



## A European aerosol phenomenology—2: chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe

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### Abstract

This paper synthesizes data on aerosol (or particulate matter, PM) chemical characteristics, which were obtained in European aerosol research activities at natural, rural, near-city, urban, and kerbside sites over the past decade. It includes only two (nearby) sites in the semi-arid Mediterranean area, and lacks data from Eastern Europe. PM chemical compositions are compared with the PM mass concentrations in PM<sub>10</sub>, PM<sub>2.5</sub>, and further size resolved PM fractions (chemical mass closure). Such data sets are more comprehensive than those currently provided by air quality monitoring networks (e.g. EMEP, EUROAIRNET). Data available from 24 sites in Europe were reviewed. They were processed and plotted to allow comparisons in spite of differences in the sampling and analytical techniques used in various studies. A number of conclusions are drawn among which are the following.

Organic matter appears to be the major component of PM<sub>10</sub> and PM<sub>2.5</sub>, except at natural and rural background sites, where sulphate contribution may be larger. Mineral dust shows up as a major component of PM<sub>10</sub> at kerbside sites. Black carbon contributes 5–10% to PM<sub>2.5</sub> and somewhat less to PM<sub>10</sub> at all sites, including the natural background sites. Its contribution seems higher (15–20%) at some of the kerbside sites, but these data may be affected by analytical artefacts. On days when PM<sub>10</sub> > 50 µg m<sup>-3</sup>, nitrate concentrations can overtake organic matter concentrations in PM<sub>10</sub> and PM<sub>2.5</sub>. High PM concentration episodes are often observed in cold periods, when the pollutant dispersion is least. Measurements indicate that the condensation in the particle phase of semi-volatile species

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like nitrate and (unspecified) organics is also favoured by cold temperatures. In particles with a diameter  $< 150$  nm (i.e., most atmospheric particles), organic matter and black carbon are by far the major components.

More data are known to be available within the scientific community, which could enrich the present data set and strengthen the conclusions made above. Most of them are not made available yet. The investment in new approaches, which would bridge the technological gap between scientific measurements and regulatory monitoring networks, is strongly needed.

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## 1. Introduction

This paper is the complement to a paper by Van Dingenen et al. (2004), which explains the scientific and policy background of this work and presents the physical characteristics of PM2.5 and PM10. Briefly, knowing the aerosol chemical composition is important to determine its sources and its potential effects. Both the physical data presented in Van Dingenen et al. (2004) and the chemical data presented here were obtained from research projects of the last 10 years. Such parameters are presently not measured in regulatory monitoring networks (such as EMEP and EURO-AIRNET).

When entitling this work “phenomenology”, we clearly made the choice of presenting the European aerosol characteristics as they *appear* when measured using the sampling and analytical techniques currently available. We wanted to make an instantaneous picture illustrating what we know—and what we do not know—of the European aerosol chemistry. This was an opportunity to discuss the uncertainties arising from comparing data produced by various institutes using different techniques (see Section 2) and to suggest directions for improving the aerosol monitoring capacities in Europe for the next decade. We considered only projects providing data representative for a site during at least a season (i.e. minimum 6 weeks of continuous measurements within the same season). However, the yearly averages presented here were calculated only for measurements covering at least one full year. Additionally we requested that, together with the chemical analysis of PM2.5 and/or PM10, mass concentration was determined independently in the same experiment.

Fig. 1 shows the location of the 24 sites, operated by 10 institutes. The list of sites consisting “The Network”, their coordinates, and a brief overview of instrumental techniques used for sampling and analysis can be found in Appendix A. We have categorized these sites using criteria proposed by the European Environment Agency (Larssen et al., 1999). Among those criteria are the distance of the station from large pollution sources such as cities, power plants and major motorways and the traffic volume.

Natural background	distance from large pollution sources $> 50$ km
Rural background	distance from large pollution sources 10–50 km
Near city background	distance from large pollution sources 3–10 km
Urban background	$< 2500$ vehicles/day within a radius of 50 m
To which we have added Kerbside	within street canyons

## 2. Representativeness of the collected data

Comparing data obtained from various research groups using different techniques over one decade implies the assumption that these data accurately describe the aerosol for the period during which they were collected, and that the temporal variations that occurred over the decade were negligible with respect to the spatial variations.

### 2.1. Possible systematic errors

#### 2.1.1. PM10 and PM2.5 mass concentrations

The PM mass concentrations reported in this work are all based on gravimetric measurements. However, aerosol samples were collected on various substrates using various sampler types (stacked filter units, sampling heads, impactors) and gravimetric measurements were performed at various relative humidity (see Appendix A). It is quite unlikely that all these devices lead to equal 50% cut-off diameters (and efficiency curves). However, the filtration devices (including sampling heads) used at most sites were all equivalent to reference methods. For the sites where less standard methods were used, the aerosol mass concentration was usually quite low around the 2.5 and  $10\mu\text{m}$ , so that a slight error in the cut-off diameters would lead to very small changes in PM mass concentrations. In contrast, sampling artefacts can sometimes seriously affect the performances of certain devices. According to Hering et al. (1997), negative artefacts due to the volatilization of

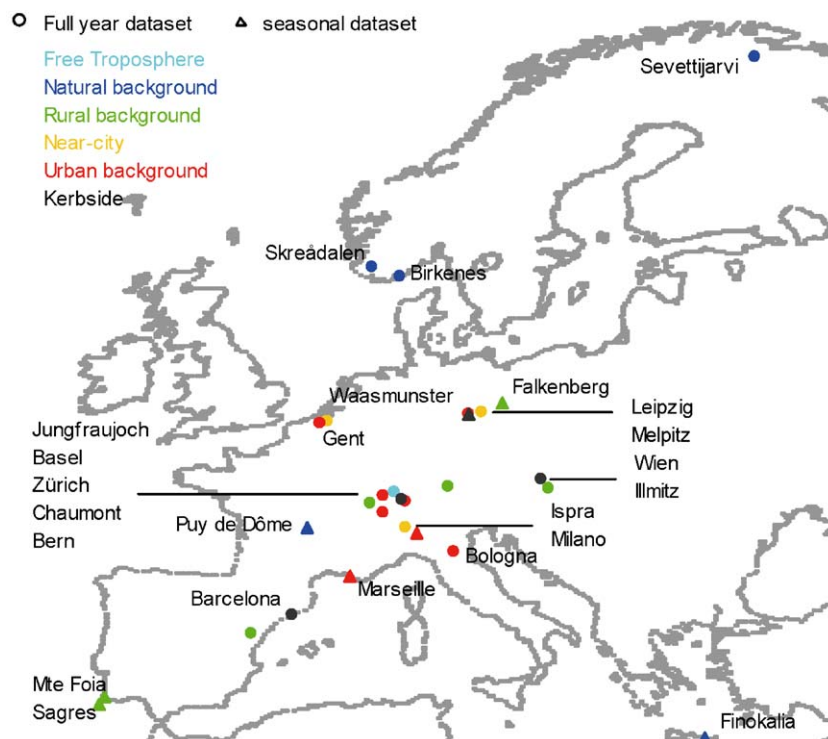


Fig. 1. Location of the sampling sites.

semi-volatile compounds in low-pressure impactor stages and to losses on impactor walls are generally  $<4\%$ . On the contrary, sampling on inert filters (e.g., quartz fibre filters) leads to variable losses of  $\text{NH}_4\text{NO}_3$  at  $T > 10^\circ\text{C}$  (Hering and Cass, 1999), and to both positive and negative artefacts for particulate organic matter, OM (Eatough et al., 1993, 1996). In Europe, the amount of  $\text{NH}_4\text{NO}_3$  and OM collected on quartz fibre filters, cascade impactors and artefact-free wet aerosol collectors was compared during laboratory (Petten wind tunnel, 1999) and field (Pipapo 1998; Melpitz Intercomp, 2000) experiments. Preliminary data can be found in the EUROTRAC-AEROSOL annual reports 200 and 2001 (see <http://aerosol.web.psi.ch/>). These experiments demonstrated that in summer time conditions ( $T > 20^\circ\text{C}$ ), up to 100% of  $\text{NH}_4\text{NO}_3$  and can be lost from quartz fibre filters, even for sampling times of a few hours (Schaap et al., 2004). For carbonaceous aerosol, the concentrations derived from cascade impactors were on average  $65 (\pm 10)\%$  of that obtained with quartz filters, due to the loss of semi-volatile carbon from the impactors or to the adsorption of volatile carbon in the filters or both (Ten Brink et al., 2004). Such artefacts can obviously affect significantly the determination of PM concentrations and seasonal variations in  $\text{NO}_3^-$  and OM contributions to PM. We highlight in the following

discussion in which way these artefacts might affect our conclusions.

Another possible source of inconsistencies among PM mass concentration measurements is the amount of particle-bound water. At 50% relative humidity, aerosol particles can contain up to 30% of water (see e.g. Guidelines for concentration and exposure response measurement of fine and ultra fine PM... in <http://www.who.int/peh/air/PM/pmtoc.htm>). At a continental site (Ispra), we found that over 1 year (2002), gravimetric measurements at 50% RH led to PM<sub>10</sub> and PM<sub>2.5</sub>, respectively, 1.09 and 1.07 times as high as gravimetric measurements at 20% RH.

#### 2.1.2. Aerosol chemical composition analyses

On top of sampling artefacts (2.1.1), the accuracy and consistency of analytical techniques have to be considered when comparing aerosol chemical composition determined by different laboratories using different methods (see Appendix B).

The measurement by ion chromatography of *inorganic species* in aerosol particles is quite easy and results from different laboratories are usually within  $\pm 10\%$  for all major species, except  $\text{Ca}^{2+}$  for which the difference can reach 50% (Putaud et al., 2000).

The accurate determination of the *organic carbon* (OC) and *black carbon* (BC) concentrations in aerosol

particles remains challenging. Several intercomparisons organised in the framework of EUROTRAC—AEROSOL (e.g., Schmid et al., 2001) showed that the uncertainty in the determination of total carbon (TC) is  $<10\%$ . It is however important to split TC between OC and BC. The latter is exclusively emitted by combustion processes, whereas OC consists of primary and secondary species from anthropogenic and biogenic origins. The split between OC and BC is instrumentally defined and largely varies from a method to another. The OC data presented in this report were provided by four laboratories, among which three participated to the Eurotrac-AEROSOL “carbon shoot out”. The last (yet unpublished) results of this intercomparison indicate that their determination of BC can diverge by up to a factor of 3. For instance, the reflectance method applied to samples collected at Gent led to BC data on an average three times as large as a thermal method with optical correction for charring (transformation of OC to BC during the analysis). Also the method used for analysing samples collected in Austria is expected to lead to BC values in the higher range, due to unaccounted charring. Consequently, the difference between the OC data derived from these methods are expected to be up to a factor of 2. The determination of particulate organic matter (OM) concentrations is also affected by the OM content of hetero-atoms (H, O, N, etc.), which is currently not measured. To account for these atoms, molecular-to-carbon ratios between 1.2 and 1.7 were proposed as correction factors (Gray et al., 1986; Malm et al., 1994; Eatough et al., 1996; Hegg et al., 1997; Turpin et al., 2000). We consistently used a ratio equal to 1.4 to convert OC to OM concentrations, although it could well be different in various aerosol types (Turpin et al., 2000). The large uncertainties in OM and BC concentrations have to be kept in mind in the discussion.

The use of elemental analysis (e.g., PIXE, INAA, ICP-MS, ICP-AES) permits to obtain the concentrations of many heavy elements, which are specific tracers of various sources. For instance, the amount and origin of mineral dust can be determined by measuring Al, Fe, and other possible soil constituents. Experimental data show that  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio in PM10 in most places range from 2.5 to 3.5. When quartz filters are used and Si cannot be determined,  $\text{SiO}_2$  values were indirectly assessed by multiplying  $\text{Al}_2\text{O}_3$  concentrations by a factor of 3. When elemental techniques are not available, only the total amount of refractory particulate compounds can be determined (by ashing ashless filter and weighing the residue). Extended data sets show that in Western continental Europe, this total amount of mineral dust is correlated with the amount of non-sea-salt calcium ( $\text{nss-Ca}^{2+}$ ). When it was impossible to determine mineral dust concentrations using others techniques, it was estimated by multiplying  $\text{nss-Ca}^{2+}$  concentrations by 4.5. The aerosol fraction called *mineral dust* therefore

includes all non-water soluble and non-carbonaceous components and consists of soil dust, road dust, fly ash and minor elements. However, considering the various techniques used to assess this aerosol fraction, the uncertainty in such mineral dust concentration estimates is large (about a factor of 2).

The discussion above shows how the chemical characterization of aerosol particles is still affected by many problems related to both sampling and analysis. In this report we show only aerosol chemical data when they can be compared with the PM10 or PM2.5 mass measured gravimetrically in the same experiment. This allows a check of internal consistency of a data set, hence a minimum of quality control. This level of chemical mass closure guarantees that no large problems (uncertainties of more than a factor of 2) exist in the weighing and analyses of the aerosol. Mass closure does not exclude, however, that the mass and chemical measurements are both affected in the same way by sampling artefacts.

## 2.2. Temporal variations at a limited number of sites

On the top of potential systematic errors, the comparability of data collected over a decade might be affected by significant temporal changes. It was possible to retrieve  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  data for 6 among 26 stations of the network from the EMEP database (<http://www.nilu.no/projects/ccc/>). A general decrease in  $\text{SO}_4^{2-}$  concentrations can be observed over the 1991–2001 period (Fig. 2a). A significant year-to-year variability (up to  $>30\%$ ) can also be noticed. In contrast, there is no clear long-term trend in  $\text{NO}_3^-$  concentrations (Fig. 2b). Year-to-year variability can however reach  $>50\%$ . These observations are used to interpret the comparison among sites in the following discussion.

## 3. PM10 and PM2.5 chemical composition

Fig. 3 shows annual average concentrations of the main aerosol components in (a) PM10, (b) PM2.5 (the fine fraction) and (c) PM10–PM2.5 (the coarse fraction). A table with numerical values is on-line available from Putaud et al. (2003).

BC, nitrate ( $\text{NO}_3^-$ ), and ammonium ( $\text{NH}_4^+$ ) concentrations result directly from measurements. As already mentioned in Section 2, OM concentrations were calculated by multiplying OC concentrations by a constant factor of 1.4 (e.g., Eatough et al., 1996) to account for the non-C atoms contained in particulate OM. Sea-spray was clearly identified as a component of the aerosol at sites located  $<50$  km from seashore. For consistency, the sea-salt concentration was calculated from  $\text{Na}^+$ ,  $\text{Cl}^-$  concentrations, and a standard seawater composition, even when the purely marine origin of

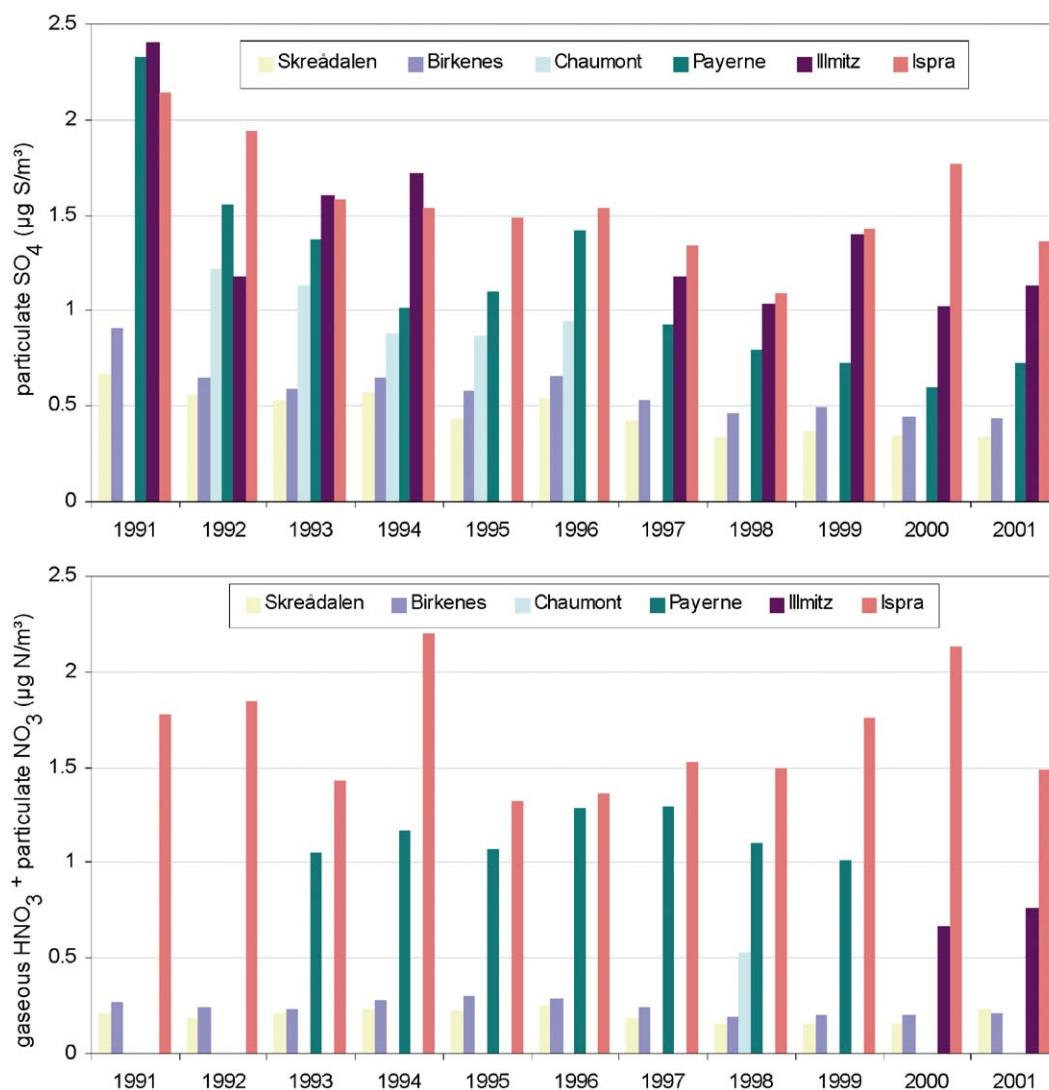


Fig. 2. Long-term trend in (a)  $\text{SO}_4^{2-}$  and (b)  $\text{NO}_3^-$  concentrations at some EMEP sites of the network.

$\text{Na}^+$  was not obvious. Likewise, nss-sulphate (nss- $\text{SO}_4^{2-}$ ) concentrations were calculated from measured  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ , and a standard sea water composition. The total amount of mineral dust (min. dust), including silicates, carbonates, calcium sulphate and trace elements, was directly determined, or estimated based on measurements of tracers such as Al or nss- $\text{Ca}^{2+}$ , as described in Section 2. The unaccounted mass (obtained as the difference between the gravimetrically measured aerosol mass concentration and the sum of the aerosol component concentrations) includes different species for the various sites of the network. Table 1 specifies what components make up the unaccounted mass for each site.

In Fig. 3, the top of the bars indicates gravimetrically determined PM10, PM2.5 and coarse fraction (PM10–PM2.5) mass concentrations. Roughly, PM10 and PM2.5 increase when shifting from natural background to kerbside sites. It is however interesting to note that in Belgium, both PM10 and PM2.5 concentrations are very similar at a near-city compared to an urban background site. It can also be noticed that PM10 and PM2.5 mass concentrations can be as high at rural or near city sites like Illmitz or Ispra, as at urban background sites like Zurich and Basel. These data are directly comparable since they were obtained with similar sampling and analytical methods, all between 1998 and 2001. They highlight that the PM concentrations inside cities also

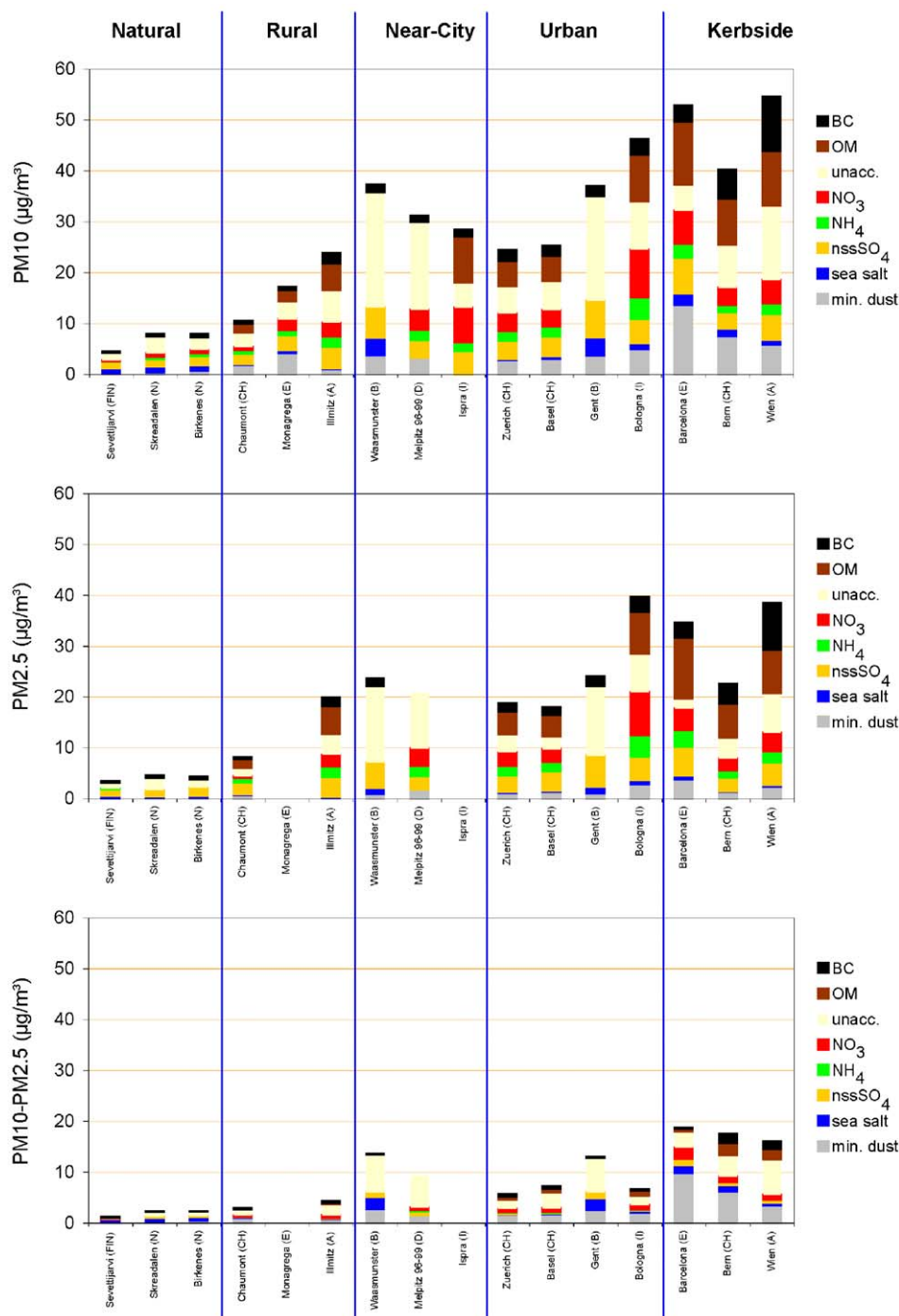


Fig. 3. Absolute annual average concentrations of the main aerosol components in (a) PM10, (b) PM2.5 and (c) PM10-PM2.5.

depend on the background PM of the region where they are located. Also the coarse fraction mass concentration is generally higher at the more urbanized sites. This

shows that even coarse particles have predominantly anthropogenic sources. As the aerosol coarse fraction mass and components are mostly obtained by

Table 1  
Species contributing to “unaccounted mass,” i.e. the difference between quantified and gravimetrically determined mass

Site			Unaccounted mass		
Sevettijarvi (FIN)			OM	Water	
Skreådalen (N)		NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	OM	Water
Birkenes (N)		NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	OM	Water
Chaumont (CH)					Water
Monagrega (E)					Water
Illmitz (A)					Water
Waasmunster (B)		NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	OM	Water
Melpitz (D)				OM	Water
Ispra (I)	Min. dust	Sea salt			Water
Zuerich (CH)					Water
Basel (CH)					Water
Gent (B)		NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	OM	Water
Bologna (I)					Unknown
Marseille (F)					Unknown
Barcelona (E)					Water
Bern (CH)					Water
Wien (A)					Water

Note: OM = organic matter.

difference (PM<sub>10</sub>–PM<sub>2.5</sub>), uncertainties in the coarse fraction concentrations are large. Let us just notice that min. dust represents generally the major single component. It may be interesting to note that the min. dust concentrations observed Barcelona, using methods similar to those used at e.g., Bern, is the highest in the Network. This might be due to the aridness of the surroundings, or to the most frequent occurrence of Saharan dust transport. On the contrary, the relatively large amounts of BC observed in the aerosol coarse fraction at Bern and Vienna, is probably for a large part due to an analytical artefact (charring).

In PM<sub>10</sub> and PM<sub>2.5</sub>, as expected, BC concentrations increase when shifting from natural background to kerbside sites. However, large differences in BC concentrations may just come from analytical inaccuracies. At natural background sites, BC was measured using an optical method. It is therefore really light absorbing material, with no possible analytical artefact due to charring. BC at remote location may result from long range transport of combustion aerosol. At a number of sites including Chaumont, Illmitz, Zurich, Basel, Bern and Vienna, in contrast, BC concentrations are likely to be affected by charring. As a consequence, BC concentration is probably not higher at Illmitz compared to Waasmunster, or at Vienna or Bern, compared to Barcelona or Bologna. On the other hand, the gradient observed between the Swiss rural site (Chaumont), urban sites (Zurich, Basel) and kerbside site (Bern) is certainly true, since the same technique was used for analyzing the samples

collected at these four sites. Taking charring into account, the OM concentration observed at the three kerbside sites would be quite similar. Outstanding is the OM concentration in PM<sub>10</sub> observed at Ispra: it is larger than at urban sites such as Zurich and Basel, and comparable to Bologna. As OM concentrations at Ispra were corrected for positive sampling artefacts (1 µg m<sup>-3</sup> yearly average), they represent a lower limit. In contrast, the OM concentration reported for Bologna might be too low by 4 to 35% (see Section 2) since samples were collected with a low-pressure impactor.

NO<sub>3</sub><sup>-</sup> concentrations do not follow the general trends of PM<sub>10</sub> and PM<sub>2.5</sub> concentrations: the largest concentrations are observed at Ispra and Bologna, both located in Italy. This cannot be due to sampling artefacts since quartz fibre filters were used in Ispra, like at all the other rural to kerbside sites, whereas a low-pressure impactor was used at Bologna, which is expected to also lead to negative artefacts as filters. NO<sub>3</sub><sup>-</sup> data might be affected by even larger sampling artefacts at the Spanish sites (Monagrega and Barcelona) only, where summer temperatures are higher. However, it is not unexpected to find the highest NO<sub>3</sub><sup>-</sup> concentrations in the Po valley, where are located both large anthropogenic sources of NO<sub>x</sub> and agriculture-related sources of NH<sub>3</sub>, necessary to stabilize NO<sub>3</sub><sup>-</sup> in the particulate phase as NH<sub>4</sub>NO<sub>3</sub>. It should be noted that the NO<sub>3</sub><sup>-</sup> concentrations observed at Ispra was not exceptionally large in 2003 (Fig. 2b). NH<sub>4</sub><sup>+</sup> concentrations generally follow NO<sub>3</sub><sup>-</sup> + nss-SO<sub>4</sub><sup>2-</sup> concentrations in PM<sub>2.5</sub> and PM<sub>10</sub> and will not be further discussed. In contrast with NO<sub>3</sub><sup>-</sup>, nss-SO<sub>4</sub><sup>2-</sup> does

not present very large spatial variations, above all in PM<sub>2.5</sub>. This is in line with the fact that most sulphate is produced from cloud processing over large scales rather than from direct (local) gas phase oxidation of SO<sub>2</sub>.

However, it should be noted that the spatial gradient in nss-SO<sub>4</sub><sup>2-</sup> would have been somewhat larger if recent data for the natural background data were considered (see Fig. 2a).

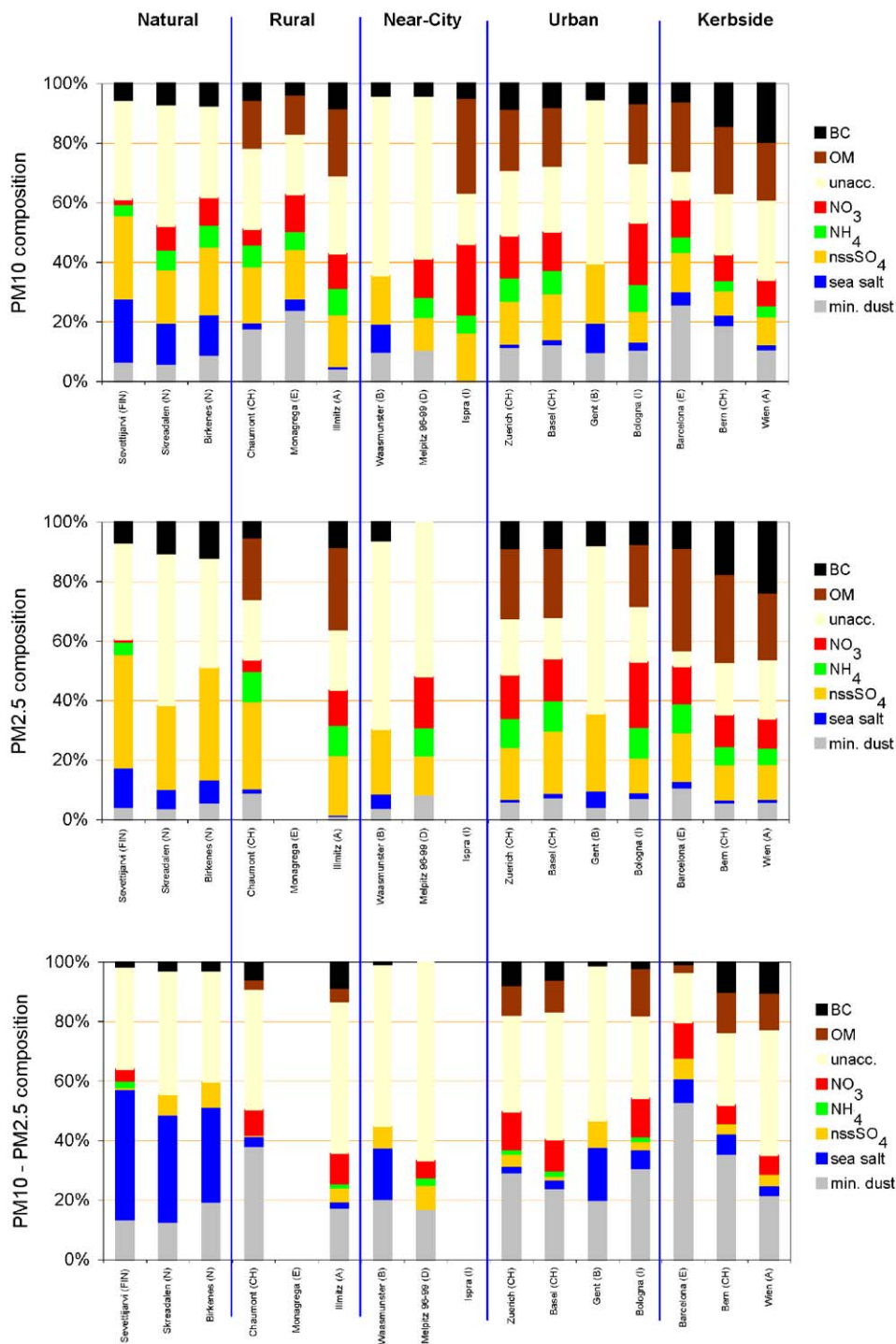


Fig. 4. Annual averaged chemical composition of (a) PM<sub>10</sub>, (b) PM<sub>2.5</sub> and (c) PM<sub>10</sub> - PM<sub>2.5</sub>.

Sea salt (or possible sea-salt components) was observed in PM10 as well as in PM2.5. The largest concentrations were observed in Belgium (Waasmunster and Gent), and Barcelona. Rather small concentrations of sea salt were observed at the Norwegian sites (Skreådalen and Birkenes), more distant from the shore line. Min. dust concentrations derived from trace element measurements show low values for natural background sites, similar values for rural to urban background sites, and higher values for kerbside sites. The difference between Barcelona and Bern in mineral dust concentration (about a factor of 2 in both PM10 and PM2.5) is certainly true since data derive from trace element measurements for both sites. Mineral dust values derived from  $\text{nss-Ca}^{2+}$  measurements (Illmitz, Melpitz, Bologna, Vienna) do not seem inconsistent with the others, but should not be directly compared.

Fig. 4 shows the annual averaged relative contributions of various species to (a) PM10, (b) PM2.5, and (c) PM10–PM2.5. Relative contributions are independent of dilution and reflect differences in the sources and processes controlling the aerosol composition. Depending on the relative contribution of the fine and coarse fractions, the chemical composition of PM10 and PM2.5 can be significantly different (e.g., Barcelona) or similar (e.g., Bologna). When all main aerosol components are analyzed (i.e. at nine sites only), they typically account for 70% of the PM10 and PM2.5 mass or more. The remaining unaccounted mass fraction (*unacc.*) is thought to result from aerosol-bound water and from random and possibly systematic errors, like for instance non-C atoms associated with particulate OM that are not adequately accounted for by using a molecular mass-to-carbon mass ratio of 1.4. All components are present in both the fine and the coarse fractions, but their contributions in each fraction are often different. Min. dust and sea salt contribute more to the coarse fraction, whereas  $\text{NH}_4^+$ ,  $\text{nss-SO}_4^{2-}$ , OM, and BC contribute more to the fine fraction. Also  $\text{NO}_3^-$  contributes generally more to the fine fraction, but its contribution to the coarse fraction is only slightly less. OM in the fine fraction may result from primary emissions from combustion processes or from the oxidation of volatile organic compounds (VOC), whereas OM in coarse fraction may also include biological debris.  $\text{NO}_3^-$  in the fine fraction is bound by ammonia, whereas in the coarse fraction it is bound by alkaline sea salt and/or min. dust particles. BC in the coarse fraction might come from tire debris or soot deposited on re-suspended dust. However, it may also well result largely from charring. Indeed, we estimated that using a charring-free method, the contribution of BC to the coarse fraction e.g., in Vienna, might be reduced to 3–4% only.

Considering that this analytical artefact might affect above all the BC values calculated for Chaumont,

Illmitz, Zurich, Basel, Bern and Vienna, we could not detect any change in BC contribution to any aerosol fraction when shifting from natural background to kerbside sites. It is quite the same for OM, which is further affected by the (probably wrong) assumption that the molecular mass-to-carbon mass ratio is the same at all site types, ranging from rural background to kerbsides (Turpin et al., 2000). However, the contribution of total carbon (which is a very robust piece of data) seems significantly higher at kerbsides compared to e.g., rural background sites, especially in PM2.5. The case of  $\text{NO}_3^-$  is interesting since the smallest contribution are observed at some of the natural to rural background sites, but also at 2 of the kerbside sites. This cannot be due to enhanced negative sampling artefacts, since the places where the minimum  $\text{NO}_3^-$  contribution are observed are not located in specially warm areas. Low contributions of nitrate at the natural background sites can be explained by the absence of local sources of  $\text{NO}_x$ , precursor of particulate  $\text{NO}_3^-$ . The time needed to form particulate  $\text{NO}_3^-$  from  $\text{NO}_x$  or the default of  $\text{NH}_3$  (necessary to form particulate  $\text{NH}_4\text{NO}_3$ ) in city centres might explain that nitrate contribution to PM10 and PM2.5 is higher at near-city sites than at kerbside sites. The relative contribution of  $\text{nss-SO}_4^{2-}$  to PM10 and PM2.5 presents a clear decreasing trends when moving from natural background to kerbside sites (see also Fig. 5). Can this be due to the fact that natural background data go back to 1991–1996, whereas most other data sets correspond to 1998 and beyond? From the data presented in Fig. 2a, it can be calculated that  $\text{nss-SO}_4^{2-}$  concentrations decreased by >30% from 1991–1996 to 1998–2001 at Skreådalen and Birkenes. Unfortunately, lacking PM mass concentration measurements for this last period, we cannot determine the current contribution of  $\text{nss-SO}_4^{2-}$  to PM10 and PM2.5 at these sites. In contrast, we were able to estimate that the contribution of  $\text{nss-SO}_4^{2-}$  in PM10 at Illmitz and Ispra over the 1991–1996 period were 22% and 13%, respectively. The spatial gradient in  $\text{nss-SO}_4^{2-}$  contribution to PM10 was therefore certainly existing in the mid-1990s. Whether it is still the case at the beginning of the 21st century should be verified. Sea salt obviously accounts for a significant fraction of PM10 and also PM2.5 at the natural background sites of the network, which happen to be close to seas. Its contribution to PM10 and PM2.5 drops to negligible values at urban and kerbside sites, except at Gent and Barcelona (especially in PM10), which are not far away from shore lines. Finally, sticking to sites where mineral dust was determined based on trace element analyses, it can be observed that the contribution of mineral dust to PM10 is very similar at rural sites (Monagrega and Chaumont) and kerbside sites (in Barcelona and Bern) located in the same country, although its sources are certainly different at these two site types.

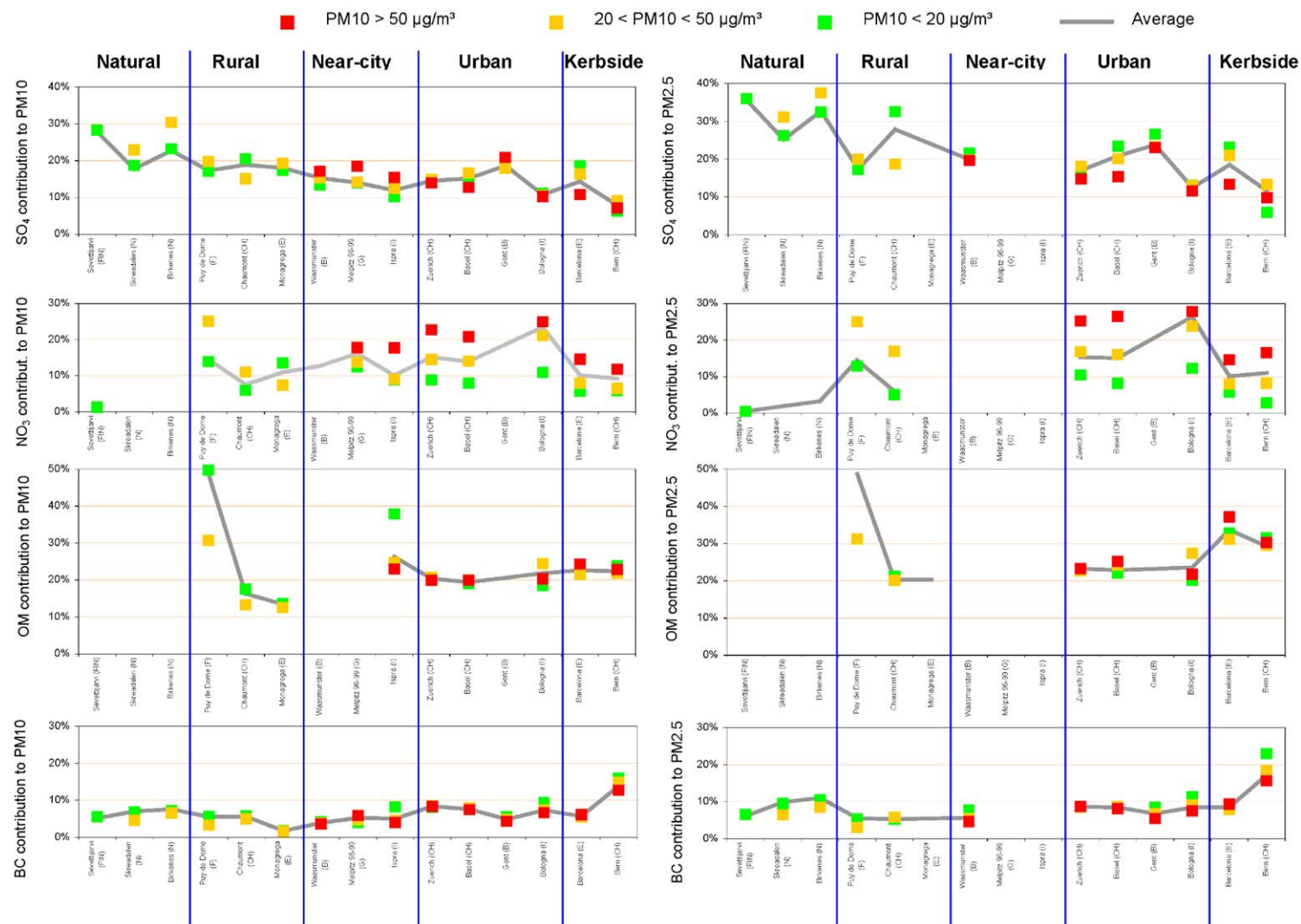


Fig. 5. Annual mean relative contribution of individual chemical species to PM10 categorized according to PM10 mass concentration: PM10 > 50 µg m<sup>-3</sup> (red), 50 > PM10 > 20 µg m<sup>-3</sup> (yellow), PM10 < 20 µg m<sup>-3</sup> (red). Average is indicated with grey line.

Table 2  
Relative contribution (%) of various chemical species to PM mass in 3 site categories

	PM10				PM2.5				PM10–PM2.5		
	Natural & rural background	Near-city & urban background	kerbside	Natural & rural background	Near-city & urban background	kerbside	Natural & rural background	Near-city & urban background	Natural & rural background	Near-city & urban background	kerbside
Black carbon	6	5	13	8	8	17	4	3	4	3	7
Organic matter	16	20	22	23	22	29	4	8	4	8	10
Nitrate	7	15	10	5	17	11	8	7	8	7	8
Ammonium	6	7	4	8	10	7	1	1	1	1	0
Sulfate	19	13	10	29	17	13	3	5	3	5	5
Sea salt	8	4	3	3	3	1	20	9	20	9	6
Min. dust	10	9	19	5	7	8	21	22	21	22	37
Unknown <sup>a</sup>	28	27	19	20	17	15	40	46	40	46	28

<sup>a</sup> Calculated only when all the main aerosol components were measured.

Table 2 gives “grand average” aerosol compositions (%) by averaging the annual mean contributions of each component to either PM10, PM10–PM2.5 or PM2.5. OM is the main single component of both PM10 and PM2.5, except perhaps at natural and rural background where it is overtaken by  $\text{SO}_4^{2-}$ , which is however boosted by higher values observed during the 1991–1996 period. Min. dust might be the major component of the coarse fraction, although mineral dust values are affected by large uncertainties. For a given site, however, the chemical composition is not constant, and may change e.g. with the degree of pollution at the site.

Figs. 5a and b show  $\text{nss-SO}_4^{2-}$ ,  $\text{NO}_3^-$ , OM and BC relative contributions to PM10 and PM2.5 as a function of PM10 mass concentration ranges. The contribution to PM10 and PM2.5 of most aerosol components including mineral dust (not shown), does not vary much when PM10 mass concentration shifts from  $<20 \mu\text{g m}^{-3}$  to  $>50 \mu\text{g m}^{-3}$ . This shows that high PM concentration episodes are mainly related to meteorological situations during which pollution dispersion is reduced, leading to an increase of all the pollutants. An exception is  $\text{NO}_3^-$ , for which contributions to PM10 and PM2.5 increase with PM10 concentration at all sites, except at Monagrega. It should be noted that at most sites, maximum PM10 and PM2.5 concentrations are observed during cold seasons (Putaud et al., 2003), except at... Monagrega. This is at least partially due to the fact that the dispersion of pollutants is least on cold days, when the mixed boundary layer height is reduced. The variations in  $\text{NO}_3^-$  contributions to PM10 and PM2.5 can therefore be at least partially due to seasonal changes in gas/particulate phase partitioning of  $\text{NO}_3^-$  (and  $\text{NH}_4^+$ ) and/or to seasonal changes in the amplitude of  $\text{NH}_4\text{NO}_3$  sampling artefacts.

#### 4. Size-segregated aerosol chemistry

Fig. 6 shows examples of the median size-segregated aerosol chemical composition observed at (a) Gent (Belgium), (b) Bologna (Italy) and (c) Marseilles suburb (France) for the September–October periods 1999 and 2000, and June–July 2000, respectively (Maenhaut et al., 2002; Matta et al., 2003).

Size distributions of BC,  $\text{nss-SO}_4^{2-}$  and mineral dust are similar at the three sites. BC and  $\text{nss-SO}_4^{2-}$  are found mainly in the sub-micron aerosol fraction, whereas min. dust is mainly in the coarse fraction (as is sea salt in Gent and Marseilles). Particulate OM is mainly in the sub-micron fraction in Bologna and Marseilles, and quite evenly distributed over the 50 nm–10  $\mu\text{m}$  size range in Gent.  $\text{NO}_3^-$  is also mainly in the sub-micron fraction in Bologna, whereas it is almost exclusively in the coarse fraction in Marseilles, due to the presence of sea salt, which shifts  $\text{NO}_3^-$  towards the aerosol coarse mode.

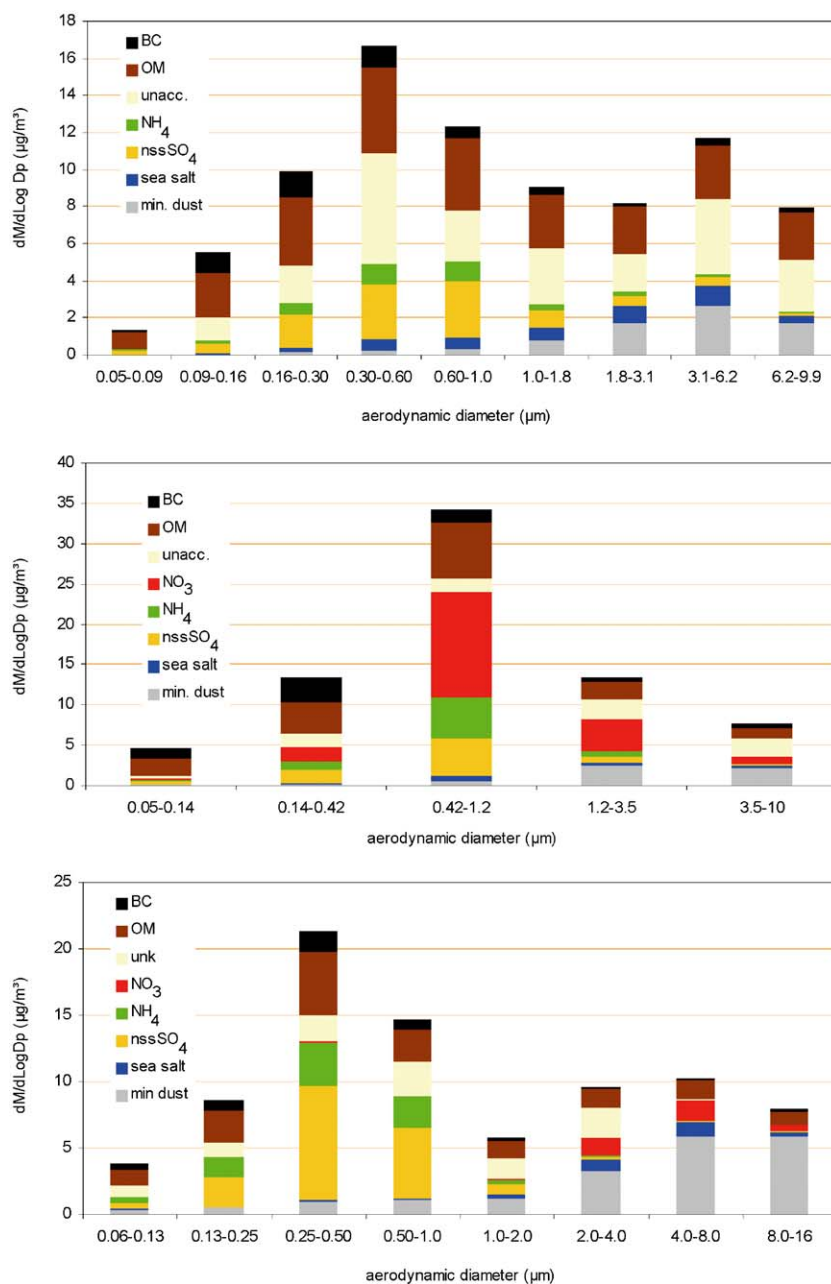


Fig. 6. Median size segregated aerosol chemical composition observed at (a) Gent (B), (b) Bologna (I), and (c) Marseilles suburb (F).

Particles smaller than about 150 nm (i.e. more than 80% of the atmospheric particles, see the companion paper by Van Dingenen et al., 2004) consist mostly of carbonaceous components (OM and BC). This kind of information is essential to understand the impact of particles on health and radiative forcing.

## 5. Summary and conclusions

Datasets on aerosol chemical properties have been compiled from 24 European sites. “The Network” includes a wide variety of environmental conditions but covers only Western Europe: two (nearby) sites only

might be representative for semi-arid Mediterranean conditions, and no data were collected from Eastern Europe. We chose to present the aerosol chemical composition as measured with current sampling and analytical methods. We know that these techniques may lead to significant sampling and analytical artefacts, the importance of which was considered along the data discussion.

When all main chemical components of the aerosol are measured, they account for about 70% or more of the PM<sub>10</sub> and PM<sub>2.5</sub> mass. The rest is thought to be due to the presence of water or to the underestimation of the molecular mass-to-carbon mass ratio when calculating organic matter concentrations. Organic matter (OM) seems to be the main contributors to the annual average PM<sub>2.5</sub> and PM<sub>10</sub> mass concentration, except at natural and rural background sites where non-sea salt (nss-SO<sub>4</sub><sup>2-</sup>) may be the first contributor to both PM<sub>10</sub> and PM<sub>2.5</sub>. More recent data from natural background sites would be needed to confirm this. In spite of large uncertainties in mineral dust contribution, it appears that it is a major contributor to PM<sub>10</sub> at kerbside sites.

No clear relationship exists between PM<sub>2.5</sub> or PM<sub>10</sub> mass concentrations on the one hand, and PM chemical composition on the other, except for nitrate (NO<sub>3</sub><sup>-</sup>). This indicates that high PM concentration episodes are primarily due to meteorological conditions that reduce the dispersion of pollutants. However, when selecting only polluted conditions (PM<sub>10</sub> > 50 µg m<sup>-3</sup>), then NO<sub>3</sub><sup>-</sup> becomes the main contributor to PM<sub>10</sub> and PM<sub>2.5</sub> together with organic matter (OM). This is at least partially due to the fact that most serious PM pollution episodes are encountered during cold periods, which favour the stability of particulate NH<sub>4</sub>NO<sub>3</sub> in the atmosphere and also reduce the amplitude of NH<sub>4</sub>NO<sub>3</sub> sampling artefacts. Black carbon (BC) contributes 5–10% to PM<sub>2.5</sub> and somewhat less to PM<sub>10</sub> at all sites, including the clean background sites. Its contribution seems to increase to 15–20% at some of the kerbside sites, but this may well be completely due to uncontrolled charring, an analytical artefact which transforms organic carbon to black carbon during analyses. Impactor measurements show that the smallest aerosol fractions (particle diameter < 150 nm), which contain more than 80% of the atmospheric particles (Van Dingenen et al., 2004), consist largely of carbonaceous components (OM and BC).

The analysis presented in this paper and the accompanying paper Van Dingenen et al. (2004) shows that research programs can provide fundamental data to understand the sources and transformation of aerosols. They could also be used to assess their effects on human health and climate, but this is outside the scope of these papers.

Simultaneous measurements of physical and chemical data allow for consistency checks between the data at a single site. However, the lack of harmonization in measuring techniques between research groups renders a comparison between sites more difficult. Monitoring networks aim at harmonized approaches, but are (presently) weak in providing the full range of aerosol parameters needed for tracking their sources and assessing their effects.

Documenting temporal and spatial variation in aerosol characteristics is needed for both process studies and modelling effort supports. The research community must work together with the users' community (health, climate, visibility, ..., legislators) to bridge the gap between scientific measurement programs and monitoring programs. The establishment of a number of super-sites, like the ones funded by the EPA in the United States (<http://www.epa.gov/ttn/amtic/supsites.html>), is presently being discussed in Europe and might offer a solution. The development of such a network should be considered a high priority, and requires a strong link between regulatory monitoring networks (e.g., EMEP) and the research community (e.g., EU, ESA-GMES, WMO-GAW and national research programs) as well. There is currently an evolving cooperation between the major networks in this respect i.e. through the EU FP5 GMES project CREATE (construction, use and delivery of a European aerosol database) to which both EMEP and the World Data Centre for Aerosols under the WMO are involved. Further, the impact of particulate matter on global change also calls for a close cooperation with non-European activities.

However, apart from an investment in new measurement/monitoring approaches, funds should also be made available for analysing existing data. More research data are known to be available. The fact that they are not analyzed has also to do with a funding system, which tends to pay for generating new data rather than fully analyzing existing ones.

## Appendix A

Data availability, data sources, instruments and sampling devices is shown in Table 3.

## Appendix B

Sampling substrates and analytical techniques for chemical analyses is shown in Table 4.

Table 3

Institute	Site	Reference (see notes)	Lat	Long	Altitude	Category	Period	PM10 sampling for chemical analysis	PM2.5 sampling for chemical analysis	PM10 mass measurements	PM2.5 mass measurements	Size-segregated che- mical composition
Gent Univ.	Sevettijarvi (FIN)	1	69.35	28.50	130	Natural	Nov 93–Jan 96	Virtual impactor	Virtual impactor	Weighing (40% RH)	Weighing (40% RH)	
Gent Univ.	Skreådalen (N)	2, 3	58.82	6.72	465	Natural	Feb 91–Feb 96	Stacked filter unit	Stacked filter unit	Weighing (50% RH)	Weighing (50% RH)	
Gent Univ.	Birkenes (N)	2, 3	58.38	8.25	190	Natural	Feb 91–Feb 96	Stacked filter unit	Stacked filter unit	Weighing (50% RH)	Weighing (50% RH)	
IIT	Melpitz 97-99 (D)	unpub- lished	51.53	12.93	86	Near-city	Dec 96–Nov 97	Hi vol sampler Partisol (weekly)	Partisol (weekly)	Weighing (50% RH)	Weighing (50% RH)	
IIT	Melpitz 99-01 (D)	unpub- lished	51.53	12.93	86	Near-city	Dec 99–Nov 01	Hi vol sampler Partisol (weekly)	Partisol (weekly)	Weighing (50% RH)	Weighing (50% RH)	
Gent Univ.	Waasmunster (B)	4	51.12	4.08	20	Near-city	Jul 94–Nov 95	Stacked filter unit	Stacked filter unit	Weighing (50% RH)	Weighing (50% RH)	
Gent Univ.	Gent (B)	4, 5	51.02	3.73	10	Urban	May 93–July 94	Stacked filter unit	Stacked filter unit	Weighing (50% RH)	Weighing (50% RH)	10-st. MOUDI + 12-st. SDI
		6					Sep 99–Oct 99					
Umweltbundesamt	Illmitz (A)	7	48.23	16.36	117	Rural	Oct 99–Oct 00	Hi vol sampler	Hi vol sampler	Weighing (50% RH)	Weighing (50% RH)	
Umweltbundesamt	Wien-Spittelauer Lände (A)	7	47.75	16.75	160	Kerbside	Oct 99–Oct 00	Hi vol sampler	Hi vol sampler	Weighing (50% RH)	Weighing (50% RH)	
EMPA	Basel (CH)	8	47.53	7.58	316	Urban	Jan 98–Mar 99	Hi vol sampler	Hi vol sampler	Weighing (50% RH)	Weighing (50% RH)	
EMPA	Zürich-Wiedikon (CH)	8	47.37	8.53	415	Kerbside	Jul 98–Feb 99	Hi vol sampler	Hi vol sampler	Weighing (50% RH)	Weighing (50% RH)	
EMPA	Zürich (CH)	8	47.37	8.53	409	Urban	Jan 98–Mar 99	Hi vol sampler	Hi vol sampler	Weighing (50% RH)	Weighing (50% RH)	
EMPA	Chaumont (CH)	8	47.05	7.58	1136	Rural	Jan 98–Mar 99	Hi vol sampler	Hi vol sampler	Weighing (50% RH)	Weighing (50% RH)	
EMPA	Bern (CH)	8	46.95	7.43	545	Kerbside	Jan 98–Mar 99	Hi vol sampler	Hi vol sampler	Weighing (50% RH)	Weighing (50% RH)	
EMPA	Payerne (CH)	8	46.80	6.93	409	Rural	May 98–Oct 98	Hi vol sampler	Hi vol sampler	Weighing (50% RH)	Weighing (50% RH)	
JRC	Ispra (I)	unpub- lished	45.82	8.63	209	Near-city	Feb 00–Dec 00	Klein filter Gerät	Klein filter Gerät	Weighing (30% RH)	Weighing (30% RH)	
LaMP	Puy de Dome (F)	9	45.77	2.97	1465	Rural	Feb 00–Mar 01	ELPI & SDI impactors	ELPI & SDI impactors	Weighing (50% RH)	Weighing (50% RH)	ELPI & SDI impactors
JRC	Milano-Bresso (I)	10	45.53	9.20	130	Urban	May 98–Jun 98	Virtual impactor	Virtual impactor	Weighing (20% RH)	Weighing (20% RH)	
ISAC	Bologna (I)	11, 12	44.53	11.29	88	Urban	Jan 00–Dec 00	6-st. Berner impactor	6-st. Berner impactor	Weighing (20% RH)	Weighing (20% RH)	6-st. Berner impactor
JRC	Marseille-Vallon Dol (F)	unpub- lished	43.35	5.40	150	Urban	Jun 01–Jul 01	9-st. Berner impactor	9-st. Berner impactor	Weighing 20% RH	Weighing (20% RH)	9-st. Berner impactor
CSIC	Barcelona (E)	13	41.37	2.12	30	Kerbside	Jun 99–Jun 00	Hi vol sampler	Hi vol sampler	Weighing (50% RH)	Weighing (50% RH)	
CSIC	Monagrega (E)	14, 15	40.50	−0.20	598	Rural	Mar 99–Jul 00	Hi vol sampler	Hi vol sampler	Weighing (50% RH)	Weighing (50% RH)	
IIT	Mte. Foia (P)	unpub- lished	37.32	−8.62	902	Rural	Jun 97–Jul 97			Weighing (60% RH)	Weighing (60% RH)	
IIT	Sagres (P)	16	36.98	−8.95	50	Rural	Jun 97–Jul 97	6-st. Berner impactor		Weighing (60% RH)	Weighing (60% RH)	6-st. Berner impactor
Univ. of Crete	Finokalia (GR)	17	35.32	25.67	150	Natural	Jul 00–Jan 01	11-st. Berner impactor	11-st. Berner impactor	Weighing (50% RH)		11-st. Berner impactor

MOUDI: micro orifice uniform deposit impactor; SDI: small deposit area low-pressure impactor; ELPI: electrical low-pressure impactor.

1—Virkkula et al., 1999; 2—Maenhaut et al., 2000; 3—Tørseth et al., 1999; 4—Maenhaut and Cafmeyer, 1998; 5—Maenhaut et al., 1996; 6—Maenhaut et al., 2002; 7—Schneider and Lorbeer, 2002; 8—Hüglin and Gehrig, 2000; 9—Sellegrì et al., 2003; 10—Putaud et al., 2002; 11—Decesari et al., 2001; 12—Matta et al., 2002; 13—Querol et al., 2001; 14—Rodríguez et al., 2002a; 15—Rodríguez et al., 2002b; 16—Neusüss et al., 2000; 17—Bardouki et al., 2003.

Table 4

Institute	Site	Category	Period	Sampling substrate	Min.	SO <sub>4</sub> <sup>2-</sup>	NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	Sea salt	OC	EC
Gent Univ.	Sevettijarvi (FIN)	Natural	Nov 93–Jan 96	Polycarbonate	PIXE & INAA	PIXE & IC	IC	IC	INAA		Light reflectance
Gent Univ.	Skreådalen (N)	Natural	Feb 91–Feb 96	Polycarbonate	PIXE & INAA	PIXE			INAA		Light reflectance
Gent Univ.	Birkenes (N)	Natural	Feb 91–Feb 96	Polycarbonate	PIXE & INAA	PIXE			INAA		Light reflectance
IFT	Melpitz 97-99 (D)	Near-city	Dec 96–Nov 97	Quartz (hi vol)	Estim. from nss-Ca <sup>2+</sup>						
				PTFE (low vol)							
IFT	Melpitz 99-01 (D)	Near-city	Dec 99–Nov 01	Quartz (hi vol)	Estim. from nss-Ca <sup>2+</sup>	IC	IC	IC	IC		
				PTFE (low vol)							
Gent Univ.	Waasmunster (B)	Near-city	Jul 94–Nov 95	Polycarbonate	PIXE & INAA	PIXE			INAA		Light reflectance
Gent Univ.	Gent (B)	Urban	May 93–July 94	Polycarbonate	PIXE & INAA	PIXE			INAA	Thermo-optical	Light reflectance
			Sep 99–Oct 99	Polycarbonate + Al	PIXE	PIXE			PIXE		Thermo-optical EGA
Umweltbundesamt	Illmitz (A)	Rural	Oct 99–Oct 00	Quartz (hi vol)	Estim. from nss-Ca <sup>2+</sup>						
Umweltbundesamt	Wien- Spittelauer Lände (A)	Kerbside	Oct 99–Oct 00	Quartz (hi vol)	Estim. from nss-Ca <sup>2+</sup>						
EMPA	Basel (CH)	Urban	Jan 98–Mar 99	Quartz	ICP-MS	IC	IC	IC	IC	EGA + coulometry	EGA + coulometry
EMPA	Zürich-Wiedikon (CH)	Kerbside	Jul 98–Feb 99	Quartz	ICP-MS	IC	IC	IC	IC	EGA + coulometry	EGA + coulometry
EMPA	Zürich (CH)	Urban	Jan 98–Mar 99	Quartz	ICP-MS	IC	IC	IC	IC	EGA + coulometry	EGA + coulometry
EMPA	Chaumont (CH)	Rural	Jan 98–Mar 99	Quartz	ICP-MS	IC	IC	IC	IC	EGA + coulometry	EGA + coulometry
EMPA	Bern (CH)	Kerbside	Jan 98–Mar 99	Quartz	ICP-MS	IC	IC	IC	IC	EGA + coulometry	EGA + coulometry
EMPA	Payerne (CH)	Rural	May 98–Oct 98	Quartz	ICP-MS	IC	IC	IC	IC	EGA + coulometry	EGA + coulometry
JRC	Ispra (I)	Near-city	Feb 00–Dec 00	Quartz		IC	IC	IC	IC	EGA + NDIR	EGA + NDIR
LaMP	Puy de Dome (F)	Rural	Feb 00–Mar 01	Teflon, quartz polycarbonate,		IC	IC	IC	IC		
JRC	Milano-Bresso (I)	Urban	May 98–Jun 98	Quartz + cellulose	Ashing	IC	IC	IC	IC	EGA + NDIR	EGA + NDIR
ISAC	Bologna (I)	Urban	Jan 00–Dec 00	Aluminium	Estim. from nss-Ca <sup>2+</sup>	IC	IC	IC	IC	EGA + NDIR	EGA + NDIR
JRC	Marseille-Vallon (F)	Dol Urban	Jun 01–Jul 01	Quartz + cell. + alu	ashing	IC	IC	IC	IC	EGA + NDIR	EGA + NDIR
CSIC	Barcelona (E)	Kerbside	Jun 99–Jun 00	Quartz	ICP-MS	IC	IC	IC	IC		
CSIC	Monagrega (E)	Rural	Mar 99–Jul 00	Quartz	ICP-MS	IC	IC	IC	IC		
IFT	Mt. Foia (P)	Rural	Jun 97–Jul 97	Tedlar + Alu		CZE	CZE	CZE	CZE		
IFT	Sagres (P)	Rural	Jun 97–Jul 97	Tedlar + Alu		CZE	CZE	CZE	CZE	EGA + NDIR	EGA + NDIR
Univ. of Crete	Finokalia (GR)	Natural	Jul 00–Jan 01	Polycarbonate		IC	IC	IC	IC		

PIXE: particle-induced X-ray emission; IC: IC; INAA: instrumental neutron activation analysis; EGA: evolved gas analysis; ICP-MS: inductively coupled plasma-mass spectroscopy; NDIR: non-dispersive infra red; CZE: capillary zone electrophoresis.

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