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Urban PM source apportionment mapping using microscopic chemical imaging

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HIGHLIGHTS

- Applies particle fluorescence for PM source apportionment
- Method can provide PM source apportionment results in near-real time.
- Rapid source contribution information can be used for source mapping.

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ABSTRACT

To evaluate the health impacts of particulate matter and develop effective pollutant abatement strategies, one needs to know the source contributions to the observed concentrations. The most common approach involves the collection of ambient air samples on filters, laboratory analyses to quantify the chemical composition, and application of receptor modeling methods. This approach is expensive and time consuming and limits the ability to monitor the temporal and spatial impacts from different pollutant sources. An alternative method for apportioning the sources of ambient PM is the application of microscopic chemical imaging (MCI). The MCI method involves measuring individual particle's fluorescence and source attribution is based on the individual particle analysis coupled with identification from a source library. Using this approach, the apportionment of ambient PM can be performed in near real time, which allows for the generation of temporal and spatial maps of pollutant source impacts in an urban area.

1. Introduction

Over the past 20 years, an ever-increasing number of epidemiological studies have shown significant associations between the mass concentration of ambient air particulate matter (PM) and adverse respiratory and cardiovascular health effects (e.g., Dockery et al., 1993; Pope et al., 1995; Krewski et al., 2009). PM air pollution has long been linked to both acute and chronic health effects, including asthma, cardiac disease, and other conditions (e.g., Koenig et al., 2005; Shah et al., 2008). In addition, many studies indicate that fine particles (PM with aerodynamic diameter $\leq$2.5 μm) have a greater impact on human health than coarse particles (PM with aerodynamic diameter 2.5–10 μm) (e.g., Dockery and Pope, 2006). Based on these and other studies, a US National Ambient Air Quality Standard (NAAQS) for $PM_{2.5}$ was established on 1997 and modified in 2006. The current standard is 35 μg/m^3 in a twenty-four hour period and annual average of 15 μg/m^3. At these levels, a significant number of urban areas in the US are in violation of the NAAQS and in order to develop effective abatement strategies, there is an increased need for determining the sources of $PM_{2.5}$.

One important approach used to aid in the development of cost-effective control strategies to control $PM_{2.5}$ is determining its sources through the application of various receptor modeling methods (Watson and Chow, 2004; Watson et al., 2008). These methods are implemented by collecting PM at a receptor (a location in the community), chemically analyzing the collected material, and working backwards to determine the source contributions. Meteorological data (e.g., wind speed and direction) are not required but can provide additional information in identifying specific sources. It should be noted that receptor oriented methods are complementary to source models (i.e., dispersion models, etc.) and applying them to the same ambient case will point out deficiencies in each of the approaches (Watson and Chow, 2004).

Watson et al. (2008) presented a review of the advantages and disadvantages of a number of receptor modeling methods. There are a number of receptor models, including chemical mass balance (CMB),

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non-negative least squares (e.g., PMF), edge detection (e.g., UNMIX), etc. These models tend to fall into two different categories: 1) a single variable or sample type (e.g., Chemical Mass Balance—CMB), or 2) a multivariate/multi-sample type (e.g., Principal Component Analysis (PCA), Positive Matrix Factorization (PMF), and UNMIX target transformation factor analysis). Inputs to the CMB include a speciated chemical profile for the observed ambient PM along with speciated profiles for the potential sources. The CMB then performs a linear least squares regression analysis to predict the relative source contributions to the observed ambient data. Prior to performing the CMB, the chemical profiles have to be developed. This generally involves the collection of source samples followed by detailed chemical analysis. In order to reduce model uncertainty and enable the identification of additional sources, polyaromatic hydrocarbons have, in some cases, been added to the chemical profiles (Watson et al., 1998; Fujita et al., 1998; Chow et al., 2007; Fujita et al., 2007). The multivariate approaches do not require chemically speciated source profiles but do require large, speciated ambient data sets (>100 samples). All these approaches are effective in providing estimates of source contributions to observed ambient PM; however, they are expensive (requiring multiple analytical methods) and time consuming (completion of the analysis generally takes weeks or months followed by data base development and receptor modeling).

In this paper we describe an alternative approach using microscopic imaging (MCI) to rapidly and inexpensively apportion observed ambient PM to specific source categories. Validation and limitations of the technique, along with an example of the application of the method are also presented.

2. Description of the MCI method

Taback et al. (1999) reported on a microscopic chemical imaging approach to characterize in real time particles in air or water based on their fluorescence. The original system coupled optical microscopy with spectroscopic imaging of particle fluorescence to non-destructively monitor impurities and microorganisms. One of the tests reported was the assessment of PAHs on particles. This led Gertler and Gillies (2001) to propose the application the MCI method for PM source apportionment based on the florescence spectra of PAHs. Their hypothesis was based on the use of PAHs as source markers in previous CMB apportionment studies (Watson et al., 1998; Fujita et al., 1998; Chow et al., 2007; Fujita et al., 2007). The approach taken was to analyze previous collected ambient and source filters using an MCI instrument (FIPA-20/40, GreenVision Systems, Ltd., Tel Aviv, Israel) and apply the system software (similar to the linear least squares regression technique employed by the CMB) to determine the sources of the PM, and compare the results against those obtained using the CMB.

The MCI system used in this earlier study is described in Taback et al. (1999) and Gertler and Gillies (2001). Briefly, the MCI instrument (FIPA-20/40) employs microscopic chemical imaging coupled with adaptive learning algorithms to identify chemical species that may be present on particles. Fig. 1 contains a schematic of the principle of operation. The instrument scans the collected particles and records the particle-by-particle spectra for the wavelength region of 400–900 nm using an interferometer based imaging Fourier spectrometer coupled to a fluorescence microscope with UV optics. The wavelength accuracy of the latest version FIPA-20/40 interferometer is 2 nm and quantification of pixels to 0.25 μm (equivalent to a particle of the same size) resolution is possible (in a sense, this is similar to scanning electron microscopy with an electron microprobe). The image is then digitized and pixel-by-pixel spectral information is collected (Fig. 2). Particle size and morphology information are also recorded. The software developed for the MCI instrument compares the spectral and morphological data collected for the sample with data in the source library and reports the presence of identified sources and their percent contribution to the mass of sample collected.

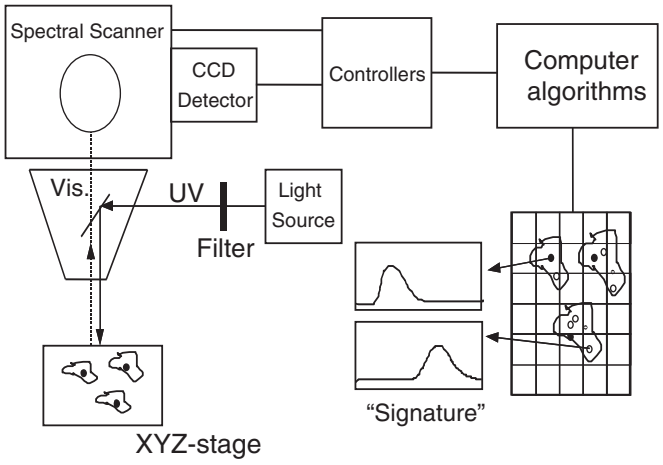

Fig. 1. Schematic of the FIPA-20 instrument for MCI analysis of particle samples.

The procedure employed by Gertler and Gillies (2001) consisted of two main parts, the first part was building a source profile data base using source samples collected as part of the Cairo Air Improvement Project (Abu-Allaban et al., 2002) and the second one was the routine scanning of ambient filters. Building the source profile data base enabled the system to recognize target sources (Fig. 3). Different source samples were scanned into the system and analyzed. Their spectral output was then saved to a database. One important criterion they used was the samples had to have been analyzed using standard analytical methods coupled with CMB source apportionment in order to validate the MCI apportionment results. Spectral and morphological information were also obtained. The key in the identification process was a coupling of the maximum and peak shape in the observed spectrum and the comparison of these parameters with the same parameters for sources contained in the source library. As part of this preliminary work only the spectral data were used.

3. Method validation

Gertler and Gillies (2001) initially evaluated the apportionments predicted using the MCI method by comparison with those obtained using the CMB method. When compared against the previous CMB results, the regression analysis had a slope of 1.14 and $R^2 = 0.93$.

Recently we expanded the initial Gertler and Gillies (2001) work using additional source and ambient samples and an upgraded MCI instrument (the upgrade was a more advanced interferometer). In addition, we performed a two-step evaluation: (1) comparison against saved images to test correct identification and (2) comparison against a more complete CMB analysis performed by Abu-Allaban et al. (2002). In the first step, we observed correct classification in 83% of the cases. The results for the second comparison are presented in Fig. 4 and show a good agreement, with a slope of 0.945 and R^2 of 0.726. Based on this assessment, we conclude that the method is able to predict the sources of the observed PM. It should be noted that inherent in this comparison is the assumption that the CMB is the "gold standard" for source apportionment. Different source apportionment methods will yield variations in predicted PM apportionment. Given this variability and uncertainty (likely on the order of 20%), the conclusion of comparability seems warranted.

4. Spatial mapping

Following validation of the method, we applied the MCI technique to develop spatial maps of PM source contributions to observed ambient PM for a number of cities including Singapore, Hyderabad (India), and

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