

Validation of a Microscopic Chemical Imaging System for PM Source Apportionment

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ABSTRACT

Many urban and industrial areas suffer from high levels of PM₁₀ and PM_{2.5}. In order 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 analysis to quantify the chemical composition (e.g., ion chromatography, atomic absorption, automated colorimetry, thermal/optical reflectance, x ray fluorescence, etc.), and application of receptor modeling methods such as the chemical mass balance (CMB) and Positive Matrix Factorization (PMF) models to determine the source contributions. This approach is expensive and time consuming. An alternative method for physically characterizing and apportioning the sources of ambient PM is the application of microscopic chemical imaging (MCI) to identify and apportion the sources of the ambient particulates. The MCI method involves measuring individual particle fluorescence coupled with morphological data to develop unique source profiles that form the basis of a source identification library. Ambient filter samples are then analyzed using the MCI method and the source attribution is based on the individual particle analysis coupled with identification using the source library. Using this approach, the apportionment of ambient PM to specific sources can be performed in near real time. In this paper we describe a study comparing the source apportionments predicted by MCI method against those derived using the CMB model in order to evaluate the applicability of the MCI methodology for PM source apportionment.

INTRODUCTION

Over the past 15 years, an ever-increasing number of epidemiologic studies have shown significant associations between the mass concentration of ambient air particulate matter (PM) and adverse respiratory and cardiovascular health effects.¹ Particulate air pollution has long been linked to both acute and chronic health effects, including asthma, cardiac disease, and other conditions.² In order to reduce these impacts, the US Environmental and Protection Agency (EPA) developed regulations to control ambient levels of particulate matter (PM). Further, polycyclic aromatic hydrocarbons (PAHs) are a common constituent of PM and are known to be toxic, carcinogenic and mutagenic.³ Many studies indicate that fine particles (particulate matter with aerodynamic diameter less than 2.5 μm) have a greater impact on human health than coarse particles⁴ (particulate matter with aerodynamic diameter 2.5-10μm).

Numerous studies have focused on the concentration and sources of PAHs bound to PM₁₀ and PM_{2.5} in the urban air.⁵ These studies have found it is important to determine the abundance, distribution and potential sources of PAHs associated with PM₁₀ and PM_{2.5} in order to reduce the health impacts of these pollutants

The new National Ambient Air Quality Standard (NAAQS) for PM_{2.5} is 35 µg/m³ in a twenty-four hour period and annual average of 15 µg/m³. At these levels, most of the urban areas in the US are likely to be in violation of the NAAQS and there would be an increased need for determining the sources of PM_{2.5}. Potential sources of PM_{2.5} include mobile sources, industrial emissions, geological material, secondary particles, vegetative burning, emissions from cooking, etc.

Understanding the sources of PM allows air quality managers and community stakeholders to pinpoint emission sources for Airshed Management Plans. Further information on the relative contribution of each source to air pollution allows planners to develop effective pollution reduction schemes to protect human health.⁶

Receptor models are used to identify the sources of emissions, and the quantities from those sources. These models 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 contribution. Meteorological data (e.g., wind speed and direction) can also provide additional information in identifying specific sources. Analyzing particulate matter and its chemical constituents has led to an improvement in our ability to determine source contributions to ambient PM.

There are two basic types of receptor models: 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 (i.e., ion chromatography for sulfate, nitrate, and chloride, colorimetric analysis for ammonium, atomic absorption for potassium, calcium, x-ray fluorescence for metals, and thermal optical reflectance for organic and elemental carbon). In order to reduce model uncertainty and enable the identification of additional sources, a recent advance has included the addition of polycyclic aromatic hydrocarbons (PAHs, quantified by GC/MS) to the chemical profiles.^{7,8} The CMB approach is effective; however, it is expensive (requiring multiple analytical methods) and time consuming (completion of the analysis generally takes weeks or months followed by data base development and CMB modeling).

Taback et al. reported on a microscopic chemical imaging approach (MCI) to characterize PM_{2.5} aerosols.⁹ The results of this work indicated the MCI technique had the potential to identify PAHs present on aerosol particles, along with characterizing particle morphology. Given the applicability of PAH identification for use in CMB source apportionment, Gertler et al.⁶

undertook a preliminary study to test the applicability of the MCI method for PM source apportionment, and they reported the results of the preliminary study to develop and validate the technique coupled with an image processing algorithm to attribute observed PM to specific sources. Given the potential of this method to enable near-real time identification of the sources contributing to ambient PM a study was undertaken to further improve and validate the MCI technique for PM source apportionment. In this paper we report the results of this study.

TECHNICAL APPROACH

The approach undertaken was to analyze filters using an MCI instrument (FIPA-20, GreenVision Systems, Ltd., Tel Aviv, Israel), 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. In addition, we prepared an MCI source profile library by analyzing previously collected source samples for the region of interest. The following sections describe this approach in more detail.

Description of the MCI Method

The MCI instrument (FIPA-20) is composed of a number of components and employs microscopic chemical imaging coupled with adaptive learning algorithms to identify chemical species that may be present on particles. The device has been described by Taback et al.⁵ Figure 1 contains a schematic of the principle of operation. Briefly, the instrument scans the collected particles and records the particle-by-particle spectra for the wavelength region of 390-900 nm using an interferometer based imaging Fourier spectrometer coupled to a fluorescence microscope with UV optics. The wavelength accuracy of the interferometer is 2 nm. (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 (Figure 2). Particle size and morphology information is also recorded. The software developed for the FIPA-20 compares the spectral and morphological data collected for the sample with the data in the source library and reports the presence of identified sources and their percent contribution to the mass of sample collected.

By digitizing the spectral data and obtaining pixel-by-pixel spectra information, the FIPA-20 can identify low concentrations of fluorescing chemical species that may be present on individual particles. This capability would enable the user to qualitatively determine the presence of fluorescing compounds such as soil, combustions emissions, explosive residue, etc. Since the intensity is proportional to the concentration of the chemical compounds of interest, quantitative information on the concentration of the compounds can be obtained. Taback et al. reported detection limits of 3.5 pg and 2.0 pg for pyrene and perylene, respectively, on quartz crystals.⁵

The procedure employed technique consists of two main parts, the first part is building the Source profile data base and the second one is the routine operation. Building the source profile data base enables the system to recognize target sources. Different source samples are scanned into the system and analyzed. Their spectral output is then saved to database. As the spectral database grows, the definition of the sources becomes more accurate.

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

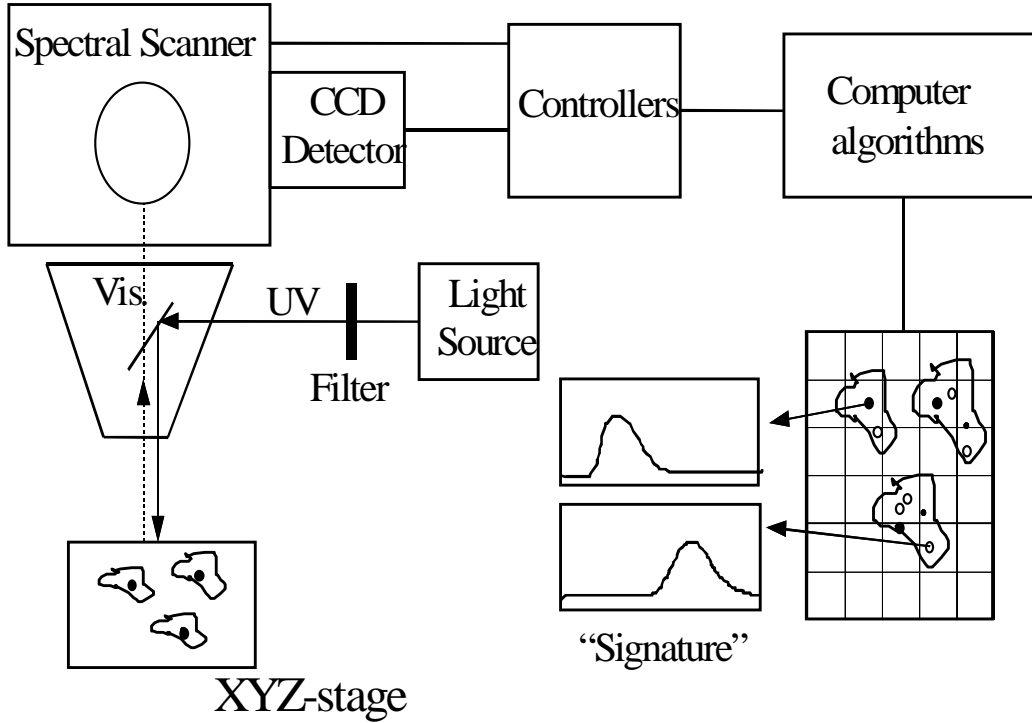
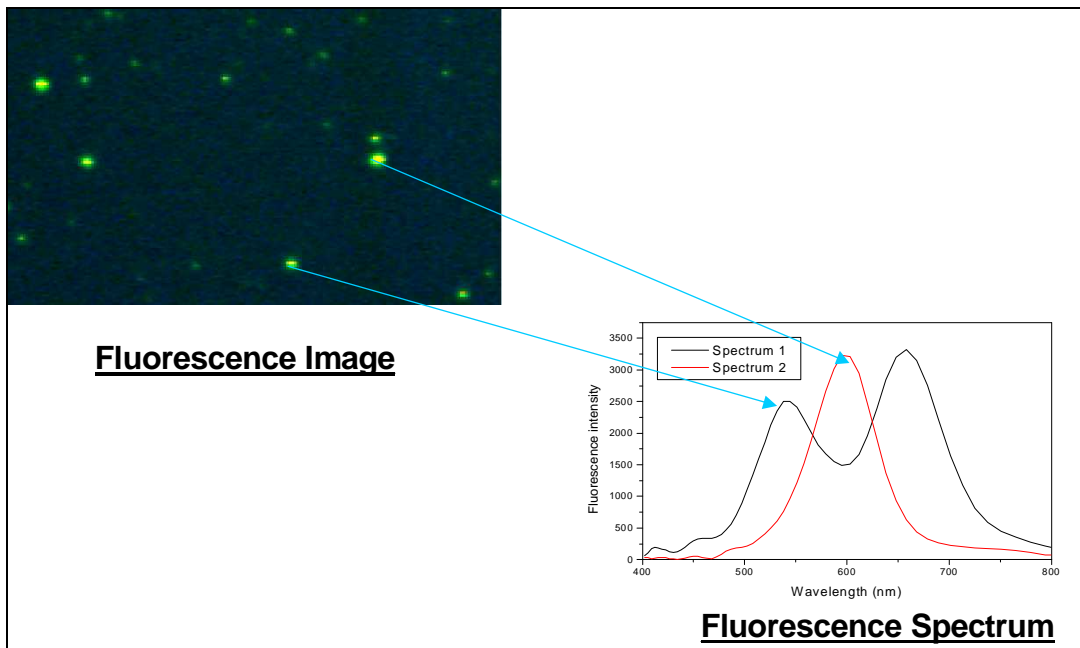


Figure 2. Example of pixel-by-pixel spectral information collected using the FIPA-20.



The tasks involved with preparing the source profile database are as follows:

- 1- Gathering appropriate source samples. This involves the collection of source emissions on Teflon filters.
- 2- Creating a software “scenario”, to store the scanned sample data (magnifying power, the area of region of interest, exposure time ... etc) and spectral output.
- 3- Scanning source samples.
- 4- Setting the target detection which is a process that enables the system to separate between target and background pixels of an image
- 5- Creating a database either manually or automatically and processing the spectra by enabling to group, name, and save different spectra according to a desired similarity.
- 6- Performing Target Identification: after creating the spectral database, defining how the target pollutant will be identified will be required by one of three different methods
 - a- Classical: in which the exact spectra used for identification will be chosen from the spectral database.
 - b- Decomposition: in which the emitter (target) will be decomposed pixel by pixel for identification.
 - c- Grouping: from the spectral database the relevant spectra will be chosen to group them into families.
- 7- Routine Operation: once the system has been setup, routine operation can begin. Routine operation consists of two main tasks:
 - a- Scanning samples by placing the filter on the xyz stage(stage tray) and loading the a scenario that consist of parameters and setup information.
 - b- Running the analysis
- 8- Performing control tests: at least once per day before starting to scan any of the filters and it is done by choosing the white light and three different color filters (Red, Green, and Blue).

Source Profile Library

For this study, we made use of previously collected ambient and source samples that had been used in earlier source apportionment studies (e.g., the Cairo Source Apportionment Study).¹⁰ Source samples were chosen to represent a mix of potential sources. One important criterion 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 was 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. For this work we relied solely on the spectral data and did not use the morphological information.

Twenty source filters (Table1) were scanned to build the source library. Initially we performed hundreds of scans per filter but analysis of the results found we could reduce the number of scans

to twenty-five to obtain sufficient resolution. Examples of the data output for a number of sources are shown in Figures 3 and 4 where different sources with different particles show different spectra.

Table 1. Source filters chosen for this study.

Coke Factory	Coal Power Plant (Fairfield)
Garbage Burning	Coal Power Plant, (Houston)
Rice Straw Burning	Soil (Clark County, Las Vegas)
Iron/Steel Furnace	Creosote Wood
Restaurant	Soil (Black Rock Desert)
Mazout	Road Dust (Cairo)
Motorcycle	Downwind Mazout
Lead Smelter	Diesel Bus
Roadway Tunnel (cars)	Diesel Van
Roadway Tunnel (mixed fleet)	Gasoline Car

METHOD EVALUATION AND VALIDATION

The method evaluation and validation component of this study consisted of two phases. These were as follows:

- Assessment of the ability of the MCI method to correctly discriminate and identify aerosols from known sources. This was accomplished by sequestering a fraction of the source filter images (i.e., spectra from individual particles) and then analyzing these spectra against the full source library to determine if the method could classify them correctly. In addition, this step enabled us to evaluate the impact of spectra that were collinear (i.e., the sources emitted particles with similar chemical composition).
- Comparison of the MCI predicted apportionments with those predicted using the CMB methodology. While there is uncertainty in the CMB results, since this is one of the most commonly accepted techniques for source apportionment, we took this to be “the gold standard” for our comparison.

Figure 3. Particles and their spectra from the coke factory source. Note the difference between peak maximum and shape when compared with the spectra in Figure 4. These differences allow for source differentiation.

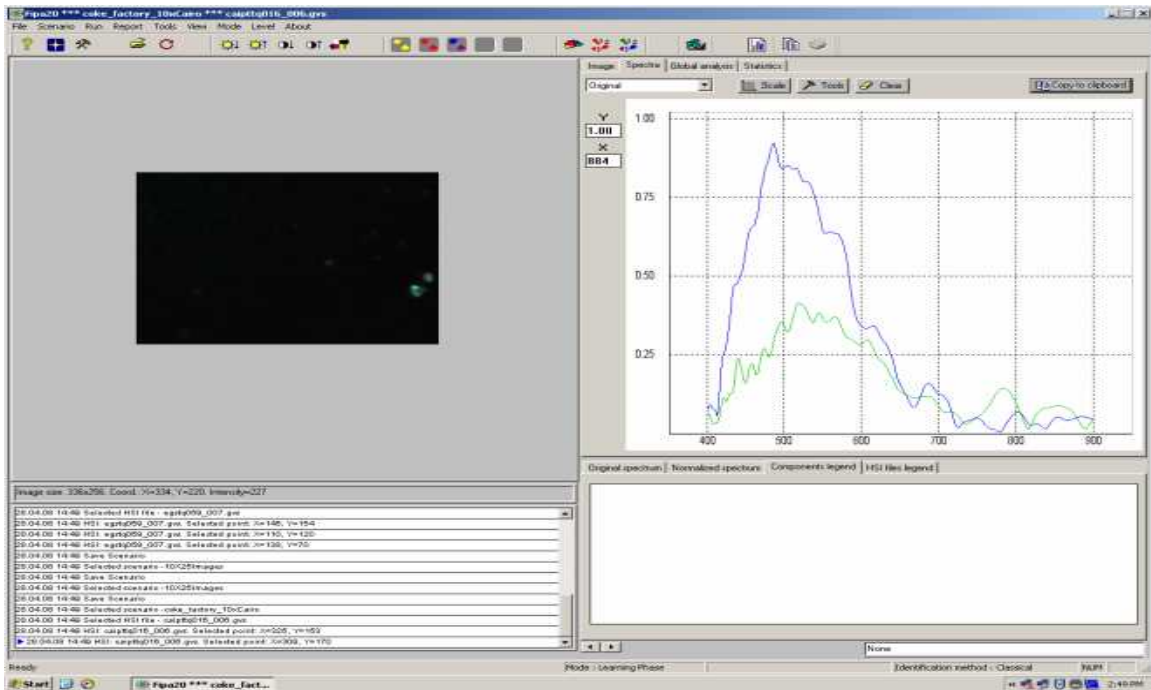
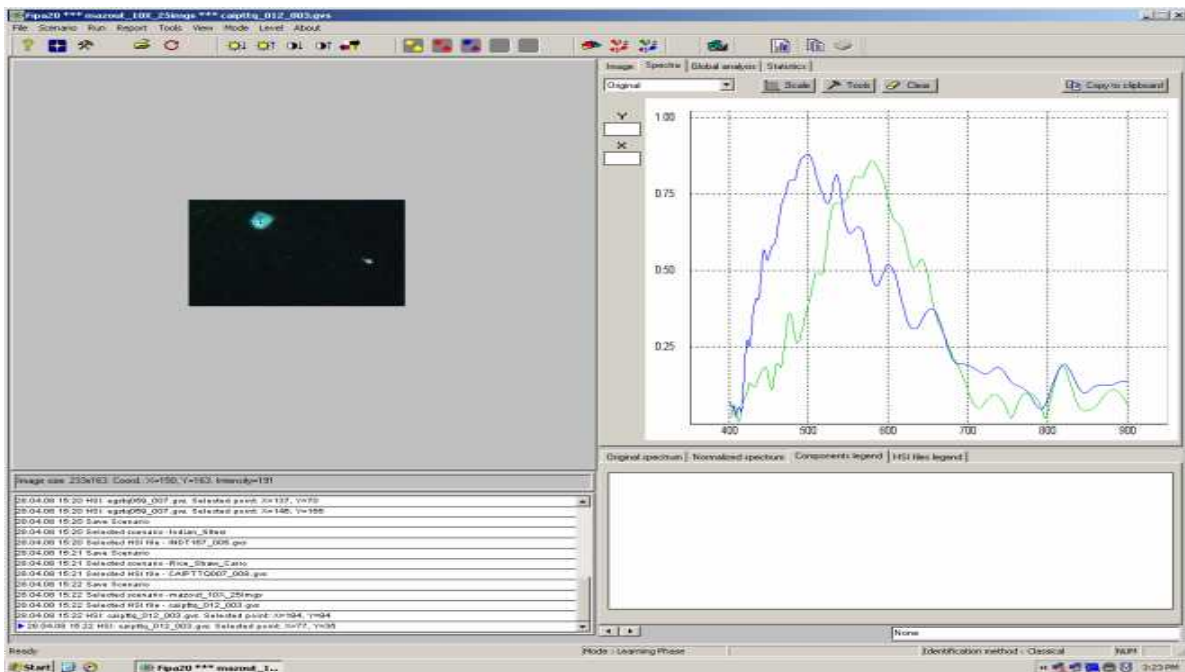


Figure 4. Particles and their spectra from the Mazout source.



When we performed the initial assessment using the saved images, the method was able to correctly classify 61% of the observed particles to a specific source. By expanding the comparison to include a four source categories (mobile, soil, vegetative burning, and industrial emissions), the correct classification improved an additional 22%, leading to an overall performance of 83% for correct results based on source categories. We believed we can improve this result by adding the size and morphological information, along with incorporating additional information on spectral intensities.

For the MCI/CMB comparison component of this work, we made use of previously collected ambient samples that had been collected as part of a study performed in Cairo.¹⁰ These samples had been previously analyzed using standard laboratory techniques and source attribution was performed using the CMB. Both the PM₁₀ and PM_{2.5} ambient samples were analyzed as described previously. The same instrument parameters were used for ambient filter analysis as were used for the development of the MCI source library. One limitation in the MCI approach is it only identifies particles that fluoresce. Hence particulate sulfate and nitrate could not be identified. For the comparison, the % source apportionments of fluorescing sources identified using the CMB (i.e., mobile sources, industrial sources, cooking/burning, and geological sources) were used in the comparison.

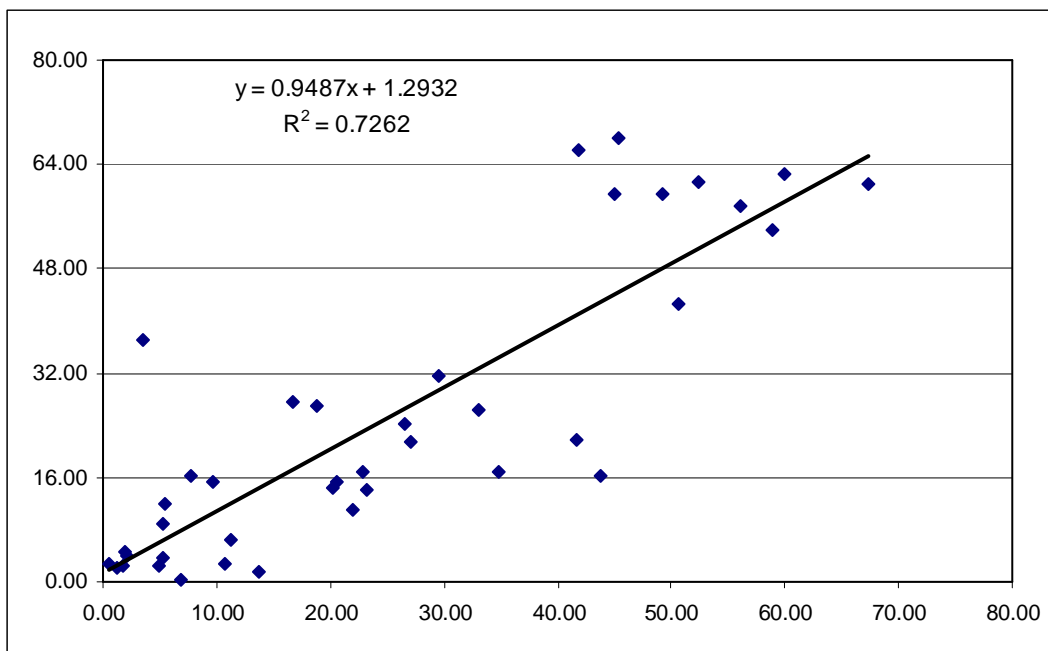
An initial comparison between CMB and MCI techniques was based on the area of the particles identified using the MCI approach. This led to the results presented in Figure 5. The agreement is fair, with a slope of 0.792 and $R^2 = 0.628$. This raised the question of whether or not a comparison of a volume based approach (laboratory analysis) with an area based approach (MCI) was reasonable. This might be the case if the particles were similarly sized; however, in the ambient samples, this was not the case.

Based on this result, we reassessed the MCI apportionments based on the total intensity of the fluorescence spectra, assuming that intensity was a better surrogate for concentration. These results are shown in Figure 5. The agreement between the two techniques (CMB and MCI) is greatly improved as judged by an R^2 of 0.726 and slope of 0.948. Based on this analysis, it appears that the MCI approach can yield similar results as the commonly accepted CMB method. The advantage; however, of the MCI technique was the results were obtained in near-real time and avoided the expensive and time consuming approach required for application of the CMB method.

SUMMARY

The MCI technique was evaluated for use in apportioning the source contributions to ambient PM using a commercially available MCI system (FIPA-20). Previously collected PM ambient and source samples were scanned using the device. A source profile library was also developed and apportionments were predicted based on the MCI approach. Using fluorescence intensity as a surrogate for concentration we found the MCI and CMB apportionments to be in good agreement, having an R^2 of 0.726 and slope of 0.948. These results indicate the potential of the MCI technique to provide near-real time source attribution results for ambient PM samples.

Figure 5. Comparison of MCI percent source contribution predictions developed based on the area of particles identified with CMB source contribution predictions (each point represents a direct comparison for a specific source contributions using the CMB and MCI approaches).



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KEY WORDS

Particulate matter, source apportionment, receptor modeling, chemical mass balance, particle characterization, microscopic chemical imaging.