

A quantitative method for clustering size distributions of elements

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Abstract

A quantitative method was developed to group similarly shaped size distributions of particle-phase elements in order to ascertain sources of the elements. This method was developed and applied using data from two sites in Houston, TX; one site surrounded by refineries, chemical plants and vehicular and commercial shipping traffic, and the other site, 25 miles inland surrounded by residences, light industrial facilities and vehicular traffic. Twenty-four hour size-segregated ($0.056 < D_p$ (particle diameter) $< 1.8 \mu\text{m}$) particulate matter samples were collected during five days in August 2000. ICP-MS was used to quantify 32 elements with concentrations as low as a few picograms per cubic meter. Concentrations of particulate matter mass, sulfate and organic carbon at the two sites were often not significantly different from each other and had smooth unimodal size distributions indicating the regional nature of these species. Element concentrations varied widely across events and sites and often showed sharp peaks at particle diameters between 0.1 and $0.3 \mu\text{m}$ and in the ultrafine mode ($D_p < 0.1 \mu\text{m}$), which suggested that the sources of these elements were local, high-temperature processes. Elements were quantitatively grouped together in each event using Ward's Method to cluster normalized size distributions of all elements. Cluster analysis provided groups of elements with similar size distributions that were attributed to sources such as automobile catalysts, fluid catalytic cracking unit catalysts, fuel oil burning, a coal-fired power plant, and high-temperature metal working. The clustered elements were generally attributed to different sources at the two sites during each sampling day indicating the diversity of local sources that impact heavy metals concentrations in the region.

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1. Introduction

Size distributions of elements in ambient particulate matter have been used to suggest sources of elements in urban areas such as Los Angeles (Singh et al., 2002) and in regions with large numbers of point sources such as an area with many coal-fired power plants (Dodd et al., 1991). Supermicrometer particles, primarily generated

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by mechanical processes including soil, sea spray or industrial mechanical processes, are composed of largely crustal elements (Seinfeld and Pandis, 1998). High-temperature processes, like combustion and metal working, emit submicrometer heavy metals (Ondov and Wexler, 1998). Condensational growth of particles during the cooling stages of high-temperature processes produce narrow size distributions of elements which peak between 0.1 and 0.3 μm (Dodd et al., 1991).

In addition to source information, size distributions can provide information about the proximity of the sources to the sampling site. For example, levels of primary ultrafine particles (D_p) particle diameter $<0.10\ \mu\text{m}$ have been shown to be highest close to their source (Reponen et al., 2003). Size distributions with peaks above 0.3 μm may be due to particle growth during transport and or due to changes in relative humidity, and therefore particle size, during the sampling (Ondov and Wexler, 1998). Broad size distributions dominated by sulfate which peak around 0.7 μm result from slow condensation of gas-phase species and cloud processing of particles (Ondov and Wexler, 1998) and are regional in nature.

Other approaches used to identify sources of heavy elements in ambient particulate matter are principle component analysis (PCA) techniques used on bulk aerosol samples (Kim et al., 2003; Song et al., 2001) and cluster analysis techniques used on single particle data (Osan et al., 2001; Phares et al., 2003). The PCA approach relies on a large data set (usually greater than 60–100 sample events) to obtain statistical significance and therefore typically cannot exploit size-resolved chemical composition information due to the extreme cost required to analyze such large numbers of samples. Large data sets from single particle analysis have been analyzed using cluster analysis to group particles with similar composition (Hoornaert et al., 2003; Osan et al., 2001). Phares et al. (2003) used this approach to analyze ultrafine particle composition in Houston, TX, during TEXAQS 2000.

Our goal in the present study was to elucidate sources of elements at two locations in Houston, TX, a highly industrialized city, using size-resolved elemental concentration data. ICP-MS was used to quantify the fine and size-segregated concentrations of 32 elements from sodium to uranium with concentrations ranging from picograms to micrograms per cubic meter. The current study exploits the idea, suggested by Ondov and Wexler (1998), that elements with similar size distributions often originate from the same source. To our knowledge, the present study is the first to use a *quantitative* method to cluster the size distributions of elements with similar shapes. Sources of the clustered elements are suggested based on the clustered elements and the shape of the size distribution. In addition to element concentrations, fine and size-segregated concentrations of inorganic ions and

elemental and organic carbon (OC) were analyzed to give the overall composition of the aerosol at the two sites.

2. Experimental methods

2.1. Sampling

Size-resolved particulate matter samples were collected at two TEXAQS 2000 sites in Houston, TX, during August 2000. One sampling site, LaPorte, is located near the Houston ship channel, which has a high density of oil refineries, chemical plants and vehicular and ship traffic (Russell et al., 2004). The second site, Aldine, is located approximately 25 miles inland, north of downtown Houston and is characterized by vehicular traffic and light industry. Twenty-four hour, $\text{PM}_{1.8}$ ($D_p < 1.8\ \mu\text{m}$) were collected on 23, 25, 27, 29, and 31 August at both sites. Each $\text{PM}_{1.8}$ sampler contained two Teflon filters (Gelman Teflo, 47 mm) and one quartz filter (Pallflex, 47 mm) and operated at a nominal flowrate of 24 liters per minute (lpm). Simultaneously, three sets of impactor samples were collected using Micro-Orifice, Uniform Deposit Impactors (MOUDI, MSP Corp.) at both sites during all events except 25 and 29 August at Aldine. At each site, two MOUDIs were loaded with Teflon filters (Gelman Teflo, 47 mm) and one MOUDI was loaded with aluminum substrates (MSP Corp., 47 mm). The MOUDIs were operated at 30 lpm with an AIHL-design cyclone separator upstream of the inlet to remove particles larger than 1.8 μm . Particles were collected in six aerodynamic particle size bins: 0.056–0.1, 0.1–0.18, 0.18–0.32, 0.32–0.56, 0.56–1.0 and 1.0–1.8 μm . Flowrates of all impactors and samplers were measured before and after each sampling event. Sampled filters and substrates were frozen until physical and chemical analysis was performed.

2.2. Physical and chemical analysis

Gravimetric mass was determined by weighing each teflon filter and aluminum substrate a minimum of three times before and after sampling using a Mettler Toledo Model M-55 microgram balance at a constant temperature ($20.5 \pm 1.6\ ^\circ\text{C}$) and relative humidity ($44.5 \pm 4.3\% \text{ RH}$).

Sulfate, nitrate and chloride concentrations were obtained from teflon filters using ion chromatography (Mulik et al., 1976) and for ammonium by colorimetry (Bolleter et al., 1961). Elemental and OC concentrations were obtained using the thermal optical methods as described by Birch and Cary (1996) for quartz filters and the method described by Kleeman et al. (1999) for foil substrates. Organic compound concentrations were calculated from the OC by multiplying by a factor of 1.4 to account for atomic species associated with the OC. Foils and quartz filters were baked prior to

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