Available online at www.sciencedirect.com
ScienceDirect
Science of the Total Environment 386 (2007) 42–52
Science of the Total Environment
An International Journal for Scientific Research into the Environment and its Relationship with Humankind
www.elsevier.com/locate/scitotenv

Source apportionment of $PM_{2.5}$ and selected hazardous air pollutants in Seattle

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Received 15 January 2007; received in revised form 17 July 2007; accepted 17 July 2007
Available online 22 August 2007

Abstract

The potential benefits of combining the speciated $PM_{2.5}$ and VOCs data in source apportionment analysis for identification of additional sources remain unclear. We analyzed the speciated $PM_{2.5}$ and VOCs data collected at the Beacon Hill in Seattle, WA between 2000 and 2004 with the Multilinear Engine (ME-2) to quantify source contributions to the mixture of hazardous air pollutants (HAPs). We used the 'missing mass', defined as the concentration of the measured total particle mass minus the sum of all analyzed species, as an additional variable and implemented an auxiliary equation to constrain the sum of all species mass fractions to be 100%. Regardless of whether the above constraint was implemented and/or the additional VOCs data were included with the $PM_{2.5}$ data, the models identified that wood burning (24%–31%), secondary sulfate (20%–24%) and secondary nitrate (15%–20%) were the main contributors to $PM_{2.5}$. Using only $PM_{2.5}$ data, the model distinguished two diesel features with the 100% constraint, but identified only one diesel feature without the constraint. When both $PM_{2.5}$ and VOCs data were used, one additional feature was identified as the major contributor (26%) to total VOC mass. Adding VOCs data to the speciated $PM_{2.5}$ data in source apportionment modeling resulted in more accurate source contribution estimates for combustion related sources as evidenced by the less 'missing mass' percentage in $PM_{2.5}$. Using the source contribution estimates, we evaluated the validity of using black carbon (BC) as a surrogate for diesel exhaust. We found that BC measured with an aethalometer at 370 nm and 880 nm had reasonable correlations with the estimated concentrations of diesel particulate matters ($r>0.7$), as well as with the estimated concentrations of wood burning particles during the heating seasons ($r=0.56$–0.66). This indicates that the BC is not a unique tracer for either source. The difference in BC between 370 and 880 nm, however, correlated well exclusively with the estimated wood smoke source ($r=0.59$) and may be used to separate wood smoke from diesel exhaust. Thus, when multiple BC related sources exist in the same monitoring environment, additional data processing or modeling of the BC measurements is needed before these measurements could be used to represent the diesel exhaust.

Keywords: Receptor modeling; Hazardous air pollutants; Aethalometer; Black carbon

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doi:10.1016/j.scitotenv.2007.07.042

1. Introduction

The federal Clean Air Act Amendments of 1990 mandate that the U.S. EPA determine a set of urban hazardous air pollutants (HAPs, or 'air toxics') that potentially pose the greatest risks in urban areas, in terms of contribution to population health risk. The current set of 188 HAPs includes toxic metals and volatile organic compounds (VOCs). The U.S. EPA identified 33 urban HAPs based on emissions and toxicities in a 1995 ranking analysis (U.S. EPA, 1999a) and developed concurrent monitoring and modeling programs to evaluate potential exposures and risks to these top-ranked 33 HAPs. The National-scale Air Toxics Assessment (NATA) estimated potential cancer and non-cancer risks associated with the ambient concentrations of these urban HAPs (U.S. EPA, 2002a, 2006). Results from the NATA project, which rely heavily on HAPs emission inventories and modeling approaches, will be used to set priorities for the collection of additional emissions data, ambient concentration data, and information on adverse effects to health and the environment.

Developing effective control strategies to reduce population exposure to certain HAPs requires identifying sources and quantifying their contributions to the mixture of HAPs and the associated health risks. One approach is to use receptor-based source apportionment models to distinguish sources. Most source apportionment studies focus on analyzing either VOCs (e.g. Mukund et al., 1996; Jorquera and Rappengluck, 2004) or fine particle ($PM_{2.5}$) mass (e.g. Kim et al., 2003; Larsen and Baker, 2003; Kim et al., 2004a). Only few studies used source apportionment modeling to identify common sources of both VOCs and $PM_{2.5}$. However, in these studies, the monitored PM species were mostly organic compounds (Harrison et al., 1996; Schauer and Cass, 2000; Schauer et al., 2002; Larsen and Baker, 2003), rather than the metals, ions, and carbon constitutes that are more routinely measured at current PM monitoring network. In other source apportionment studies that included both non-organic trace elements on PM and gaseous pollutants (Swietlicki et al., 1996; Kim et al., 2005a; Zhou et al., 2005; Liu et al., 2006), the gaseous species usually were non-VOCs (such as CO, SO_2, and NO).

Among the HAP sources commonly found in urban areas, diesel engine exhaust is of special interest as it is a likely lung cancer hazard (U.S. EPA, 2002b). Emerging evidence has also indicated that diesel exhaust exacerbates existing allergies and asthma symptoms (U.S. EPA, 2002b). Another HAP source of interest is wood smoke, which is a major contributor to the air pollution in the west coast of U.S. during winter months (Schauer and Cass, 2000; Maykut et al., 2003). Exposure to wood smoke has been linked to both acute and chronic illnesses (Naeher et al., 2007). Both diesel exhaust and wood smoke contain a complex mixture of gases and particulates. In this paper, we apportioned the diesel exhaust and wood smoke sources using the speciated PM with and without additional VOC measurements. For diesel exhaust, it is also commonly characterized by diesel particulate matter through measurements of black carbon (BC). Aethalometers are increasingly used in the field to provide continuous BC measurements to represent diesel exhaust (e.g. Edgerton et al., 2006; Zanobetti and Schwartz, 2006). However, other sources, such as wood smoke, also contribute to BC. Thus, complications of using the BC measurements as diesel exhaust marker in high and low wood smoke seasons need to be addressed.

In this study we applied source apportionment models to a combination of VOCs and non-organic elemental $PM_{2.5}$ speciation measurements to identify sources of selected HAPs in Seattle, WA. We evaluated the performance of the models with and without the addition of VOCs data. Using the source apportionment results, we examined the validity of using BC as a marker for diesel exhaust during different seasons.

2. Methods

2.1. Sample collection and analysis

Speciated $PM_{2.5}$ and VOCs measurements at the Beacon Hill monitoring site in Seattle from 2000 to 2004 were used for modeling. This urban-scale site, located in a highly populated neighborhood, has been shown to represent average $PM_{2.5}$ concentrations in a typical Seattle residential neighborhood (Goswami et al., 2002). It is located within 2 km of two major interstate freeways and arterial roads, as well as within 4 km of a warehousing area and a major seaport. Thus it is impacted by a mixture of urban sources including vehicle emissions and wood burning. A map and photograph of the monitoring site and the surrounding area can be found in Maykut et al. (2003) and Larson et al. (2006). The Beacon Hill site, as part of the U.S. EPA Speciation Trends Network (STN), collects $PM_{2.5}$ samples using the URG (Chapel Hill, NC) sampler equipped with Teflon, Nylon, and quartz filters, which were analyzed for (1) $PM_{2.5}$ mass and elemental compositions; (2) sulfate (SO_4^{2-}), and nitrate (NO_3^-), and (3) organic carbon (OC) and elemental carbon (EC), respectively (Kim et al., 2005b). VOCs samples also were