

**New Simpel Aerosol
Mass Closure**

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Geochemical perspectives from a new Aerosol chemical mass closure

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Abstract

The aerosol chemical mass closure is revisited and a simple and inexpensive methodology is proposed. This methodology relies on data obtained for aerosol mass, and concentration of the major ions and the two main carbon components, the organic carbon (OC) and the black carbon (BC). Atmospheric particles are separated into coarse (AD $>2\mu\text{m}$) and fine (AD $<2\mu\text{m}$) fractions and are treated separately. For the coarse fraction the carbonaceous component is minor and assumption is made for the conversion factor k of OC-to-POM (Particulate Organic Matter) which is fixed to the value of 1.8 accounting for secondary species. The coarse soluble calcium is shown to display a correlation (regression coefficient f , y axis intercept b) with the missing mass. Conversely, the fine fraction is dominated by organic species and assumption is made for dust which is assumed to have the same f factor as the coarse mode dust. The fine mode mass obtained from chemical analyses is then adjusted to the actual weighed mass by tuning the k conversion factor. The k coefficient is kept different in the two modes due to the expected different origins of the organic particles. Using the f and k coefficients obtained from the data set, the mass closure is reached for each individual sample with an undetermined fraction less than 10%. The procedure has been applied to different urban and peri-urban environments in Europe and in Beijing and its efficiency and uncertainties on f and k values are discussed. The f and k coefficients are shown to offer consistent geochemical indications on aerosol origin and transformations. f allows to retrieve dust mass and its value accounting for Ca abundance in dust at the site of investigation may serve as an indicator of dust origin and aerosol interactions with anthropogenic acids. f values were found to vary in the 0.08–0.12 range in European urban areas, and a broader range in Beijing (0.01–0.16). As expected, k appears to be a relevant proxy for particle origin and ageing and varies in the 1.4–1.8 range. For Beijing, k exhibits high values of about 1.7 in winter and summer. Winter values suggest that fresh coal aerosol might be responsible for such a high k value, which was not taken into account in previous works.

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1 Introduction

Aerosols are found in different size-classes which account for their various environmental effects, such as respiratory diseases, visibility impairment, and radiative forcing (Donaldson et al., 2001; Zhang et al., 2004; Penner et al., 2004). They also contribute to numerous atmospheric processes, and may also serve as nuclei on which clouds form (Kaufman et al., 2002). Of interest too are nucleation and heterogeneous chemical reaction sequences producing condensable particulate products from precursor gases such as sulphur dioxide, nitrogen oxides and organic vapours. Particles thus formed are defined as secondary aerosols, and are present in the whole size spectrum both for number and mass distributions (Seinfeld and Pandis, 1998).

One of the major challenges in aerosol science is to account for aerosol sources and transformation processes at local, regional and global scales in order to better understand their effects on the environment, and subsequently support relevant environmental protection policies. This challenge calls for a broad field of investigations, from the relatively simple situations encountered in developed countries to the intense multi-sources pattern observed in developing cities. Mass closure attempts represent a unique tool to accept the challenge.

For this purpose, experimental campaigns generally consist in allocated samplings on different filter types, running simultaneously at a representative site. Such experiments allow an extensive aerosol characterisation at different possible time-scales, from diurnal to inter-annual. Particle size segregation is a critical parameter to identify the most important contributors to the aerosol fine and coarse masses and to assess their origin and behaviour - primary or secondary, natural or anthropogenic, and state of mixing (Ten Brick et al., 2004; Berner et al., 2004).

An aerosol mass closure is achieved when the gravimetric measurement of filter samples matches the sum of masses of the individually identified chemical species (the reconstructed mass). Any attempt, however, includes hypotheses to estimate dust material and organic matter, which possibly largely contribute to the aerosol mass. Pre-

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vious works present a diversity of approaches to constrain the uncertainties associated to these hypotheses (Andrews et al., 2000; Putaud et al., 2004a; Rees et al., 2004). But no general pathway clearly emerges.

Here, we attempt to define a simple and inexpensive filter-based protocol which may apply to urban and peri-urban sites of various complexities. This methodology provides Ca^{2+} /dust (f) and OC/POM (k) conversion factors and has been validated on approximately 500 samplings from 11 field campaigns conducted in different environments in Europe and in Beijing, China. This paper details the methodology and furthermore shows that estimated coefficients (f) and (k) may provide an interesting insight on particle origin and transformations.

2 Experimental

2.1 Sampling protocol

All field experiments have used the following protocol. Considering a complex multi-source aerosol phase, a distinction between fine and coarse particles is relevant since they are remarkably distinct in origin and nature. Each mode is indeed closely related to a type of source, or to characteristic physical and chemical generation processes. Coarse particles (larger than 1000 nm) are usually primary particles mechanically generated from wind erosion of dust material or sea surface. Interestingly, these particles provide a surface of basic material on which volatile species, and especially acidic ones, may attach. Primary particles from combustion, like fly ash, may also be found on this coarse mode. Fine particles comprise the nucleation (less than 20 nm), the Aitken (ranging from 20 to 90 nm) and the accumulation mode (90 nm < AED < 1000 nm). They are generated from both primary sources (combustion) and secondary processes (conversion of gaseous precursors) (Whitby, 1978; Hoppel and Frick, 1990; Covert et al., 1992).

In our work, distinction between coarse and fine particles is operationally defined

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using stack filter unit (SFU) samplers working at $1 \text{ m}^3 \cdot \text{h}^{-1}$ with two filters of different pore size used as follows: Nuclepore $8.0 \mu\text{m}$ filters collect particles with aerodynamic diameters higher than $2 \mu\text{m}$, while downstream $0.4 \mu\text{m}$ filters collect particles smaller than $2 \mu\text{m}$ (John et al., 1986). In order to maintain the cut-off and the analysis reliability, sampling duration is adapted to obtain aerosol loadings $< 500 \mu\text{g}/\text{filter}$. Aerosols are weighed from these SFU samples prior to dissolution for Ion Chromatography (IC). Bulk measurements of carbonaceous aerosols are performed using Whatman QM-A quartz-fibre filters. Insoluble species (other than BC) are assessed as dust material.

Chemical size distributions are achieved using DEKATI 13-stage cascade impactors, mounted with either quartz-fibre or Zefluor filters for the analysis of carbonaceous matter and soluble species, respectively.

2.2 Gravimetric measurements

All Nuclepore filters are weighed before and after sampling, using a Mettler Microbalance UMT3 with $1 \mu\text{g}$ sensitivity. Filter weighing is achieved after 24-hour equilibration at room temperature with atmospheric relative humidity (RH) maintained below 30%. RH is set to refer to a dry aerosol in order to minimize uncertainties due to water adsorption-desorption by the filter media and aerosol particles (MacMurry, 2000). Typical uncertainty for our gravimetric measurements (Δm) is of the order of $\pm 5 \mu\text{g}$, which represents 1 to 2% of the total aerosol mass in all the datasets involved in this work.

Zefluor filters used for cascade impactors are weighed using the same protocol. Averaged uncertainty on the mass value presents significant differences between the stages, from $\Delta m = 3\text{--}5\%$ for the 10 first stages ($> 150 \text{ nm}$), whereas the uncertainty is up to 20% for the 3 other stages ($< 150 \text{ nm}$).

2.3 Inorganic soluble species

After weighing, Nuclepore filters are analysed by IC for the determination of the major anions and cations using the following protocol. Filter samples are extracted in 15 ml

of Milli-Q water for 45 min in a sonic bath. Fifty micro-litres of chloroform are then added to each sample to prevent bacteria activity. Samples are filtered just before the analysis using Acrodisc filters (Pall Gelmann) with a porosity of $0.4\ \mu\text{m}$. Analysis of cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}) takes place on a 4 mm CS12 column and Dionex IC (Model DX-600) equipped with a reagent free system (automated eluent generation and self-regenerating suppression). Analysis of the major inorganic anions (Cl^- , NO_3^- , SO_4^{2-}) takes place on an 4 mm diameter AS11 column and Dionex IC (Model DX-600) also equipped with a reagent free system. Blank filters were systematically taken in the field without showing any significant contamination during sampling, handling or shipment.

In our mass closure attempts it must be noted that organic acids (which are identified on chromatograms and provide useful indication about sources, transformation processes and state of mixing) are not included in the fraction hereafter termed ions, as they are already included in estimates of the particulate organic matter.

Averaged uncertainty on the major ions results is of the order of 10 ppb, which represents less than 2% of uncertainty in atmospheric ion concentrations for most of our field campaigns.

2.4 Carbonaceous fraction

The total carbon fraction (TC) includes black carbon (BC) and organic carbon (OC). In our 2-step procedure (Cachier et al., 1989), carbonate (CO_3^{2-}) is systematically evolved prior to analysis to avoid any interference with the other BC or OC components. This point is particularly important at sites highly impacted by dust aerosols (e.g. in Beijing).

Carbon determination encounters two major difficulties, one related to sampling, the other to analysis. By itself, carbon particles sampling may create two contradictory artefacts. The positive artefact enhances the carbon content by the capture of volatile organic carbon (VOC) which is favoured by the fibrous matrix of the quartz filter. To minimize the artefact, our cleaning procedure consists in burning during 48 h

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the quartz filter at relatively lower temperature (400°C) than what is generally performed (600 to 900°C), leading to satisfactory blank values of $0.8 \pm 0.05 \mu\text{gTC}\cdot\text{cm}^{-2}$ and $0.20 \pm 0.1 \mu\text{gBC}\cdot\text{cm}^{-2}$. On the other hand, the negative artefact lowers the carbon content by stripping the particle coating of the semi-volatile organic matter (SVOM). We eventually get rid of both positive and negative artefacts by heating samples at 60°C for 15 min prior to analysis, as similarly reported by Malm et al. (2005).

The analytical determination of BC and OC is still open to discussion (Ten Brink et al., 2004). Regarding the split between BC and OC, the main problems encountered in the analysis are related to two contradictory artefacts: the charring of OC, or the incomplete removal of organic compounds, which may lead to an overestimate of BC; and conversely the untimely departure of BC. To assess the quality of our 2-step approach for the BC-OC split, we compared our reference method to two thermal protocols both implemented in the Sunset Inc. OCEC instrument working in transmission for the laser beam. The first of these two protocols uses the temperature programme from the Desert Research Institute method (DRI) developed by Chow et al. (1993), and is hereafter referred to as DRI_a. The second one is the NIOSH method (Birch and Cary, 1996), which currently serves to determine BC and OC in the NIOSH 5054 protocol.

These three methods were applied to two sets of filters, collected (i) 5 km North from Beijing downtown, at the top of the National Research Centre for Environmental Analysis & Measurements, in January 2003 (Results refer to Beijing IntercompC campaign in Table 1), and (ii) at Florence, July 2002–June 2003. An additional comparison of our reference method with the DRI_a method was performed during Pek1, in January 2003 in Beijing downtown. All samples were previously treated to remove carbonate. Intercomparison data are presented in Table 1. TC results are found similar and highly correlated whatever the analytical method used (r^2 higher than 0.99) whereas BC and OC results show higher discrepancy. In previous intercomparison exercises (Schmid et al. 2001; Ten Brink et al., 2004), our laboratory simple method was found to provide results situated in the middle of the range of values. It is also the case for the inter-comparisons conducted in this work. OC uncertainty from our reference method to the

others ranges within 20–25%. Because of the large abundance of OC especially in the fine fraction of urban aerosols, the analytical split between BC and OC may bring non-negligible bias in the chemical mass closure which relies on the OC-to-POM (Particulate Organic Matter) conversion achieved using an adequate coefficient k (see part 4.3). A 20% OC uncertainty may influence a typical $PM_{2.5}$ chemical mass by 10%, which implies up to 20% variability in k values.

2.5 Dust material

Multi-element techniques such as XRF, INAA and PIXE are commonly used for analysing mineral dust, but they still need assumptions regarding the unaccounted presence of heteroatoms (Andrews et al., 2000). Dust material is made of elements, in various relative amounts, depending on the source location but many works rely on the “Bowen ratios” characterizing a mean desert composition to account for dust composition (Bowen, 1966). In regions where desert dust mix with local resuspension, this may not fully picture the actual dust composition.

Calcium is a major component of dust, along with Si, Al and Fe, where it is mainly found as calcium carbonate. It has been recently suggested that Ca^{2+} could be used to estimate the concentration of dust matter in the atmosphere. Putaud et al. (2004a) estimated the dust component at Monte Cimone in Italy during two identified dust episodes. They found a fair regression between Ca^{2+} from IC and mineral dust from weighing. They also reported two different typical abundances of Ca^{2+} in dust material depending on dust origin: 5.6% for non-Saharan dust periods, and 15% for Saharan dust periods. Using a slightly different approach, during the MINOS campaign in Crete Island, Sciare et al. (2005) compared $nss-Ca^{2+}$ ($nss-Ca^{2+} = Ca^{2+} - (0.038 \times Na^+)$) obtained directly from IC and indirectly from aluminium and iron concentrations obtained by PIXE, using typical elemental ratios. A proportion of $10.96 \pm 1.0\%$ of $nss-Ca^{2+}$ in dust was found. Both above-cited works therefore suggest that the Ca^{2+} to dust ratio could serve as an indicator of dust origin. In this purpose, one key feature of our experimental protocol is the systematic and total dissolution of calcium during the aerosol extraction stage, which

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can thus be analysed by IC as soluble calcium (Sciare et al., 2005). We therefore attempt to use soluble calcium analysed by IC to obtain an indirect and simple estimate of dust mass concentration. In the calculations, for simplification, we do not distinguish soluble calcium (Ca^{2+}) from non sea-salt calcium $nss\text{-Ca}^{2+}$ in any of our experiments.

5 It may be noted that in our work dust material always refers to insoluble species including CaCO_3 , and excluding the carbonaceous BC fraction. The soluble fraction termed ions comprises neither calcium nor carbonate.

3 Field campaigns: Site description and dataset presentation

In the frame of various projects, the aerosol chemical composition was investigated from analysis of filters obtained in the frame of eleven campaigns during variable time sampling durations. However, similar instrumentation, analytical protocol and data processing were performed. Details on field experiments are summarized in Table 2. This chapter presents the different sites with their characteristics, and our attempts for data quality and consistency.

15 3.1 European experiments

In the frame of the European projects CARMEL and SELF CLEANING GLASS, atmospheric particles were sampled at European urban sites on a weekly basis or twice a month in order to capture their seasonal variations. All sites are primarily impacted by traffic but however might display some differences concerning the relative influence of diesel-powered mobile sources. Some data from the intensive experiment ESCOMPTE are also presented. Site to site variability also originates from meteorological conditions which largely determine possible regional influence and the occurrence of secondary formation for inorganic and organic particles.

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3.1.1 Paris and peri-urban site Gonesse, France

Two sites were investigated using filter sampling in the French capital city: Downtown, at the top of Saint-Eustache church (40 m); and in a peri-urban environment, at Gonesse, 15 km away in the northeast, close to the International Charles-de-Gaulle Airport. Paris Centre (Paris) experiment consisted in bi-monthly samples from June 2004 to July 2005, for both the coarse and the fine aerosol fractions. Gonesse experiment was conducted on a weekly basis from September 2004 to July 2005.

According to the ion balance yearly-averaged data, fine aerosols are neutral, which suggests that ammonium is fully neutralised by sulphate and nitrate. In the coarse mode, the ion balance is systematically in favour of cations since only Ca^{2+} , but not carbonate, from CaCO_3 , is taken into account. Carbonate might thus be estimated from the excess number of moles of Ca^{2+} .

3.1.2 Florence, Italy

Florence filter-based experiment was conducted on a weekly basis from July 2000 to June 2003 (Cachier et al., 2004). Figure 1a compares the TEOM PM_{10} mass with that obtained by gravimetric measurements. In autumn and winter, the gravimetric mass is systematically higher than the TEOM data. This disagreement appears correlated to nitrate concentrations and atmospheric ambient temperatures (Fig. 1b), pointing out the general risk of volatilisation of a significant fraction of the aerosol in the TEOM sampling procedure. The loss of ammonium nitrate is generally quoted to explain the TEOM missing mass. However, in our data ammonium nitrate represents about 50% of the missing mass and it may be concluded that other species, most likely semi-volatile organic matter (SVOM), are also lost when heated inlets are used as in the recommended TEOM design. In Florence, this loss is estimated at 20% of the total aerosol mass, and might be sensitive to an air temperature threshold below which TEOM data may be biased. From this experiment, it may be argued that TEOM data are not always adequate for chemical mass closure.

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3.1.3 Marseilles and peri-urban site Realtor, South of France

The international project ESCOMPTE (Cros et al., 2004) which took place in the Marseilles region, offered the opportunity to investigate the aerosol composition in one of the most polluted regions in France during time periods (June–July 2001, and July 2005) of important photochemical activity. In the present work, Marseilles dataset is used for one DEKATI 13-stage cascade impactor results obtained in July 2005, whereas filter data are from Realtor which is a peri-urban background site, located 50 km north of Marseilles city. Filter samples were there collected on a day/night basis from 9 June to 6 July, 2001.

3.2 Beijing experiments

Over the years 2003–2004, an intensive filter-based experiment was conducted in Beijing City and its region in the frame of the scientific cooperation between the Beijing Municipality and the Ile-de-France Region. The experiment included one-month duration intensive studies in winter 2003 (Pek1) and summers 2003 and 2004 (Pek2 and Pek3) and routine filter samplings in-between (for total mass, carbon and inorganic ions determination). This approach participated to solve a number of key questions on the particle emissions and gas-particle interactions in a complex multi-source atmosphere. Three sites were investigated: (1) Downtown, on Chegongzhuang Road, 4 km West from Tiananmen Square, between the Second and Third Ring Road. Samplings were performed on the roof of Beijing Municipal Environmental Monitoring Centre (BMEMC), about 30 m above the ground. This site was investigated during Pek1, Pek2 and Pek3 experiments; (2) 40 km north of Beijing downtown, in a relatively clean background environment, during Pek1 and Pek3; and (3) 50 km south of Beijing downtown, in an environment influenced by local industries and city plumes, during Pek1 and Pek3.

At all sites, fine aerosols are found neutral (Fig. 2). Interestingly, in the coarse mode, more than two thirds of Ca^{2+} (in addition with the other cations) are not balanced by anions which thus indicates that a large fraction of calcium is available for carbonate.

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This would also suggest that a significant portion of Ca^{2+} is possibly present as CaSO_4 or $\text{Ca}(\text{NO}_3)_2$.

4 Methodology: Reconstructing the mass

All steps of the methodology are illustrated by the Pek3 experiment results (Fig. 3). The coarse mode and the fine mode mass balances are worked out separately following a 2-step methodology where mass reconstruction relies on two hypotheses applied separately to the main component of the fine and coarse fractions (Fig. 3a):

1. In the *coarse* mode, the first hypothesis concerns the mass of total dust material, which is estimated from soluble Ca^{2+} ion concentration using a conversion factor termed f ;
2. In the *fine* mode, the critical point is the OC-to-POM conversion factor k , which accounts for unmeasured hydrogen, oxygen, and other hetero-atoms in organic materials.

For each mode, the mass closure attempt can be expressed as:

$$m_{\text{aerosol weighed}} \geq m_{\text{aerosol retrieved}} = \Sigma[m_{BC}, m_{\text{POM}}, m_{\text{ions}}, m_{\text{dust}}, m_{nd}] \quad (1)$$

where:

m_{BC} mass of BC determined by the reference thermal method

m_{POM} mass of POM estimated from OC obtained from the reference thermal method, using a conversion factor k

m_{ions} sum of the masses of water-soluble inorganic species determined by IC, except Ca^{2+} and organic ions (respectively accounted for in dust and POM)

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m_{dust} Mass of total insoluble and soluble dust material estimated from soluble calcium using the conversion factor f and including calcium carbonate

m_{nd} not determined mass: difference between $m_{\text{weighed aerosol}}$ and the sum of m_{BC} , m_{POM} , m_{ions} and m_{dust} (see definition m_{dust});

5 4.1 Estimating the dust concentration from Ca^{2+} in the coarse mode

The first step of this method consists in balancing the weighed aerosol mass of the coarse mode with the chemically retrieved mass, which includes ions, BC, and POM. In this first step, we deliberately fixed the OC-to-POM conversion factor k to 1.8. This relatively high conversion factor may be considered as representative of oxygenated and/or functionalised organic species (Gelencsér, 2004), as one might expect at first approximation for secondary organic material condensed onto coarse particles. In our datasets, as POM generally accounts for 5 to 20% of the total mass in the coarse mode, sensitivity tests show that conversion factors variability ranging from 1.4 to 2.2 influences the coarse mode chemical mass to $\pm 5\%$ at most. Any error on this estimation would therefore have little importance for the coarse mode chemical balance.

The difference between the reconstructed coarse mass (sum of BC, POM and ions masses) and the weighed coarse mass provides a substantial missing mass. This missing mass includes species which are not analysed among which the most common are oxides of aluminium, silicon and iron and calcium carbonates (CaCO_3). It must be recalled that calcium is assumed to be totally dissolved as Ca^{2+} during the extraction phase and may be obtained by ion chromatography (see part 2.5).

In all cases, this missing mass is found to be highly correlated to Ca^{2+} obtained by IC (Fig. 3b).

$$\text{Ca}^{2+} = f \cdot \text{missing mass} + b \quad (2)$$

The slope f is related to the abundance of Ca^{2+} in mineral dust Eq. (3). As detailed later in the text (§ 5) it is shown to be a sensitive indicator of the different dust mixtures.

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At all sites, the correlation between Ca^{2+} and missing mass is sufficiently good ($r^2 > 0.78$) to support the consistency of this simple approach for the evaluation of dust in the coarse fraction of the aerosol. So it may be assessed that the regression coefficient f may be used to calculate mineral dust amounts (including CaCO_3^-) from soluble

5 Ca^{2+} (obtained by IC) following:

$$\text{mineral dust} = \text{Ca}^{2+} / f \quad (3)$$

Using this dust estimate, mass closure of coarse aerosols is achieved with an efficiency ranging between 97% and 107% (Fig. 3c).

10 The intercept b accounts for Ca^{2+} which is not associated to insoluble dust, most likely calcium nitrate and sulphate. Conversely, the intercept with the x axis may account for non-calcium containing dust. These two influences may compete, however at our sites of investigation, b was always found positive or almost null underlining the presence of calcium sulfate and/or nitrate in the coarse mode.

4.2 OC-to-POM conversion factor k in the fine mode

15 Because carbonaceous particles generally account for 50% to 70% of the fine aerosol mass, the OC-to-POM conversion factor, k , is a crucial parameter in the adjustment of the chemical mass to the gravimetric mass of this fine fraction. k is generally taken in the range 1.2–1.6 for urban aerosols (Putaud et al., 2000; Gelencsér, 2004) with higher values (1.6–2.1) for non urban aerosols (Turpin and Lim, 2001).

20 Up to now, knowledge on the OC chemical structure remains hardly workable to properly estimate the OC-to-POM conversion factor. Excluding aerosol mass spectrometer (AMS)-based experiments which are able to directly provide POM data, at least three types of approaches are found in the literature:

25 (1) The best-guess approach is operational and consists in determining k in order to keep closure exercises as close as possible below 100% (Hueglin et al., 2005 in Switzerland; He et al., 2001 and Sun et al., 2003 for Beijing particles). Noteworthy, 1.4

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is often taken as a common arbitrary conversion factor for urban aerosols (Putaud et al., 2004b).

(2) An interesting consideration consists in looking at the nature of the organic matter. WINSOC (Water insoluble organic carbon) are generally fresh primary particles containing organic compounds largely saturated with only few oxygenated functional groups. For WINSOC, a conversion factor of 1.2 may be relevant, following Zappoli et al. (1999). Turpin and Lim (2001) argued for high conversion factors of 1.6 ± 0.2 for urban (Los Angeles), and 2.1 ± 0.2 for non urban. In the work on Singapore aerosols by Balasubramanian et al. (2003), a different k value is attributed to the two distinct fractions WSOC (Water soluble organic carbon) and WINSOC (Water insoluble organic carbon). Their respective contribution to the OC mass will determine the k value for the total OC fraction. In their work, the adopted WSOC to WSOM conversion factor is 1.8 which is justified by the presence of oxygenated and multifunctional groups. The abundance of WINSOC in the total OC fraction explains the total OC k value of 1.44. As aerosol ageing results in an increase of WSOC abundance, the ageing is also marked by an increase of k value.

(3) At last, several studies consider the origin of particles (distinguishing between fresh and aged aerosols) and determine the OC-to-POM conversion factor by analogy with similar environments previously described in the literature (typically *urban* and *non urban*). Following this approach, “consensus” values claimed for aerosols in Europe and in the US has become as high as 1.7 ± 0.3 (Putaud et al., 2000, Rees et al., 2004; Kiss et al., 2002).

Some crossing views emerge from the two latter approaches relative to the origin and the age of the particles which are determinant for both the importance WSOC component in the organic aerosols and the k factor value. One may expect k to increase under the influence of aged aerosols at remote locations, or secondary organics at source sites.

The second step of the present method provides k estimates for the aerosol fine mode using the following arguments. Dust is a minor fraction, in the range 0 to 15 %

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in mass for our dataset. We hypothesize that in both size fractions (fine and coarse modes) dust particles display a similar average composition, which is suggested by previous dust characterizations achieved in Beijing (Cao et al., 2002; Sun et al., 2004). So we calculated dust concentration from fine Ca^{2+} using the same f coefficient (within the uncertainty range, see part 4.3) determined for the coarse mode. Ions and black carbon masses are obtained straight from analyses of the fine fraction. Finally, k is modulated in order to obtain a reconstructed mass as close as possible below the weighed mass (Fig. 3d) and a value of 1.65 is obtained.

4.3 From sampling to data processing

This chapter presents the different uncertainties, assumptions and processing features associated to our protocol.

4.3.1 Uncertainties

The major uncertainties are brought by the gravimetric measurements and the carbon measurements as both may influence the aerosol mass from 1% to 2%. IC analysis uncertainties are found to be one order of magnitude lower. On average, 2% mass uncertainty may affect the f estimates up to 15% in the coarse mode (i.e. $\Delta f = \pm 0.01$), and the k estimates of 20% in the fine mode (i.e. $\Delta k = \pm 0.3$). As noticed in part 2.4, the BC/OC split may itself be responsible for a similar uncertainty on k values.

The small discrepancy remaining between the reconstructed mass and the actual weighed mass may be partly explained by the amount of species not estimated in dust (b intercept in Eq. 2). This fraction is referred to as n.d.(not determined) in our datasets (see Eq. 1).

4.3.2 Data processing

Regression data (slopes and intercepts) are obtained from 70% or more of the available samples, which leads to correlation coefficients (r^2) mostly better than 0.80. Mass clo-

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sure regression slopes are forced to zero. Correlation coefficients (r^2) are even better if the sampling time period is focussed on a characteristic condition, as achieved during Beijing experiments particularly, distinguishing between up to four different periods per 24 h.

5 We compared our regression data (slope and intercept) to results estimated from an ordinary least squares regression, and obtained a consistency higher than 95% for both the fine and coarse modes.

5 Interpretation and limitation

5.1 Dust origin and reactions of neutralization

10 In our protocol f might be addressed as a proxy of mineral dust origin. Interactions with other species however may influence this value. Interestingly, in a given region, f exhibits seasonal, temporal and spatial variability. We attempt in this part to assess this approach consistency and its limitations by applying it primarily to our Beijing and Europe data sets. Additional value given by the intercepts is also discussed.

15 For the Beijing experiment, at each site, f values reflect competing influences between long-range transported dust and more local dust produced by re-suspension. Indeed, each of these two types of dust presents different calcium contents. Long-range transport minerals are likely to be desert dust and to contain important amounts of quartz and feldspar, whereas local dust produced by abrasion processes due to local mechanical stress (wind, traffic, construction) are characterised by calcium-rich minerals like calcite and dolomite (Shi et al., 2003; Kuang et al., 2004). Thus in the Beijing region where dust particles have a mixed origin, an increased influence of desert dust will mark the f coefficient towards smaller values whereas important local dust inputs will shift f towards higher values. Table 3a shows quite similar f values for Beijing South and Beijing North sites. This feature could point to a regional dust pattern, driven by
25 long-range transport. Both sites display a similar seasonal change (respectively 0.062

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and 0.055 in winter, and 0.069 and 0.068 in summer) which could be related to a change of dust source region (Zhang et al., 2003; Washington et al., 2003). Whereas in Beijing Centre, f values are always higher indicating a very active production of local dust probably by traffic and construction works. Dust f values for Beijing Centre are markedly higher in summer (Pek3, $f=0.091$), than in winter (Pek1, $f=0.072$) which again may be due to the predominance of local dust in summer. In this respect, the remarkably high values obtained for Pek2 (Pek2, $f=0.125$), are easily explained by the importance of construction works carried out in the vicinity of the sampling site during the experiment. Additionally, our f results also suggest lower resuspension at night which might be in relation with a decrease of local activities.

Y axis intercept values confirm the similarity of the peri-urban Beijing South and Beijing North station dust. Interestingly in Beijing center, a higher sampling frequency allows to point to a significant formation of calcium nitrate and sulfate in the coarse mode during the day especially in the afternoon when photochemical reactions are very active.

The Europe dataset appears consistent too, despite a different sampling procedure regarding frequency (continuous bi-monthly sampling) and experiment time-period (12 months). Dust f values are found higher at Paris Centre than at the peri-urban site of Gonesse (0.150 and 0.072, respectively). It may be recalled that Paris Centre site is situated at the top of a church where renovation works on calcareous stones are regularly undergone which may influence the dust fraction. Same situation may be quoted for Realtor which is situated close to the calcareous region of Rhone river-delta. f is also influenced by gas-to-particle interactions as CaCO_3 is sensitive to acidic species which may create a loss of insoluble material through the formation of condensed calcium salts and subsequent volatilisation of CO_2 . These interactions are clearly evidenced on cascade impactor data showing associations of Ca^{2+} , NO_3^- , and SO_4^{2-} in the coarse mode (Cachier et al., 2005). Therefore, these neutralisation processes are likely to increase the f values and deciphering the respective roles of sources and processes in the f values is difficult. As sulphate and nitrate formations

are sensitive to photochemistry, a more important abundance in summer than in winter, and during daytime than at night time, may also explain the temporal trends observed in Table 3a. The photochemical formation of secondary sulfate and nitrate and their attachment to the very active calcium-rich dust at Realtor may also explain the high intercept b at this site .

5.2 OC-to-POM conversion factor k

In organic aerosols, k reflects the presence of functionalities and is thus very sensitive to the presence of secondary organic particles. Therefore k displays a significant increase with ageing from urban to receptor sites. It is also expected to be higher during time periods when photochemical processes are effective and to display diurnal and seasonal trends at a given site. These general considerations apply in simple situations with a predominant single source, which is the case of urban areas in developed countries where traffic is the overwhelming source.

At our European sites, results obtained are in accordance with these expectations. As shown in Table 3, k 12-month averages show an expectable value of 1.4 in Paris and 1.5 in Florence, while the peri-urban sites, Gonesse and Realtor, exhibit a higher k value (1.6). The small difference between the urban Paris and Florence sites might be explained by the influence of 2-strokes engines and biomass burning in the Florence traffic fleet (Cachier et al., 2004).

In Beijing region however, the pattern looks different. k values appear high (1.6–1.7) and do not exhibit conclusive trends. This feature is here attributed to changes in the source mix. Among the four major sources prevailing over the year in Beijing: industries, traffic, coal combustion, and biomass burning, some of them display a pronounced seasonality. In winter, during the heating season, the major source is coal combustion either in industrial settings or for domestic purposes. Coal combustion emissions are expected to contain large amounts of organic aerosols. In winter, coal is certainly the main contributor to the particulate OC fraction of the aerosol and the observed high k values may subsequently characterize the coal combustion source.

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In summer, coal consumption lowers, and photochemistry and biomass burning (Duan et al., 2004) progressively take over, which maintains high k values. Of interest, while not investigated here, are the effects of meteorological parameters, and precipitations particularly, which are likely to significantly lower k values by subtracting highly functionalized WSOC.

Noteworthy is that the k dataset points to different conditions at night especially during the last experiment (Pek3) where sampling was matching closely the different sources. From other measurements and tracers such as the BC/CO ratio (Cachier et al., 2005; Guinot, 2006) it has been hypothesized that a significant additional combustion source was prevailing at night in centre Beijing which is also reflected in the lower calculated k value (1.5). Finally whatever the season, the Beijing South station exhibits remarkably high k values (1.85) whereas the Beijing North station k values remain similar to those obtained in Beijing downtown. This could classify the south site as a *receptor* site with aged aerosols and indicate that general transport is maintained southwards all year long in spite of different local wind conditions (northerlies in winter, breezing southwest to west winds in summer). The influence of an additional local combustion source however may not be excluded, but up to now remains unidentified.

5.3 Mass closure attempts from cascade impactor data

The aim is to assess the consistency of our protocol based on fine/coarse distinction with results extracted from the different modes of the mass distribution provided by the dynamical segregation of particles with a cascade impactor. We therefore applied the simple methodology detailed in this paper to selected stages of chemical size distributions obtained using 13-stage DEKATI cascade impactors. Tests were performed on four impactors sampled in Beijing, Paris and Marseilles. The mass distribution generally presents two main modes. In Figure 4 data are detailed for the Marseilles sample. It may be seen that both the reconstructed mass and the actual mass display the same profiles.

It appears from our experience that the selection of representative stages is highly

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critical to properly estimate the conversion factors k and f from the mass closure of a given mode, either the accumulation mode or the super-micron modes. This problem is probably due to overlapping of modes, but it may be solved by a careful selection of stages. The accumulation mode is well represented by the 4th or 5th stage (50% efficiency cut-off: 170 and 270 nm, respectively), and the coarse mode by the 10th or 11th stage (50% efficiency cut-off: 2.5 and 3.2 μm).

For the two modes, k and f coefficient values appear similar, although calculated on single samples, to what is obtained for the corresponding aerosol set (Table 4). This good agreement validates both the methodology and the interpretation of results.

6 Conclusions

This new methodology for aerosol chemical closure gets rid of heavy sampling and analytical means, as it relies on a limited number of allocated sampling lines, and the characterisation of the carbonaceous components and the ion fractions only. As fine and coarse particles are dominated by strikingly different sources, the operational segregation between fine and coarse particles allows to formulate hypotheses separately for these two different modes (with little incidence on the final result) and to retrieve the two parameters which are necessary for the mass closure. In the coarse fraction, which is dominated by dust, the OC-to-POM conversion factor k is fixed arbitrarily supposing OC mainly of secondary origin ($k = 1.8$) and the dust abundance is retrieved by calculating f , the Ca^{2+} /missing mass correlation coefficient. Conversely, on the fine fraction, as the aim is to obtain the actual conversion factor k , the dust conversion parameter f is fixed assuming that dust particles have the same origin as the coarse particles. It must be recalled however that k values may be significantly biased according to the OC/BC separation method, and by the lack of carbonate removal.

In the contrasted environments where we applied this methodology, in Paris and in Beijing regions mainly, correlations leading to the f and k coefficients were found very satisfactory and the aerosol mass closure could be attained for each individual sample

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whatever the sampling durations and frequencies.

Through the calcium-to-dust relationship (f coefficient), our methodology provides simple but reliable tools to access to some geochemical perspectives: dust origin is discussed as local versus long-range transport inputs becomes. Although of possible competing influence, evidence is also given for gas- particle interactions in the coarse mode, according to the abundance of secondary acidic species (nitrates, sulphates) in the atmosphere. This dust neutralisation calls for a better understanding of the influence of dust particles on anthropogenic gases.

In addition, this methodology allows an original approach and provides useful arguments for the debate on actual k values. As expected k appears to be a relevant proxy for particle origin and ageing and varies in the 1.4–1.8 range in the case of European aerosols dominated by traffic. But in multi-sources urban situations, k reflects the dominant source and may notably differ to what was previously assumed. This is illustrated by the Beijing case, where fresh aerosols produced by coal combustion could have a k value as high as 1.7. This unexpected value suggests that at this location carbonaceous particles could be still more important than assumed previously (as k adopted values are generally of the order of 1.4) In complex environments such as those encountered in megacities, we may recommend a careful analysis of sources for the choice of an adequate k value.

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Table 1. Carbon analysis : Correlation between the 2-step thermal method and thermal optical method data (slope and correlation coefficients (r^2))

	Beijing Intercomp C n = 14	Beijing Pek1 n = 35	Florence n = 42
TCThermal/DRI _a	1.005 (0.99)	–	0.988 (0.98)
BC Thermal/DRI _a	0.975 (0.82)	0.846 (0.81)	0.742 (0.61)
BC Thermal/NIOSH	1.196 (0.91)	–	1.233 (0.63)
OC Thermal/DRI _a	1.079 (0.99)	1.233 (0.89)	1.089 (0.95)
OC Thermal/NIOSH	0.971 (0.99)	–	1.039 (0.94)

n accounts for the number of samples.

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Table 2. Field experiments conducted from 2001 to 2005.

Field experiments	Type	Date Sampling frequency	Sampling frequency	<i>number of samples</i>	(Mass ($\mu\text{g}/\text{m}^3$))	
					Fine	Coarse
Europe						
PARIS	urban	Jun 2004–Jul 2005	bi-monthly	28	12.3	15.8
GONESSE	peri-urban	Sep 2004–Jul 2005	weekly	40	13.7	9.9
REALTOR	peri-urban	Jun–July 2001	day/night	49	13.8	10.4
FLORENCE	urban	Jul 2002–Jun 2003	weekly	52	19.2	22.8
China						
BEIJING Pek1	urban	10–31st Jan 2003	day/night	43	48.3	83.7
Pek1 North	peri-urban	<i>idem</i>	day/night	47	45.6	64.2
Pek1 South	peri-urban	<i>idem</i>	day/night	41	31.8	71.7
BEIJING Pek2	urban	28th Aug–19th Sep , 2003	4 samples/day	85	55.5	75.3
BEIJING Pek3	urban	9–27th Aug 2004	3 samples/day	60	58.4	72.3
Pek3 North	peri-urban	<i>idem</i>	day/night	36	37.4	34.0
Pek3 South	peri-urban	<i>idem</i>	daily	18	52.3	52.6

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Table 3. (a) Results from Ca^{2+} to the missing mass regressions obtained from the different field campaigns: slope f and intercept b . Coarse mode mass closure efficiency using f .

	f	Intercept b	r^2	n	%Closure	r^2	n
Europe							
PARIS	0.150	+0.39	0.67	20	99.7	0.78	20
GONESSE	0.072	+0.19	0.90	26	99.3	0.77	26
REALTOR	0.201	+0.84	0.54	34	97.0	0.72	40
FLORENCE	0.120	+0.33	0.56	44	99.6	0.73	46
Beijing							
WINTER 2003							
Pek1 Day	0.082	+0.43	0.88	15	99.8	0.95	20
Pek1 Night	0.062	+0.63	0.94	14	97.9	0.96	20
<i>Pek1 North</i>	<i>0.055</i>	<i>+1.07</i>	<i>0.90</i>	<i>29</i>	<i>97.5</i>	<i>0.90</i>	<i>29</i>
<i>Pek1 South</i>	<i>0.062</i>	<i>+1.07</i>	<i>0.78</i>	<i>27</i>	<i>98.9</i>	<i>0.85</i>	<i>28</i>
SUMMER 2003							
Pek2 8–12 h	0.165	+0.99	0.79	15	99.6	0.66	15
Pek2 12–16 h	0.159	+0.99	0.91	13	99.9	0.94	13
Pek2 16–20 h	0.160	+1.79	0.92	14	99.7	0.86	14
Pek2 20–8 h	0.090	+0.23	0.94	16	98.8	0.64	16
SUMMER 2004							
Pek3 7–12 h	0.085	+0.77	0.94	13	106.7	0.94	14
Pek3 12–22 h	0.095	+0.90	0.98	12	102.5	0.93	18
Pek3 22–7h	0.099	+0.42	0.92	10	103.5	0.96	11
<i>Pek3 North</i>	<i>0.068</i>	<i>+0.011</i>	<i>0.86</i>	<i>27</i>	<i>98.9</i>	<i>0.93</i>	<i>24</i>
<i>Pek3 North</i>	<i>0.069</i>	<i>+0.007</i>	<i>0.79</i>	<i>12</i>	<i>99.4</i>	<i>0.88</i>	<i>12</i>

k coarse are fixed at 1.8.

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Table 3. (b) k results estimated from the different field experiments.

	k	%Closure	r^2	n
Europe				
PARIS	1.40	99.1	0.89	25
GONESSE	1.60	98.7	0.86	30
REALTOR	1.60	98.2	0.85	38
FLORENCE	1.50	97.9	0.85	41
Beijing				
WINTER 2003				
Pek1 Day	1.70	99.4	0.96	20
Pek3 Night	1.55	99.6	0.85	19
<i>Pek3 North</i>	<i>1.60</i>	<i>99.4</i>	<i>0.84</i>	<i>29</i>
<i>Pek1 South</i>	<i>1.85</i>	<i>99.2</i>	<i>0.90</i>	<i>28</i>
SUMMER 2003				
Pek2 8–12 h	1.75	99.0	0.96	18
Pek2 12–16 h	1.55	99.9	0.95	17
Pek2 16–20 h	1.60	98.6	0.90	18
Pek2 20–8 h	1.55	99.8	0.67	20
SUMMER 2004				
Pek3 7–12 h	1.65	99.9	0.98	14
Pek3 12–22 h	1.70	99.3	0.99	17
Pek3 22–7 h	1.50	99.0	0.87	12
<i>Pek3 North</i>	<i>1.55</i>	<i>99.8</i>	<i>0.92</i>	<i>27</i>
<i>Pek1 South</i>	<i>1.70</i>	<i>99.7</i>	<i>0.92</i>	<i>16</i>

f fine = f coarse.

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Table 4. Concentrations and mass closure achieved on selected stages from DEKATI cascade impactors sampled in Paris, Marseilles, and Beijing (Pek1 and Pek2).

	Paris		Marseilles		Beijing Pek1		Beijing Pek2	
Date	20 Jan 2005 daytime		2 July 2005 daytime		16 Jan 2003 daytime		11 Sep 2003 daytime	
<i>Dekati stage</i>	<i>10th</i>	<i>5th</i>	<i>10th</i>	<i>4th</i>	<i>11th</i>	<i>5th</i>	<i>10th</i>	<i>5th</i>
AED (μm)	2.580	0.267	2.604	0.176	3.189	0.330	2.580	0.267
Weighed mass	16.13	7.81	3.89	1.94	29.10	20.69	18.19	13.51
Reconstructed mass	15.96	7.72	3.77	1.99	29.61	20.31	18.13	13.33
<i>k</i>	1.80	1.40	1.80	1.40	1.80	1.70	1.80	1.70
<i>f</i>	0.08	0.08	0.18	0.18	0.075	0.075	0.15	0.15
OC	0.66	2.78	0.38	0.31	3.66	3.68	1.32	2.15
BC	0.18	0.90	0.17	0.15	1.71	2.02	1.05	1.31
POM	1.19	3.89	0.69	0.44	6.60	6.25	2.38	3.66
SO ₄ ²⁻	1.29	0.76	0.18	0.81	0.96	4.54	0.55	5.50
NO ₃ ⁻	1.61	0.31	0.51	0.02	0.76	2.21	1.96	0.53
NH ₄ ⁺	0.19	0.29	0.01	0.30	0.18	2.86	0.02	1.83
Cl ⁻	4.34	0.08	0.02	0.01	0.28	0.56	0.08	0.04
Na ⁺	2.11	0.07	0.09	0.01	0.12	0.25	0.17	0.01
K ⁺	0.05	0.05	0.00	0.01	0.07	0.55	0.16	0.30
Ca ²⁺	0.38	0.11	0.37	0.04	1.31	0.08	1.74	0.02
Dust	4.73	1.34	2.07	0.23	17.47	1.05	11.61	0.13
Other ions	0.28	0.01	0.03	0.01	0.13	0.08	0.15	0.01

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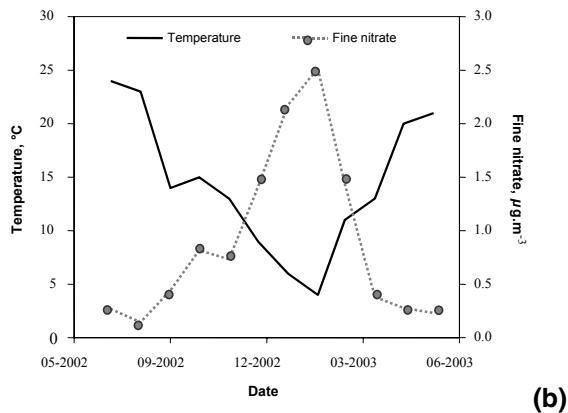
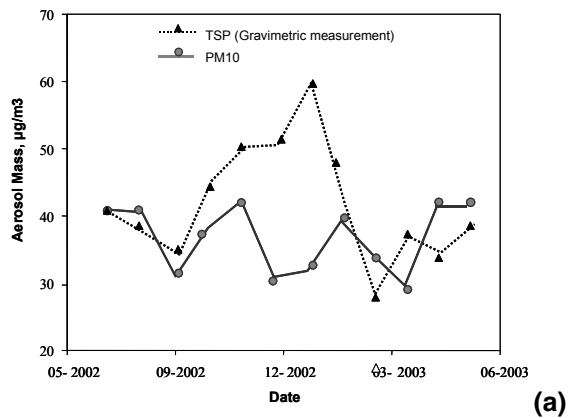


Fig. 1. Monthly averages at Florence (July 2002–June 2003). **(a)** PM-10 obtained with TEOM and TSP by filter gravimetric measurements. **(b)** TSP nitrate concentrations as a function of ambient temperature.

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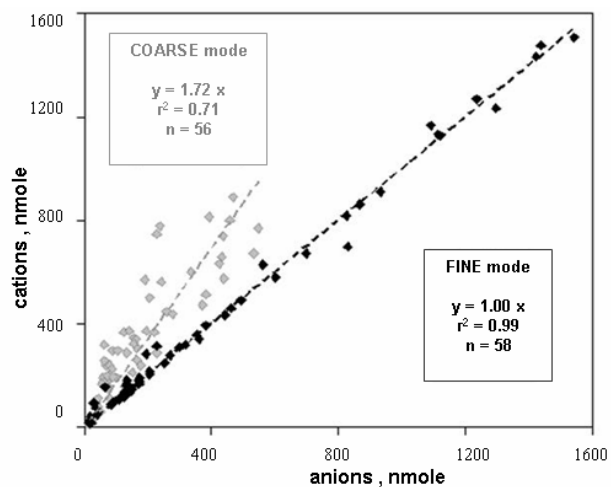


Fig. 2. Ion balance for coarse (in grey) and fine (in black) particles in Pek3 aerosols. Carbonate can be estimated from the excess of cations observed from the coarse mode slope.

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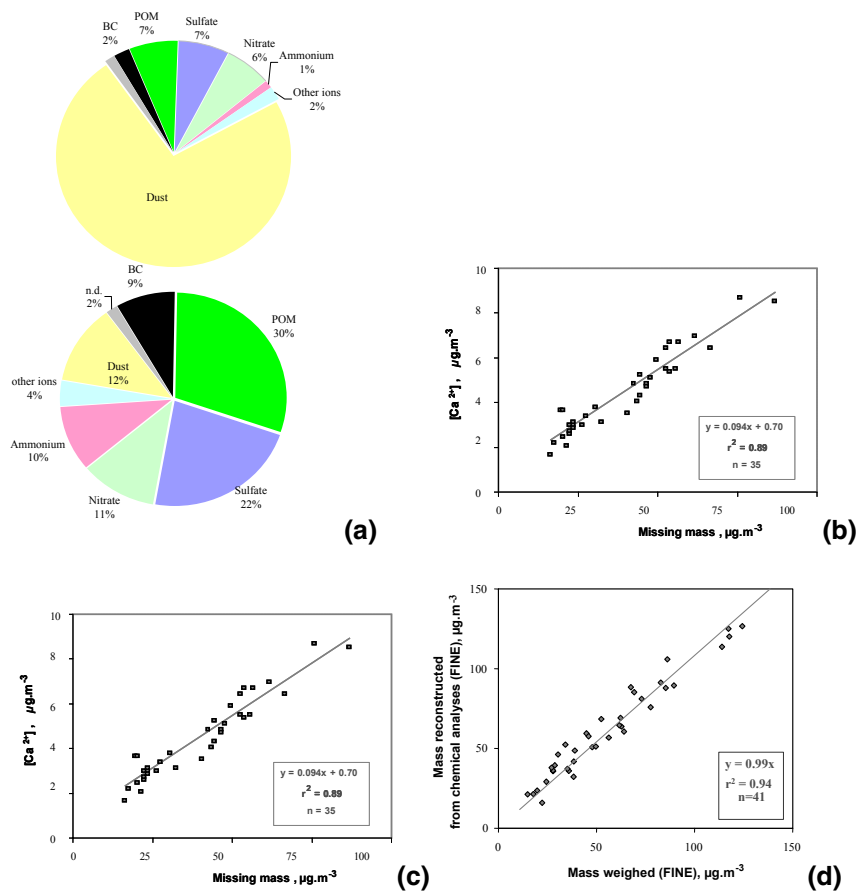


Fig. 3. Mass closure for Pek3 experiment (August 2004), all samples. **(a)** Mean chemical composition of the coarse (left) and fine (right). **(b)** Missing mass/ Ca^{2+} correlation in the coarse mode. **(c)** Mass closure of the coarse mode: Consistency between the actual weighed mass and the reconstructed mass. **(d)** Mass closure of the fine mode after k adjustment ($k=1.65$).

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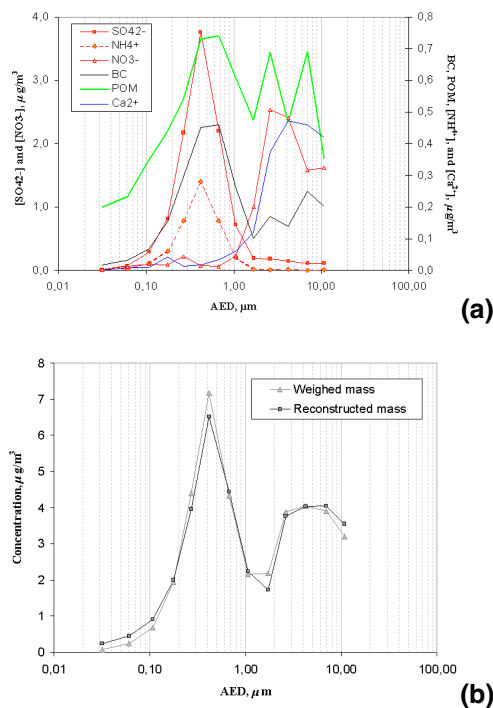


Fig. 4. Size distribution in Marseilles (2 July 2005). **(a)** Mass size distribution of BC, POM, sulphate, nitrate, ammonium, calcium. The association between Ca^{2+} and NO_3^- is particularly clear in the coarse mode. Arrows show the selected stages for f and k determination for the two modes. **(b)** Consistency between the actual weighed mass and the reconstructed mass over the whole distribution.

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