govern vehicular emissions (Shi and Harrison, 1999; Charron and Harrison, 2003; Lough et al., 2007; Phuleria et al., 2007; El Haddad et al., 2009; Pant and Harrison, 2013). A good understanding of the relative contribution of traffic to ambient air pollutant concentrations, especially particulate matter (PM) is vital for policy action. Source apportionment techniques are used widely for quantitative estimation of the contribution of different sources to ambient PM concentrations and can be implemented in many different ways, receptor modelling being one of the methods. Watson and Chow (2007) describe receptor models as models that "interpret measurements of physical and chemical properties taken at different times and places to infer the possible or probable sources of excessive concentrations and to quantify the contributions from those sources" and this category of source apportionment techniques includes microscopic and chemical models (Pant and Harrison, 2012). With the assumption that the concentrations of chemical species are preserved between sources and receptors, receptor models use the principle of mass conservation for apportionment of PM mass to different air pollution sources. Thus, the concentration of a species measured in a sample of particulate matter can be described as (Hopke, 1991):

$$X_{ij} = \sum_{p=1}^{p} g_{ip} f_{pj} \quad (1)$$

where X_{ij} is the species concentration of i in the sample j, g_{ip} is the fractional mass of species i in source p and f_{pj} is the mass contribution of source p to particulate matter in ambient air in sample j.

There are several receptor models such as the Chemical Mass Balance (CMB) model, multivariate statistical models such as Principal Component Analysis (PCA) including factor analysis models such as Positive Matrix Factorization (PMF), Multilinear Engine (ME), UNMIX and hybrid models such as Constrained Physical Receptor Model (COPREM) (Watson et al., 2002; Viana et al., 2008). Different models use different approaches to solve Equation (1), for e.g. the CMB model uses the effective-variance least squares method whereas UNMIX uses eigenvector analysis.

1.1. CMB model

The CMB model uses the ambient measurement data for chemical species together with the associated uncertainty and source profiles for different sources as inputs, and the output consists of estimates of the contribution of each source to the total mass. The model has several assumptions including non-reactivity of the chemical species and non-co-linearity of the source profiles (Watson et al., 2002). In addition, the number of species should be greater than the number of sources in order to derive results from the model. This model has been used extensively for source apportionment of PM mass (Schauer et al., 1996; Bi et al., 2007; Sheesley et al., 2007; Chelani et al., 2008; Lambe et al., 2009; Stone et al., 2010; Yin et al., 2010; El Haddad et al., 2011; Hanedar et al., 2011; Rutter et al., 2011; Guo et al., 2012; Perrone et al., 2012). A large number of markers can be used for source apportionment including elemental carbon (EC), organic carbon (OC), trace metals and organic molecular markers. However, trace metals such as Fe, Cu, Zn and Ni are often emitted from several key sources, and in some cases, it is difficult to apportion PM mass to the sources based on the trace metals alone (Lin et al., 2010). In addition, with removal of species such as Br and Pb from fuels, such markers cannot be used conclusively for source apportionment analyses. With the idea that molecular marker compounds are emitted by specific sources and can be used to distinguish between PM sources, Schauer et al. (1996) proposed CMB modelling using organic molecular markers (hereafter referred to as CMB-MM). A number of source-specific organic molecular markers have since been proposed for use in CMB modelling. Key molecular markers include levoglucosan for wood burning, hopanes and steranes for vehicular emissions, higher n-alkanes for vegetative detritus, benzothiazoles for tyre wear and cholesterols and lactones for cooking (Rogge et al., 1993a,b; Schauer et al., 1996; Lough et al., 2007; Heo et al., 2013). A detailed description of various organic markers for different sources has been compiled by Lin et al. (2010).

1.2. Source profiles

Selection of appropriate source profiles is one of the critical steps towards obtaining a good fit with the CMB model. Source profiles are defined as "the mass abundances, i.e. fraction of total mass of chemical species in source emissions, and such profiles are generally representative of source categories rather than individual emitters" (Watson et al., 2002). Such profiles are created using emission samples from a range of emitters of a particular source category and conducting physical and chemical analyses to arrive at the contributions of each tracer element/compound (Watson et al., 2002). Source profiles are used for identification and quantification of contributions of different sources to PM using the CMB model as well as to compare and validate results obtained from factor analysis models (e.g. PMF) and to a large extent the model relies on the accuracy of the source profiles used as an input. However, in the absence of locally relevant source profiles, the Source Contribution Estimates (SCE) can be prone to erroneous results. In recent years, significant differences have been observed between laboratory-tested and real world mixed source traffic emissions (Gertler et al., 2002; Yan et al., 2009; Ancelet et al., 2011). While the typical components of any source profiles are found to be more-or-less similar, the relative mass abundances vary based on location and emitter characteristics. As a result, different combinations of source profiles can provide statistically valid yet completely different solutions (Robinson et al., 2006a).

Traffic emission profiles can be generated using several different methods including lab-based dynamometer studies, tunnel studies and twin-site studies (Rogge et al., 1993a; Lough et al., 2007; He et al., 2008; El Haddad et al., 2009; Yan et al., 2009). Since the twin site/tunnel measurements are carried out in the ambient environment, and for a mixed fleet, they are seen to be more representative of real-world emissions. A number of papers have reported the estimation of the contribution of traffic emissions to