Application of single particle analysis performed by SEM-EDX to air quality studies

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Abstract. Single-particle analysis of short-term aerosol samplings can provide information on the rapid evolution of size distribution and chemical composition of pollution aerosols, notably in source areas where reactive compounds are present. The aim of this work is to evaluate the capability of automated particle analysis performed by SEM-EDX to describe such rapid evolutions. Two sampling campaigns were performed at a highly urbanised and industrialised coastal site. The first one corresponded to low atmospheric particle loads and low temporal variation of particle mass concentrations. In these conditions, the lower analysed particle number to yield representative results was 1 000 particles per impaction stage. During the second one, a pollution event with a significant increase in particle mass concentrations was recorded. The ability of automated SEM-EDX to describe short temporal variation in particle chemical composition was demonstrated here.

1. Introduction

The impact of atmospheric aerosols on human health via inhalation is now largely demonstrated. The harmful effects of aerosols depend on mass concentrations of airborne particulate matter, but also on certain characteristics such as the chemical composition and microphysical properties of the constituting individual particles. Thus, a good knowledge of physico-chemical characteristics of atmospheric particles is essential. In urban and industrial environments, physical processes like condensation or coagulation and heterogeneous reactions of particles can occur rapidly in polluted air masses to produce “aged” particles [Choël et al., 2006]. It is necessary to take into account these fast evolutions to fully quantify the impact of atmospheric particles. Sampling of aerosols generally takes several hours to collect enough particulate matter for subsequent chemical analysis. Unlike many bulk techniques, single-particle analysis by automated scanning electron microscopy combined with energy-dispersive X-ray spectrometry (SEM-EDX) requires light sample loadings with sampling times as short as a few minutes. Single-particle analysis of short-term aerosol samplings can provide information on the rapid evolution of size distribution and chemical composition of pollution aerosols, notably in source areas where reactive compounds are present. The aim of this work is to evaluate the ability of automated particle analysis performed by SEM-EDX to describe fast evolution of air quality.

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2. Materials and Methods

2.1. Sampling conditions
The sampling took place on the university campus of Dunkerque (Nord-Pas de Calais, France) on November 17th 2005 and February 1st 2007. The sampling site (51.03°N; 2.37°E) was located 100 meters north from the closest air quality monitoring station in downtown Dunkerque and approximately 1000 meters east from the industrial area housing a major steel manufacturing plant and a large oil refining complex. Atmospheric particles were collected during 10 min each at the top of a 4-m high mast, by a 3-stage cascade impactor (Dekati PM-10) with a flow rate of 30 L min⁻¹. Dekati PM-10 impactor has three consecutive stages to separate coarse and fine fractions: Stage 1 removes particles of equivalent aerodynamic diameter larger than 10 \( \mu \)m, stage 2 collects particles below 10 \( \mu \)m and above 2.5 \( \mu \)m in diameter (PM10-2.5 size fraction), stage 3 collects particles below 2.5 \( \mu \)m and above 1 \( \mu \)m in diameter (PM2.5-1 size fraction). Particles impacted on a substrate material made of boron specifically developed for the purpose of particle microanalysis [Choël et al., 2005].

2.2. SEM-EDX measurements
Single-particle analysis was performed with a LEO 438VP SEM outfitted with a ultrathin-window energy-dispersive X-ray detector. Automated particle analysis was performed using the commercially available Link ISIS Series 300 Microanalysis system (Oxford Instruments). The software uses a two-step process to locate and analyze particles. Electron images were acquired using a backscattered electron detector with a magnification of 6000×. A preset grey level threshold is applied so that particles are outlined against the substrate. The coordinates of the particles and preset morphological measurements (area, perimeter, shape factor, Feret diameters...) are recorded during a primary analysis run. During the secondary analysis run, X-ray spectra are collected by rastering the electron beam over the surface of the particle. X-ray spectra were collected with an acquisition time of 20 s, at an accelerating voltage of 15 kV and a probe current of 200 pA. Each particle was morphologically characterized by its equivalent diameter calculated from the area of its two-dimensional projection considering it a sphere. Only particles with diameters greater than 0.3 \( \mu \)m were considered. Net X-ray intensities of 15 elements (C, N, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe) were obtained by non-linear least-squares fitting of spectra. Net intensities were then converted into atomic concentrations using a reverse Monte Carlo quantitative program [Ro et al., 2003]. To obtain data statistically representative of the collected aerosols, approximately 1000 spectra were acquired per impactor stage. This analytical methodology was successfully evaluated on airborne particulate matter, consisting of a complex heterogeneous mixture of particles [Choël et al., 2007].

2.3. In-situ measurements
The “in-situ” total size distribution of atmospheric particles was measured by an optical particle counter (Malvern 3016) by integration of data during the sampling (10 min). A weather station (Vantage Pro) recorded automatically local meteorological conditions (temperature, relative humidity, wind speed, wind direction and pressure) every half hour. PM10 and PM2.5 mass concentrations were recorded by a TEOM (Tapered Element Oscillating Microbalance) Series 1400a Ambient Particulate Monitor.

3. Results and discussion

3.1. SEM-EDX optimization
Good agreement was found between the dry size distributions of particles obtained from SEM-EDX data acquired on the same impaction spot by two operators. Analysis by automated SEM-EDX of different impaction spots of the same size fraction results in similar size distributions of particles.
The number of particles necessary to analyze so as to yield representative results about the dry size distribution of PM2.5-1 size fraction was determined. For that purpose, results obtained for subsets of data were compared against results of the full dataset (Figure 1). Physical properties of particles collected on the boron substrate are well characterized by analyzing more than 500 particles.

![Figure 1. Comparison of dry size distributions obtained for subsets of data chronologically extracted from A2 PM2.5-1 dataset.](image1)

The number of particles necessary to analyze so as to yield representative results about the relative abundances of particle types encountered on an impaction stage was also determined. Chemical properties of the same size fraction (PM2.5-1) converged to within 10% of their final values after analyzing about 1000 particles (Figures 2). Note that these threshold values depend on the number of particles populating a particle type and on the heterogeneity of the sample studied.

![Figure 2. The relative abundance of particle types according to the number of particles considered.](image2)

### 3.2. Ability to describe short temporal variability

Two sampling campaigns were performed under stable atmospheric situations. The first sampling campaign (17 Nov 2005) corresponded to low atmospheric particle loads and low temporal variation of particle mass concentrations during the preceding hours and during sampling: on average 21.3 ($\pm$ 0.5) $\mu$g m$^{-3}$ for PM10 and 7.5 ($\pm$ 0.6) $\mu$g m$^{-3}$ for PM2.5 ($\pm$ 1SD in brackets). Four aerosol samples were successively collected for 10 min each between 12H30 and 13H30. The relative abundance of...
particle types encountered was relatively constant, across all samples considered (Figure 3). That confirmed the good representativeness of data acquired by SEM-EDX.

Figure 3. Particle types obtained from SEM-EDX data of PM2.5-1 size fraction.

During the second sampling campaign (1 Feb 2007), a pollution event with a significant increase in PM10 and PM2.5 mass concentrations was recorded between 16H00 and 18H00: the higher PM10 and PM2.5 mass concentrations were respectively 63 and 37 µg.m⁻³ at 17H30. This corresponded to a plume of dusts originating from the chimneys of the nearby steel manufacturing plant. In this case, the relative abundance of particle types encountered was strongly dependent on when the sample was taken (Figure 3). The ability of automated SEM-EDX to describe short temporal variation in particle chemical composition has been demonstrated here.

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