5 Anthropogenic Fine Aerosol Distribution over Europe with special emphasis on primary PM2.5 and Black Carbon

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Abstract

Primary particles are an important component of fine aerosol mass over Europe. We present a model simulation for the year 1995 in which we account for primary aerosols. For this purpose we have developed a new emission inventory for BC, based on the CEPMEIP emission inventory for PM. For Europe and the Former Soviet Union we estimated an annual emission of 0.47 Tg and 0.26 Tg, respectively. Transport (off and on-road) and households are the most important sources for BC in Europe.

Distributions of BC and additional primary material were calculated using the LOTOS model. Modelled BC concentrations range from 0.05 $\mu g/m^3$ and lower in remote regions to more than 0.5 $\mu g/m^3$ in central Europe. Peak levels above 1 $\mu g/m^3$ are calculated over large urban areas. The BC concentration is about 25% of the total primary aerosol concentration. The primary aerosol fields were combined with previously calculated secondary aerosol concentrations to obtain an estimate of the anthropogenic fine aerosol distribution. Modelled BC levels contribute only 4-10% to the total fine aerosol mass, where sulphate and nitrate contribute 25-50% and 5-35%, respectively. Comparison with experimental data revealed that the model underestimates PM2.5 levels, caused by the underprediction of BC and additional primary material by about a factor of 2. The underestimate could be explained by (a combination) of local emissions, measurement uncertainties, representation of wet deposition. In addition, the uncertainties associated with the emission inventory play a role.

The black carbon emission inventories have evolved over the years leading to much lower emission estimates. However, using the most recent inventories the observed BC concentrations are severely underestimated. Unaccounted sources contribute at most 15 % to the total BC emission. Emission factors, most notably those for traffic, were identified as the cause of the largest uncertainty in the emission estimates.

5.1   Introduction

Atmospheric particulate matter (PM) is a complex mixture of anthropogenic and natural airborne particles. Particulate matter in ambient air has been associated consistently with excess mortality and morbidity in human populations (e.g., Dockery et al., 1993; Pope et al., 1995; Brunekreef, 1997; Hoek et al., 2002). Inhalation is the only route of exposure that is of concern in relation to the effects of PM on human health. Therefore, the European air quality standards currently focus on all particles smaller than 10 μm (PM10), which covers the inhalable size fraction of PM. Mass and composition of PM10 tend to divide into two principal groups: coarse particles, mostly larger than 2.5 μm in aerodynamic diameter, and fine particles, mostly smaller than 2.5 μm in aerodynamic diameter (PM2.5). The fine particles contain secondary aerosols, combustion particles and condensed organic and metal vapours. The larger particles usually contain sea salt, earth crust materials and fugitive dust from roads and industries (WHO, 2000). Although adverse health effects are associated with elevated levels of both PM10 and PM2.5, these health effects were most strongly and consistently associated with particles derived from fossil fuel combustion (e.g. Hoek et al. 2002), which mostly occur in the PM2.5 size range. Another reason to study PM2.5 rather than PM10 is that long range transport of aerosols also depends strongly on aerosol size.

Moreover, various components of fine particulate matter (PM2.5) in the atmosphere also have climate-forcing impacts, either contributing to or offsetting the warming effects of greenhouse gases (Kiehl and Briegleb, 1993; Hansen and Sato, 2001, Menon et al. 2002). In particular, black carbon (BC) has recently been identified as an important contributor to radiative heating of the atmosphere (Haywood et al., 1997; Myhre et al., 1998; Jacobson, 2001; 2002). Organic carbon (OC), which is often emitted along with BC, may act to offset some of the global warming impact of BC emissions (Hansen and Sato, 2001). In case of biomass burning aerosol, OC is thought to completely offset the warming potential of BC (Penner et al., 1998; Grant et al., 1999). However, for fossil fuel derived emissions this is not the case and a net positive forcing remains (Penner et al., 1998; Cooke et al., 1999). Control of fossil fuel black carbon may be a cost effective way to reduce global warming emissions (Jacobson, 2002) in conjunction with abatement of GHG emissions. So measures to abate climate-forcing by reducing BC emissions often would have collateral benefits by reducing emissions of health-related pollutants.

The main sources for carbonaceous aerosols are incomplete combustion of fossil fuel and biomass, and the oxidation of biogenic volatile organic compounds (VOC) (Seinfeld and Pandis, 1998). Carbonaceous aerosol is predominantly present in the sub-micron size fraction (Echalar et al., 1998; Cooke, et al., 1999). The global emissions of black carbon and organic carbon from fossil fuel burning has been estimated at 6 to 8 Tg/yr and 10 to 30 Tg/yr, respectively (Penner et al., 1993; Cooke and Wilson, 1996; Liousse, et al., 1996; Cooke, et al., 1999; Scholes and Andreae, 2000). However, recent studies by Bond et al. (1998, 2002), in which a different technique for the determination of black carbon emissions was used, suggest significantly lower emissions. The differences indicate that there is still a large uncertainty associated with emission estimates of carbonaceous

aerosols.

Most of the studies on primary aerosols have been performed with global models. However, satellite retrieved aerosol optical depth (AOD), a measure for the aerosol burden, over Europe shows a large spatial variation and strong gradients around industrialized areas, indicating the influence on AOD of local emissions of primary aerosols and/or precursor gases (Robles Gonzalez et al., 2000). Therefore, we expect that a model with a higher horizontal resolution is more suitable to assess aerosol fields and especially those of primary particles than global models.

In this paper we present a regional model study of the composition of anthropogenic-induced PM2.5 in Europe with special emphasis on the mass concentration of primary particles and more specifically BC. For this purpose we use a recent emission inventory of anthropogenic primary particulate matter in Europe (TNO, 2001), which is based on the fuels used in different anthropogenic activities. As BC is formed by the incomplete combustion from e.g. diesel engines, cooking fires and coal burning, a BC emission inventory can be derived from the PM inventory based on the fractions of BC in the respective (ultra) fine PM emissions (e.g. Cooke et al., 1999, Streets et al., 2001). The burdens of primary emitted particles over Europe are calculated with the LOTOS model (Builtjes, 1992; Schaap et al., 2003a). By combining these results with earlier calculations for the secondary aerosol components sulphate, nitrate and ammonium (Schaap et al., 2003a), estimates of PM2.5 levels over Europe are obtained. The consistency of the model calculations is checked with the observations at a number of European locations.

5.2   Emission data

Black Carbon (BC) is mostly released from incomplete combustion of carbonaceous fuels. We made an estimate of BC sources and their distributions over the Europe using the results of CEPMEIP (TNO, 2001), which is a spatially distributed pan-European inventory of anthropogenic PM emissions for the year 1995. Currently CEPMEIP covers nearly all of the relevant sources of primary anthropogenic TSP, PM10, PM4, PM2.5 and PM0.95 emissions, however, without chemical speciation. To derive an European BC emission inventory from CEPMEIP, the fraction of BC in PM2.5 for each of the source categories has to be attributed.

Streets et al. (2001) describe such an effort for China. These authors present a review study for BC emission factors from anthropogenic sources, in which also earlier work by Penner et al. (1993), Cooke and Wilson (1996) en Cooke et al. (1999) is discussed. We use the BC fractions from Streets et al. (2001) to estimate the BC emission from the sub-micron particle emissions in CEPMEIP. The BC fractions of the sub micron particles for different fuels, listed in Table 5.1, are almost exclusively based on western technology. Combining these data on SNAP level 2 results in a BC fraction of the PM2.5 emission. In this study, we followed the procedure for each country separately. The European BC emissions and averaged BC fractions of PM2.5 are given per major source category (SNAP level 1) in Table 5.2. The European total emission, excluding the Former Soviet Union (FSU), is 473 Gg/yr, excluding sea ships. The largest contributions are from transport followed by wood burning in house holds. Other important sources are industrial

Table 5.1 Black carbon fractions of PM0.95 emissions by fuel type used

SNAP[a]	Description	Solid fuels	Light liquid fuels	Medium/ heavy liquid fuels	Gaseous fuels	Waste/ biomass
1	Energy transformation	0.005	0.32	0.52	0.9	0.25
2	Small combustion sources	0.5	0.32	0.55	0.9	0.25
3	Industrial combustion	0.1	0.32		0.9	0.25
5	Extraction of fossil fuels				0.9	
7	Road transport	0.1	0.32	0.55	0.9	
8	Non road transport	0.1	0.32	0.55	0.9	
9	Waste handling and disposal					0.005
10	Agriculture					0.25

[a] *Selected Nomenclature Air Pollution*

combustion, energy transformation (especially with liquid fuels), gas flaring at oil platforms, agricultural waste burning and emissions from sea ships in international waters. The particle emissions have been gridded to the LOTOS grid. Area and point sources have been distinguished. For area sources, which the spatial patterns follow population density (majority of area sources), we used the CIESIN-NOAA high resolution gridded population data (NGCIA, 2000). Agricultural emissions are distributed according to animal populations by NUTS 3 regions (Eurostat,1998) and the distribution of arable land and pastures. International shipping emissions were distributed using the EMEP SO_2 ship emissions (EMEP, 2003). Large point sources (LPS) are distributed according to their exact location and characteristics (fuel types, capacities etc.). Point sources include large combustion plants, large industrial processes (steel, non-ferrous, cement etc.), waste combustors, refineries and off shore oil production platforms. Point source data has been updated to the reference year 1995 by means of a questionnaire. About 70% of all countries responded and for the remaining countries various literature sources have been used to update point source lists. The gridded emissions as input for the LOTOS model are shown in Figure 5.1.

The temporal variation of the emissions is broken down for each source category using a monthly factor. This value is divided by a factor for the day of the week (i.e. Monday, Tuesday etc.) and finally by a factor for the hour of the day (local time). The procedure was developed for ozone precursor emissions and is described by Builtjes et al. (2003).

Table 5.2 Particulate matter smaller than 2.5 μm from the CEPMEIP database, the source specific black carbon fractions and estimated black carbon emissions for anthropogenic activities in Europe excluding the former USSR.

SNAP[a]	Description	PM2.5 (Ktonnes)	Black Carbon emission (Ktonnes)	Derived Fraction Black Carbon of PM2.5[b]
1	Energy transformation	256	28	0.11
2	Small combustion sources	460	96	0.21
3	Industrial combustion	258	64	0.25
4	Industrial process emissions	197	0	0.00
5	Extraction of fossil fuels	36	30	0.85
6	Solvent and product use	81	0	0.00
7	Road transport	332	158	0.48
	• Gasoline	44	14	0.32
	• Diesel	262	144	0.55
	• Volatilisation losses	27	0	0.00
8	Non road transport	160	83	0.52
9	Waste handling and disposal	25	0.1	0.004
10	Agriculture	83	15	0.17
11	Nature[c]	n.e.	n.e.	n.e.
	Total	1889	473	
	International Shipping[d]		23	0.12

[a] *Selected Nomenclature Air Pollution* [b] *These fractions are the net result of a mix of activities and fuels within each category. The original calculations are based on the fractions presented in Table 5.1* [c] *n.e. = not estimated. The CEPMEIP database only considers anthropogenic sources* [d] *International sea going ships are not included in the inventory*

5.3   Model description

A chemistry transport model was applied to calculate the distribution of fine primary aerosol over Europe. For this purpose the LOTOS model (LOng Term Ozone Simulation) has been used. LOTOS has been applied for oxidant modelling (Builtjes, 1992; Hass et al., 1997) and for the calculation of secondary aerosol fields over Europe (Schaap et al., 2003a; Robles-Gonzalez et al., 2003). The geographical domain of LOTOS ranges from 10°W to 40°E and from 35°N to 70°N with a spatial resolution of 0.5x0.25 degrees lon-lat. The vertical domain is divided in three layers and extends to 3.5 km. The lowest layer represents the variable mixing layer on top of which two layers with equal, but variable, depth are located. Hence, due to the continuously changing mixing height, the grid volumes vary in space and time. The mixing height is part of the meteorological input for 1995, which is diagnostic and derived from ECMWF using procedures developed by the Free University of Berlin (Kerschbaumer and Reimer, 2003). Every hour, the mixing layer height is updated and the mass in the three layers is redistributed by mass conserving linear interpolation. The vertical coverage of the model is considered sufficient, since it has been shown that 80 to 90 % of the aerosol burden is located below 3 Km (Banic et al., 1996; ten Brink et al., 2001).

We assumed all BC and additional primary material (APPM) to be hydrophyllic direct after emission, thus wet and dry deposition are represented as for the highly soluble sulphate. All boundary conditions for BC were assumed to be zero. At the eastern boundary, however, the assumed boundary conditions and, hence, the model results are highly uncertain and we choose to present results only west of 30°E. For a full description of the model including the secondary inorganic aerosol formation we refer to Schaap et al. (2003a).

In this study we used LOTOS to calculate the distribution of primary emitted particles for the base year of 1995. The calculated distributions can be combined with previously calculated distributions of the inorganic species (Schaap et al., 2003a) to obtain an estimate for the total PM2.5 concentration field due to anthropogenic sources.

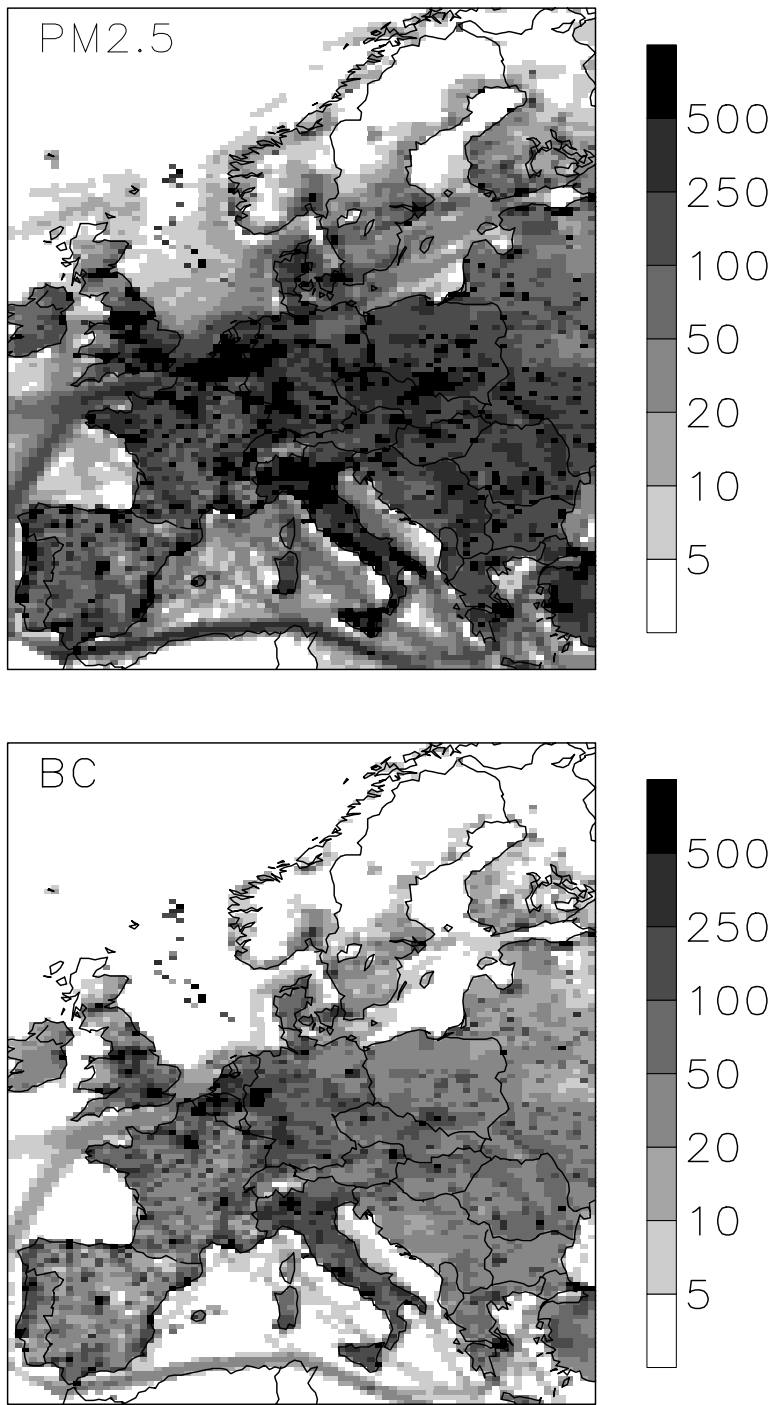*Figure 5.1 Emissions (Tonnes/yr) of PM$_{2.5}$ and black carbon for 1995*

5.4   Results and preliminary discussion

5.4.1   Primary aerosol distribution

In Figure 5.2 the simulated annual averaged distribution of the total primary material and its black carbon content are presented for 1995. Annual averaged concentrations of primary material range up to 5 µg/m³ over Europe. Areas with the highest concentrations are found in industrialised and/or densely populated regions, e.g. north western Europe, the Po valley and southern Poland. Secondary maxima can be identified over a number of large cities, such as London, Manchester, Athens, Madrid and Oslo. The local peaks over the North Sea can be explained by the emissions from oil platforms. Over more rural regions, which cover most of continental Europe, the levels of primary components are between 1 µg/m³ and 2.5 µg/m³. In Scandinavia concentrations trail off from about 1 µg/m³ in the south to less then 0.25 µg/m3 over mid and northern Scandinavia. Important ship routes are mainly located near the European continent and, hence, the concentrations of primary particles trail of from the edges of the continent to the open sea due to dry and wet deposition.

The black carbon content of the primary aerosol shows a very similar distribution as the total primary components because the source categories with the highest PM emissions also have the highest BC fractions. In western Europe the black carbon levels are about one fifth of the total primary aerosol. Over eastern Europe the BC content is calculated to be slightly less. Modelled concentrations are lower than 50 ng/m³ over remote regions such as the northern Scandinavia. In relatively clean areas over Spain and southern Scandinavia BC are about 250 ng/m³ whereas the calculated BC concentrations exceed 500 ng/m³ over central Europe and 1000 ng/m³ in the densely populated areas.

5.4.2   Comparison with measured data

For 1995 monitoring data on BC (or EC) are not available. Therefore, we have compared our calculated BC concentrations with a number of studies as shown in Figure 5.3 and in Table 5.6. The data represent a period ranging from the end of the 1980s to 2001 and are often obtained in campaigns. The comparison shows that the simulated BC concentrations underestimated those measured by about a factor of 2. The relative underestimation is found to be rather constant for remote to rural sites (see Figure 5.3). This is an indication that the distribution of the concentrations and the main sources are well represented in the model, however, the absolute concentration is not. For urban sites the underestimation is larger, which can be explained by the high influence of local emissions.

Since we do not know the chemical speciation of the non-BC emissions (APPM) direct comparison with measurements is not possible. However, using the total PM2.5 concentrations and those of OC conclusions can be drawn on this part of PM, see below.

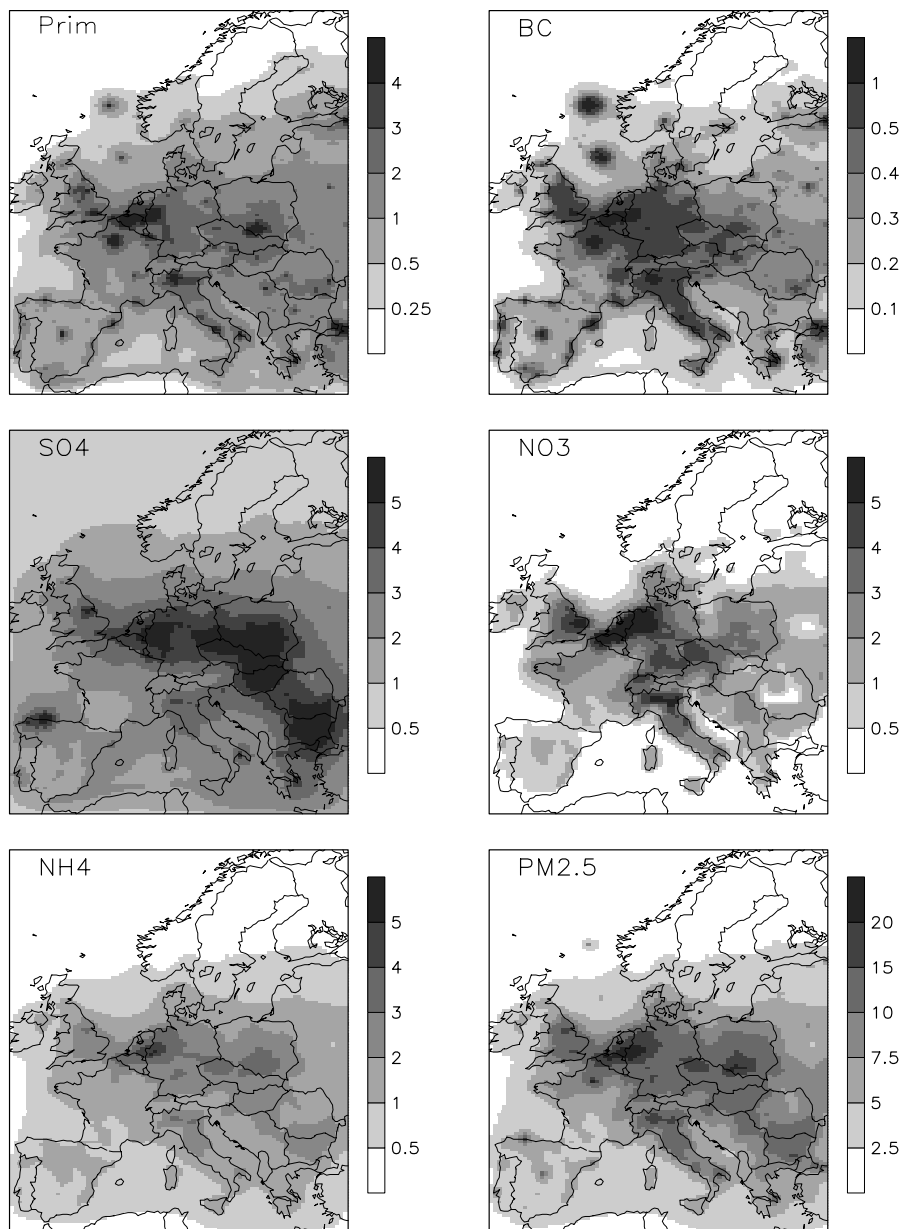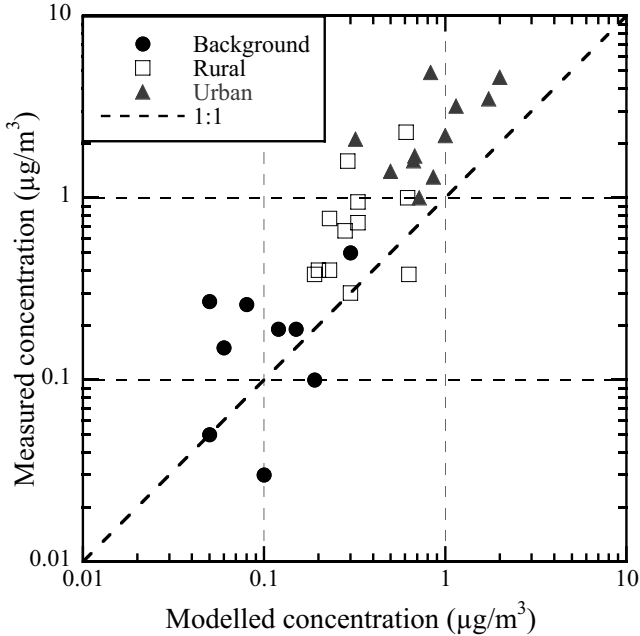*Figure 5.2 Annual average distribution of the indicated aerosol components (µg/m3)*

Figure 5.3 Comparison between modelled and measured BC concentrations at background, rural and urban locations

5.5   Fine aerosol distribution

5.5.1   PM2.5 distribution

To investigate the PM2.5 distribution over Europe we added to the primary particle simulations the fields of the inorganic components from Schaap et al. (2003a), shown in Figure 5.2 c, d and e. Sulphate contributes more than 3 $\mu g/m^3$ to PM2.5 over a region that spans from England, over north western Europe to south eastern Europe. Similar contributions are found in the Po valley and the north west of Spain. Maximum contributions are calculated in the Ruhr area, southern Poland, Hungary and Rumania and are markedly different from those of the primary aerosols. North of 57 N the annual averaged sulphate concentrations are lower than 2 $\mu g/m^3$, whereas those in more remote continental areas are between 2 and 3 $\mu g/m^3$.

High concentrations of nitrate are confined to continental areas, with maxima in north western Europe, the UK and the Po valley. Annual averaged nitrate concentrations are as high as those of sulphate in western Europe, whereas those of sulphate are higher in (south) eastern Europe and Scandinavia. In contrast to sulphate nitrate levels show a distinct seasonal variation. Maximum concentrations occur in winter, when ammonium nitrate is stabile. However, ammonium nitrate formation is limited during summer over the largest part of Europe due to high ambient temperatures. Sulphate and nitrate are neutralised by ammonium. Therefore, ammonium concentrations are significant and only

somewhat lower than those of its associated ions alone.

The sum of all modelled anthropogenic components of PM2.5 is shown in figure 5.2f. Highest concentrations of PM2.5 are found in the most industrialised and populated areas of Europe. Concentrations exceed 20 µg/m^3 over the south of the Netherlands, Belgium, the Ruhr area and southern Poland. Secondary maxima can be found in the Po valley, the Czech Republic and metropolitans of London, Manchester and Paris. Over central and south eastern Europe concentrations are calculated to range between 10 and 15 µg/m3. Towards the north the anthropogenic induced concentration of PM2.5 trails of from about 4 in southern Scandinavia to less than 2.5 µg/m^3 further north. Also, the rural areas in Spain and southern France are relatively clean with respect to anthropogenic PM2.5. As mentioned before, our simulation does not consider mineral dust, which is known to contribute strongly to PM in Spain (Rodriguez et al., 2002). Further, a number of cities can be recognised, e.g. Madrid, Barcelona and Athens.

5.5.2   Composition of PM$_{2.5}$

In figure 5.4 the relative contribution of the main components to the total fine aerosol mass is shown. Primary emitted particles (including BC) contribute 15 to 20 % of the total fine aerosol mass over continental Europe. This fraction is rather constant. Higher contributions (>30 %) are found in densely populated regions. For BC the contribution to PM2.5 ranges between 3 % and more than 10 %. Similar to the total primary contribution highest values occur over the most densely populated regions in Europe. The high values of BC over the North Sea are due to the presence of oil platforms there. The low relative contribution of BC over eastern Europe is striking; less than 4 %. The region where this applies coincides with the band of high sulphate concentrations. This minimum is only slightly visible in the contribution of total primary material and illustrates that the BC emissions are largely due to diffuse sources as traffic and off-road transport (e.g. river ships, trains) whereas the sulphur and, to a lesser extent, non-BC emissions have a large stationary point source component.

Sulphate contributes the largest calculated mass fraction to PM2.5 over Europe. Its contribution is about 30-35 % over most of continental Europe. The mass fraction increases towards more remote locations and is slightly lower in those areas where primary material and nitrate are important. The percentage of nitrate in PM2.5 over continental Europe is modelled to be 20 to 30 %. Contributions over 30 % are found in the regions with high ammonia emissions such as north western Europe and the Po valley. The nitrate contribution trails off from the coast towards the open sea, since in our model ammonia is rapidly deposited (Schaap et al., 2003a). In reality, the reaction of nitric acid with sea salt plays an important role by transferring nitrate from the fine to the coarse aerosol fraction (Vignati et al., 1999). Ammonium, which neutralises both sulphate and nitrate, contributes about 15 to 25 % to the fine aerosol mass; maxima in ammonium coincide with those of nitrate.
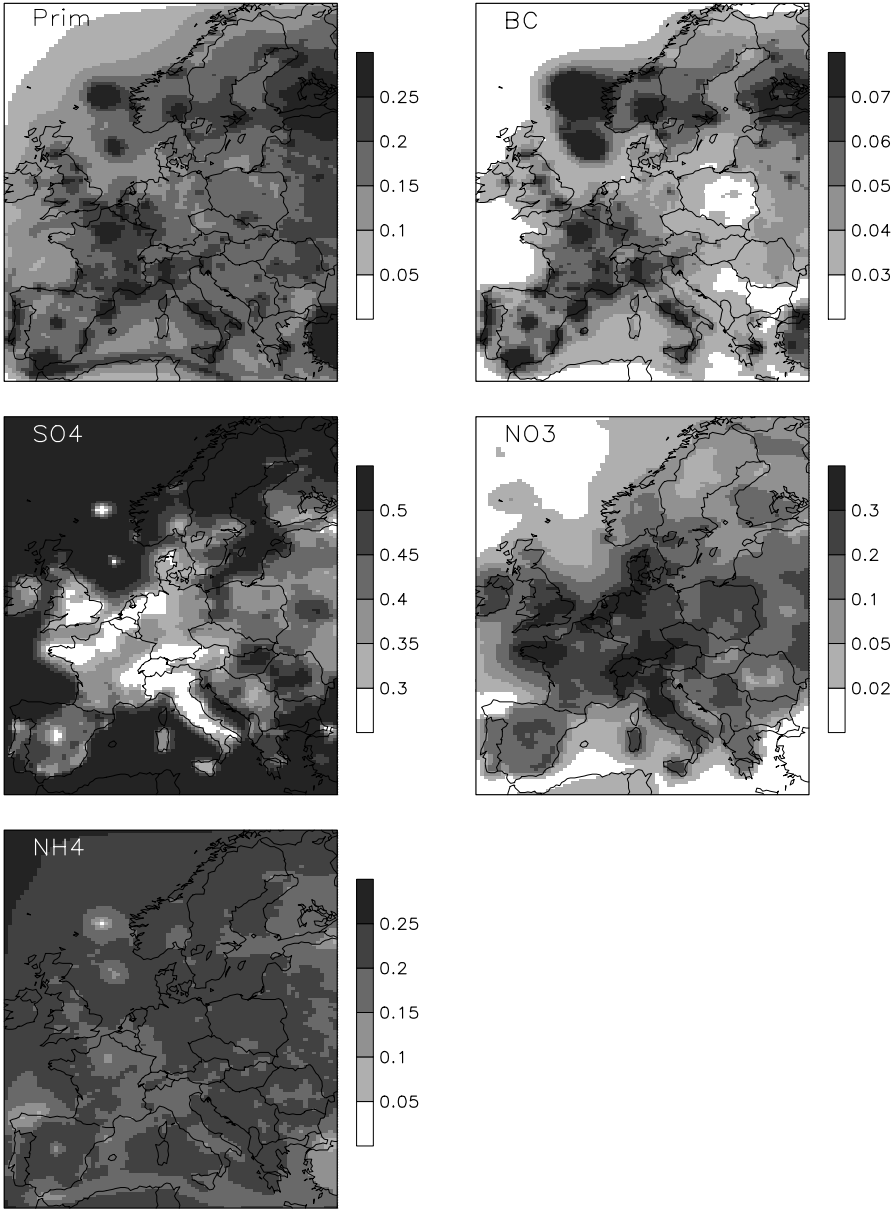
Figure 5.4 The relative contribution of different species to the modelled fine aerosol mass

5.5.3   *Comparison with measured data*

Before we compare our calculations to measured data we shortly discuss the uncertainties inherent to the sampling of PM and its composition. PM is mostly sampled using filters (Teflon, quartz, cellulose) or impactors. Several mechanisms may cause artefacts during sampling. Volatile compounds such as ammonium nitrate and a number of organic species may evaporate from inert filters (Chow, 1995). On the other hand, nitric acid or organic vapours may be adsorbed to the filter or previously collected material (Spicer and Schumacher, 1977; ten Brink et al., 2003). In case of nitrate artefacts are probably not significant during winter (Schaap et al., 2002; 2003b). However, evaporation from inert filters is thought to be significant at temperatures above 20 degrees Celsius (Hering and Cass, 1999; Schaap et al., 2003b). Such losses have not been observed for impactors (Hering and Cass, 1999). A field comparison for total carbon (the sum of OC and EC) at Melpitz showed differences between filter samplers of up to 20 % for a 10 day average (ten Brink et al., 2003). A similar range was found for the impactors although they recovered only 75 % of the TC measured on the filter samplers. The TC data agreed reasonably, however, its OC and EC content is difficult to determine. EC and BC are ideally both elemental carbon but are named according to their detection technique, thermal and optical respectively. Measured EC and BC concentrations showed differences up to a factor of three. As a consequence of these possible artefacts the determination of PM mass is associated with a rather large uncertainty.

In the analysis of the composition data part of the PM mass is unaccounted for. Putaud et al. (2003) suspect a large fraction of this gap to be water. This hypothesis is substantiated by data from Helsinki, where 5% of the ambient PM2.5 mass was found to be water (Pakkanen et al., 1999). Another part of the unaccounted mass may be due to the uncertainty in the conversion factor for the non-carbon atoms in organic carbon (Putaud et al., 2003).

Numerous studies have described measurements of aerosol composition in Europe. Very recently, a number of studies has been compiled by Putaud et al. (2003). The compilation contains data for sites at which the total particulate mass was available in combination with its chemical composition, including carbonaceous aerosols. In addition, we have compared our inorganic aerosol simulations to EMEP data (EMEP, 1997) and data compiled by Schaap et al. (2002) (Schaap et al., 2003a). We briefly summarize the main findings below. Since the EMEP data do not comprise carbonaceous aerosol and PM2.5 data, but contains a larger number of sites, the data sets should be used complementary.

The comparison of the modelled annual mean data against the compilation by Putaud et al. (2003) is shown in Table 5.6. Because sea salt and dust are not included in the model, this table also contains the measured PM2.5 concentration (PMcorr) corrected for their contributions. The model shows an increasing underestimation (listed as not modelled (NM)) with increasing PM levels. Hence, underestimation is largest at the kerbside stations. The chemical data allow us to address this increasing gap in more detail.

The secondary components compare rather well with observed data by Putaud et al. (2003). Comparison is best for sulphate showing a slight underestimation of the averaged sulphate levels by 12 %. Comparison with measured data from EMEP also revealed that the annual average modelled sulphate concentrations were slightly underestimated (6%). The correlation on a daily basis was on average reasonable (r = 0.58).

For nitrate the picture is more complicated. Except for Barcelona the modelled values are within a factor of 2 of the measured data (Putaud et al., 2003). The model overestimates the annual average concentrations at the Swiss sites (Zurich and Basel). However, independent data show annual average concentrations of 4.7 μg/m^3 for two sites in the Swiss valleys (Schaap et al., 2002). The difference may be explained by losses during sampling since inert filters were used in Zurich and Basel. The large underestimation in Barcelona, however, can not be explained by sampling artefacts. A plausible explanation is the formation of sodium or dust nitrate, which are the main nitrate compounds in this region in summer (Rodriguez et al., 2002). Comparison of the modelled nitrate concentrations to EMEP data showed that the modelled concentrations are on average 10 % too high. At single stations deviations of a factor of 2 were observed. Largest overestimation was found in the south of the Netherlands, where ammonia emissions are highest. For a detailed discussion on the comparison with measured data for nitrate, sulphate and ammonium we refer to Schaap et al. (2003a; Chapter 4).

The compilation by Putaud et al. (2003) also contains data on EC (=BC). The calculated BC concentrations are lower than those measured. Best agreement is found for the Belgian site Waasmunster, where the calculated value is within 10 % of the measured one. However, at the rural and near city stations the underestimation lies mostly about a factor of 2-3, consistent with the data presented in section 5.2. Underestimation is highest at the kerbside stations of Vienna and Bern, a factor of 9.

To address the non-BC emissions or additional primary PM (APPM) we compare the modelled APPM levels to those measured of OC. Biogenic secondary organic aerosols (BSOA, neglected in this study) cause the measured OC levels to be an upper estimate for primary OC. However, in polluted areas such as continental Europe the contribution of BSOA is probably negligible, as is anthropogenic SOA (Schell et al., 2001). In addition, although a majority of APPM is organic carbon it is not fully OC. Therefore we assume APPM to be an upper estimate for OC. The OC concentrations measured at the sites (Putaud et al., 2003) are underestimated in much the same way as BC. Hence, the same applies to the total primary particulate concentration as compared to the measured total carbon content.

The measured ratio of OC to BC ranges from 0.95 to 4.0. Surprisingly, at the three urban sites the ratio is very similar, 2.7 or 2.8. However, due to the large uncertainty in the BC levels this ratio is highly uncertain. Assuming APPM to be OC, the OC to BC emission ratio for the European countries as a whole is on average 3. This ratio for transport emissions is about 1, which indicates that in areas with large traffic emissions, e.g. cities, the ratio could be significantly lower than 3. Moreover, based on the emission estimates ratios down to 1 could be expected at sites where traffic emissions are dominant. Disregarding Barcelona, such a tendency is observed in the observations. Modelled and

measured ratios are between 2.5 and 2.8 at the urban sites. As expected for a regional model, at the kerbside stations similar ratios are simulated as for the urban background sites. In reality, APPM is not fully OC. However, we feel that the uncertainty present in the measured OC to BC ratios is much larger than that induced by the APPM=OC assumption.

Not all components of PM2.5 were determined for all sites. For instance for the Belgian sites, Waasmunster and Ghent, the nitrate, ammonium and OC contents of PM2.5 were not measured. The unaccounted fraction is therefore large at these stations. The modelled concentrations of these unaccounted species can largely fill the gap. For Ghent, the sum of the modelled fraction even exceeds the unaccounted fraction, which can be explained by an overestimation of the nitrate levels in this region (Schaap et al., 2003a). Modelling may provide a tool to assess the aerosol composition in regions without (complete) measurements as shown for this case.

5.6   Discussion

The comparison between modelled and measured BC concentrations strongly suggests that the model underestimates BC concentrations. Since the inorganic ions are simulated reasonably well (see also Schaap et al. (2003a) and discussion therein), it could be deduced that the underestimation of PM2.5 levels is mainly caused by primary carbonaceous particles. Therefore, the discussion here focuses on the gap between modelled and measured concentrations of primary carbonaceous components.

5.6.1   Comparison of modelled and measured concentrations

The BC data compiled in this study cover a large time span (1980s – 2001). Data from campaigns of only a few months may be influenced by the specific meteorological conditions prevailing during the campaign. In addition, inter annual variability and an expected decreasing trend in BC emissions (see below) may introduce variability and uncertainty in the model to measurement comparison. In addition, recent intercomparison tests show that BC measurements with different techniques are associated with an uncertainty of about a factor of 3 (ten Brink et al., 2003). However, the model results show often an underestimation of a factor of two or more for both older and more recent data than 1995, obtained with different techniques. EC/BC data may be systematically too high, e.g. due the charring (Schmid et al., 2001). However, total carbon concentrations, which are to be measured with a much higher accuracy (ten Brink et al., 2003), are also underestimated in much the same way. Since the measured and modelled BC to TC ratios are very similar, we conclude that the observation that the modelled BC values are too low appears to be robust and not obscured by the measurement uncertainties.

The modelled concentrations represent grid box average concentrations. The tendency for increasing deviation between the modelled and measured data going from rural to urban sites can be explained by the influence of local sources. It is therefore difficult to draw strong conclusions about the performance of the model, which predicts background concentrations, based on the measurements of PM2.5 and primary components (BC) in an

Table 5.3 Overview of black carbon emissions estimates for Europe and the former USSR

Year	Black Carbon (Tg yr^{-1})		Aerosol	Remark	Author
	Europe	Former USSR			
1980	3.80	5.60	Bulk	Based on BC/SO$_2$ ratio's	Penner et al. 1993
1980	2.14	1.93	Bulk	Based on emission factors and fuel use	Penner et al. 1993
1984	2.65	1.55	Bulk		Cooke and Wilson, 1996
1984	1.74	1.07	Bulk	Fossil fuel BC emission only	Cooke et al., 1999
1984	1.26	0.69	sub-micron	Fossil fuel BC emission only	Cooke et al., 1999
1996	0.44 (0.33-1.20)	0.36 (0.22-1.24)	sub-micron		Bond, 2002
1995	0.47 (0.23-0.70)	0.26 (0.12-0.40)	sub-micron	Only anthropogenic sources	This work

urban environment. Unfortunately, PM2.5 and BC measurements are mostly done in the urban environment. However, the modelled BC concentrations for the available background sites and rural sites are also associated with a systematic underestimation of a factor of 2. The influence of local emissions is assumed to be small in these locations suggesting that the representativity of the stations also does not explain our finding that the modelled values are too low.

Uncertainties in the removal of BC may also affect our results. We assume BC to be hydrophyllic at the same time scale as our emissions are mixed in the model grid, e.g. up to a few hours. The ageing time scale is under scientific debate and ranges from hours (Kohler et al., 2001; Riemer et al., 2003) to 1.5 day (Cooke and Wilson, 1996, Wilson et al., 2001). Although in our model wet deposition is not very effective (Schaap et al., 2003a) and a longer ageing time scale will probably not yield significant different results, a more detailed study using explicit aerosol dynamics seems necessary to assess this ageing time scale under ambient conditions prevailing in Europe.

5.6.2   Emission data

Comparison with previous emission inventories

The black carbon emission data used here (Table 5.2) will be compared with emission estimates presented in previous studies (Table 5.3). The year for which the emissions have been estimated is an important variable in such a comparison because PM2.5 and associated black carbon emission are expected to change considerably over time due to

Table 5.4 European BC emission (Ktonnes) based on a re-evaluation of the data from Cooke et a1(1999) for 1984 and an extension of the activity data to the year 1995.

Year	1984	1995	This study
C sector = combined traffic	299	401	241
D sector = domestic	637	295	96
I sector = industrial	510	347	137
Total	1446	1043	474

economical and technological changes. Furthermore, it is important to consider the aerosol size - bulk versus sub-micron aerosol -, which is covered by each emission inventory. This can be illustrated with the data from Cooke et al. (1999) for 1984 that indicate that about 70% of the bulk aerosol black carbon is in the sub-micron range. The contribution of the sub-micron range to the bulk aerosol has probably increased over time in Europe due to a further increase in air pollution control measures, which tend to capture coarse particles more efficiently.

The emission estimates in Table 5.3 suggest a strong decline of black carbon emissions between 1980 and 1995 for both Europe and the former Soviet Union (FSU). Emission estimates for Europe range from 2.1-3.8 Tg in 1980 (Penner et al., 1993) to 0.47 Tg in 1995 (This study). This decline is partly real due to technological improvements, air quality control measures and economical and political changes, most notably those in Eastern Europe and the USSR after 1989. For example, there is a strong trend in the FSU to the use of natural gas for power generation, which has reduced emissions, particularly in European Russia (Hill, 1997). However, the decrease of emissions over time has not been as dramatic as suggested in Table 5.3. The lower emission estimates are also caused by a more accurate assessment of the PM emitting activities in relation to their technological level, the resulting PM emissions and their fractional black carbon content. In the past such improvements resulted in revisions of inventories. For 1984 Cooke et al. (1999) revised the inventory of Cooke and Wilson (1996) resulting in a 30 % lower emission estimate.

Recently, Bond et al. (2002) presented a new bottom up BC emission inventory using the latest available emission factors. Their European emission estimate is very similar to our estimate. The range reported here is narrower than reported by Bond (2002) most likely because 1) the CEPMEIP database provides a relatively good insight in the technological level , which has a large impact on the resulting emissions, of different countries and facilities within a country and 2) Bond (2002) uses a different procedure for quantifying the uncertainty range (adding up the standard deviations for each source instead of the variances). The uncertainty range in our estimates of total BC emissions from Europe and FSU has been estimated from two components: the uncertainty in sub-micron particle emissions which has been assessed at ± 20% (Visschedijk, 2002) and the uncertainties in the BC fractions for the different fuel categories as reported in Table 5.1.

The more recent estimates (Bond et al. (2002) and this study) compare very well, but are more than a factor of 2 lower than the previous estimates. These estimates are not

necessarily in contradiction with each other since the uncertainty of the previously reported data is at least a factor of 2 (e.g., Liousse et al., 1996, Cooke et al., 1999). However, our model results and those obtained with the Bond et al. (2002) inventory both underpredict the observed BC concentrations (see also Table 5.7) whereas the results from studies using the older emission estimates as model input agreed better with observations (Cooke et al., 1999; Jacobson, 2001; Chung and Seinfeld, 2003). Are the older inventories better than the present ones and if not, why do these older emission estimates than result in more realistic simulation results?

The current emission inventories (this study and Bond (2002)) are bottom-up inventories using the relatively good insight in PM2.5 emissions to derive BC emissions. The BC emissions can be derived using the available data on the BC fraction of combustion-derived PM because we have knowledge on fuel types used in different sectors and activities. It is important to realize that this is the proper way to derive the BC emissions because the fuel type and the way it is consumed are causal factors in the process of BC production and subsequent emission. Hence, we are confident that the approach taken in the current emission inventories is an improvement. Then, why do older inventories produce a better match with observational data? A part of the discrepancy may be explained by the year of study. We revisited the data of Cooke et al. (1999) for 1984 and extended the emission inventory to 1995 by using activity data for 1995 in combination with the original emission factors by Cooke et al. (Table 5.4). The revisited emission inventory for 1984 (1.44 Tg yr^{-1}) is somewhat higher than the original figure (1.26 Tg yr^{-1}) by Cooke et al. (1999). These differences can be attributed to corrections of small errors and improvements of the activity data. More important, by changing the activity data only the estimated BC emission decreases about 30% in ~10 years. The emissions from domestic sources and industrial sources decrease significantly but this is partly compensated by the increase of especially the transport and traffic sections (Table 5.4). Since, the emission changes between 1984 and 1995 are due to changing activities only, the improved knowledge on emission factors is crucial to explain the difference between the extrapolated (1.04 Tg) and our estimate (0.47 Tg), which is still a factor of two.

Traffic emissions

Bond et al. (2002) suggested two major reasons for underprediction of BC emissions: fuel use and emission factors. Underreporting of fuel use may occur when a portion of the fuel supply (e.g. wood or coal) does not pass through official channels, or when some "fuels" are not considered at all (e.g. house fires, waste paper). Emission factors may be underestimated if measurements come from better technology or more careful practice than the average. Increased emission factors might be associated with transient operation, poor-quality or adulterated fuels, or badly maintained units. These factors are of particular interest for the traffic emissions. It should be realised that the emission factors for traffic used in earlier studies (Kohler et al., 2001; Cooke et al., 1999) are very crude. In fact, two emission factors are used: 2 en 10 gC / kg for diesel for OECD and non OECD countries respectively. In reality a range of emission factors are present without sharp differences related to technology, age of the motors used as well as maintenance. Such a crude

separation causes large uncertainties in the emissions from traffic on a regional perspective.

There are presently various sets of PM emission factors for mobile sources e.g., for the Netherlands (VROM, 2002), Germany (INFRAS, 1999) or Europe (Ntziachristos and Samaras, 1999). The proposed emission factors are influenced by e.g. sampling strategies, definitions of standard driving cycles, assumed effect of motor aging and may differ substantially for some source categories such as diesel-fuelled vehicles. In the CEPMEIP inventory (TNO, 2001) emission factors for diesel-fuelled vehicles were taken from the German inventory (INFRAS, 1999), whereas the Dutch emission factors (VROM, 2002) were taken for all other vehicles. The results were found to be in line with the COPERT estimates for country totals (Ntziachristos and Samaras, 1999) and IIASA model results (T. Pulles, 2003, personal communication). The selected emission factors are not necessarily the most representative. By applying the different emission factors the uncertainty surrounding the estimate for total traffic-related PM emissions was found to amount to a factor of ~2. Furthermore, the contribution of gasoline vehicles to daily PM levels may be substantial especially due to cold starts (Watson et al., 1998), suggesting that PM emissions due to gasoline vehicles may be underestimated. In general, it can be concluded that the emission factor methodologies need to be harmonized and further validated to come to an accurate and consistent European set of emission factors for traffic, which is however outside the scope of the present paper.

Unaccounted sources

A possible underestimation of the traffic BC emissions is caused by the PM2.5 particle emissions and not their BC fraction. Although traffic is a major source of primary particles, there are more uncertainties in the PM2.5 emissions. In Table 5.5 we present emission estimates for the US (Battye et al., 2002) from sources that are not present in the CEPMEIP database. The most important source missing in CEPMEIP is fugitive dust accounting 43 % of the total emissions in the US. Although these emissions are difficult to extrapolate to Europe due to different road and climatic conditions, it indicates that the European PM2.5 emission may be underestimated significantly, especially in southern Europe where climatic conditions compare best with the US. The most important missing industrial source is metal processing which contributes only 2 % of the total fine particle emissions in the US. For BC, these missing sources contribute only 7-11 % of the total US emission and are, therefore, not likely to explain a large underestimation of the European BC emissions.

In addition, the emissions from (controlled) vegetation fires are unaccounted for. Prescribed and/or intentional burning of grasslands and forest does not or hardly occur in Europe and is not considered in our black carbon emission inventory. Burning of agricultural residue has been considered although its importance has rapidly decreased in recent years due to policies to ban residue burning. On the other hand, accidental or lightning-ignited fires may cause an underestimation of the BC emissions in Europe. In the US these emissions are thought to be about 8 % of the total emission (Battey et al., 2002). Lavoue et al. (2000) estimated the European emissions from wildfires to be 0.01 Tg in

Table 5.5 Relative contribution of sources not included in Table 5.2 to reported US $PM_{2.5}$ emissions, BC to $PM_{2.5}$ ratio for these sources and derived relative contribution to total estimated US Black carbon emissions (recalculated from Battye et al., 2002).

Category	Percentage of reported US $PM_{2.5}$ emissions[a]	BC to $PM_{2.5}$ ratio		Percentage of total estimated BC emissions	
		Best estimate	High estimate	Best estimate[b]	High estimate[b]
Industrial - metals processing	1.6%	0.1	0.3	2.1%	3.9%
Industrial - asphalt manufacture	0.1%			0.0%	0.6%
Rubber and plastics products	0.0%			0.0%	0.3%
Fugitive dust - unpaved roads	21.8%	0.01	0.019	2.8%	3.3%
Fugitive dust - paved roads	10.5%	0.017	0.028	2.5%	2.3%
Fugitive dust - construction	6.0%		0.005	0.0%	0.3%
Fugitive dust - other	2.3%	0.006	0.013	0.2%	0.3%
Total relative contribution of the above sources to reported US emissions	42.3%			7.6%	10.9%
Wildfires	3.6%	0.072	0.12	3.5%	3.4%
Prescribed forest burning	8.1%	0.072	0.12	7.9%	7.7%

a) Total reported US PM2.5 emissions is 5894 Ktonnes/yr (Battye et al., 2002) b) Best estimate BC emissions 433 Ktonnes/yr, high estimate BC emissions 727 Ktonnes/yr (Battye et al.,2002)

1995. The annual and seasonal variation in wild fire emissions is large (Schultz, 2003, Lavoue et al., 2000) and the contribution may be 2 to 3 times higher in other years. The majority of the emissions occur in southern Europe, where the influence may be significant during specific episodes with forest fires. However, for Europe as a whole the contribution of wild fires to the BC emissions is small (2 - 5 %).

The unaccounted sources may contribute largely to PM2.5 emissions but probably less than 15 % to the European BC emissions. We therefore conclude that the traffic emission factors are associated with the highest uncertainty and need to be further addressed in the future.

5.7   Conclusions and recommendations

We presented a model study dedicated to European PM2.5 levels with special attention to primary emitted particles including BC. We used the PM emissions from CEPEIP (TNO, 2001) and combined those with estimated BC fractions to derive a European BC emission inventory on 0.5-0.25° lon-lat for the year 1995. The BC emissions were estimated to be 0.47 Tg in Europe and 0.26 Tg in the Former Soviet Union (FSU). Transport and small combustion sources (households) are the major sources of BC in

Europe and cause these emissions to have a very diffuse nature.

Calculated distributions of primary particles were combined with those previously calculated for secondary inorganic components. Sulphate was found to contribute most to the total PM2.5 mass, followed by nitrate and total primary material. The BC content of PM2.5 was estimated to range between 4-10%. The modelled PM2.5 concentrations underestimate measured concentrations, especially as compared with urban stations. The gap between modelled and measured PM2.5 concentrations appears to be strongly correlated with the primary carbonaceous particles. BC concentrations on background and rural locations are often underestimated by a factor of 2.

The underestimation may be explained by several factors. Local emissions cause an underestimation of primary pollutants in the source regions but not in remote locations. The representation of the ageing process may cause an unknown underestimation at remote locations, although it is unlikely to be a factor of 2. Unaccounted sources are estimated to cause a maximum underestimation of the BC emissions of 15 %. The most important uncertainty is still associated with the emission factors. The black carbon emission inventories have evolved over the years leading to much lower emission estimates. However, using the most more recent inventories the observed BC concentrations are severely underestimated.

At this moment we cannot conclude with certainty that we underestimate the emissions of BC in Europe, because the underestimation may be explained by a number of other factors. However, since the most important and uncertain source of BC is traffic, better emissions estimates for traffic are urgently needed.

Appendix

Table 5.6 Comparison of simulated and measured PM2.5 concentrations and its composition. PM2.5cor gives the comparison of PM2.5 correct for mineral dust and sea salt. Modelled non-BC primary material is assumed to be fully OC. The observed unaccounted mass (UA) is compared to those model components that were not determined in the measurements. NM is the difference between the PM2.5cor and modelled PM2.5. Observational data from Putaud et al. (2003). B = Background, R =Rural, U = Urban, K = Kerbside, MD = Mineral dust, SS = Sea Salt, UA = Unaccounted

Cat.	Site (Country)		PM$_{2.5}$	MD	SS	SO4	NH4	NO3	OC	BC	UA	PM2.5cor	NM
B	Sevettijarvi (F)	Obs	3.41	0.15	0.46	1.29	0.15	0.02	-	0.23	1.12	2.80	
		Sim		-	-	0.54	0.22	0.09	0.09	0.03	0.09	0.97	1.83
B	Skreadalen (N)	Obs	5.05	0.18	0.29	1.28	-	-	-	0.48	2.33	4.58	
		Sim		-	-	1.32	0.56	0.26	0.29	0.15	1.11	2.58	2.0
B	Birkenes (N)	Obs	4.66	0.25	0.34	1.61	-	-	-	0.52	1.59	4.07	
		Sim		-	-	1.42	0.61	0.34	0.38	0.18	1.33	2.93	1.14
R	Illmitz (A)	Obs	19.94	0.26	0.11	3.97	2.04	2.28	5.49	1.66	4.12	19.56	
		Sim		-	-	3.98	2.6	3.81	2.65	0.83	-	13.87	5.69
R	Waasmunster (B)	Obs	25.58	0.98	1.13	5.04	-	-	-	1.42	15.12	23.48	
		Sim		-	-	4.84	3.84	6.96	3.92	1.38	14.72	20.94	2.54
R	Melpitz (D)	Obs	16.85	1.80	-	2.69	1.99	3.43	-	-	10.83	15.04	
		Sim		-	-	5.34	2.99	3.64	1.59	0.58	2.15	14.14	0.90
U	Zuerich (CH)	Obs	18.98	1.18	0.17	3.27	1.84	2.68	4.44	1.66	3.60	17.63	
		Sim		-	-	2.72	2.27	4.28	1.77	0.65	-	11.69	5.98
U	Basel (CH)	Obs	17.85	1.40	0.25	3.80	1.83	2.47	4.21	1.54	2.57	16.21	
		Sim		-	-	2.84	2.41	4.58	1.87	0.7	-	12.40	3.81
U	Gent (B)	Obs	26.39	1.05	1.31	6.17	-	-	-	1.83	13.70	24.02	
		Sim		-	-	4.87	3.85	6.94	4.52	1.24	15.31	21.42	2.60
U	Bologna (I)	Obs	35.82	2.89	0.84	4.62	4.12	8.54	8.24	2.91	7.55	32.10	
		Sim		-	-	3.55	2.74	4.89	1.98	0.80	-	13.96	18.1
K	Barcelona (E)	Obs	34.61	3.79	0.81	5.60	3.31	4.27	11.89	2.98	1.96	30.01	
		Sim		-	-	3.61	1.19	0.27	3.44	1.76	-	10.27	19.7
K	Bern (CH)	Obs	22.65	1.35	0.21	2.67	1.40	2.32	6.68	3.95	4.07	21.09	
		Sim		-	-	2.43	1.94	3.52	1.36	0.49	-	9.74	11.3
K	Wien (A)	Obs	38.51	2.37	0.41	4.44	2.18	3.57	8.62	9.10	7.84	35.74	
		Sim		-	-	4.2	2.53	3.34	1.72	0.53	-	12.32	23.4

Table 5.7 Comparison of simulated and observed BC concentrations (μg/m³). For Mace head and South Uist the range of measured data is tabulated

Site	Lon	Lat	Period	Sim.	Obs.	Reference
Background						
Mace Head	-9.5	53.2	Jul-Aug	0.10	0.03	Krivacsy et al., 2001
Mace Head	-9.5	53.2	Year	0.09	0.05-1.0	Derwent et al., 2001
Hyytiala	24.3	61,9	Jun	0.15	0.19	Alves et al., 2002
South Uist	-7	57	Winter	0.06	0.02-0.33	Loew et al. 1996
South Uist	-7	57	Summer	0.05	0.03-0.08	Loew et al. 1996
Finokalia	25.6	35.2	May	0.09	0.26	Kouvarakis et al., 2002
Prasses	25.1	35.2	May	0.13	0.19	Kouvarakis et al., 2002
Aspvreten	17.4	58.8	Jun-Jul	0.15	0.10	Zappoli et al., 1999
NE Atlantic	-5.0	61.0	Oct-Nov	0.05	0.27	O'Dowd et al., 1993
Rural						
Kap Arkona	13.2	57.4	Year	0.21	0.4	Zier, 1991
Melpitz	12	51	Year	0.61	2.3	Heintzenberg et al., 1998
Corsica	9	42	Spring	0.23	0.38	Cachier et al., 1989
Landes Forest	-1	44	Autumn	0.30	0.3	Cachier et al., 1989
Edgbaston	-1	51	Year	0.65	0.38	Smith et al., 1996
K-Puszta	19.5	46.9	Jul-Aug	0.28	0.60	Molnar et al., 1999
K-Puszta	19.5	46.9	Jul-Aug	0.28	0.75	Krivacsy et al. 2001
Po-Valley	11.4	44.4	Sep	0.63	1.0	Zappoli et al., 1999
Anadia	-8.4	40.3	Aug	0.29	1.59	Castro et al., 1999
Areao	-8.8	40.5	Year	0.34	0.95	Castro et al., 1999
Aveiro	-8.4	40.4	Jul	0.23	0.77	Alves et al., 2002
Ebro	-0.2	40.5	Year	0.24	0.4	Rodriguez et al., 2002
Roervik	12.1	57.2	Jan-May	0.21	0.73	Brostrom-Lunden et al., 1994
Urban						
Vienna	16.2	48.1	Year	0.83	4.9	Hitzenberger and Tohno, 2001
Gent	3.4	51	Summer	0.77	1.7	Kubatova et al., 2002
Gent	3.4	51	Winter	1.24	3.2	Kubatova et al., 2002
Gorlitz	14.6	41.1	Year	0.87	1.3	Zier, 1991
Halle	12	51.3	Year	0.68	1.6	Zier, 1991
Potsdam	13.4	52.3	Year	0.73	1.0	Zier, 1991
Radebeul	13.6	51.6	Year	0.51	1.4	Zier, 1991
Gif sur Yvette	2.8	48.4	Year	1.03	1.6 / 2.7	Cachier et al., 1989; Bremond et al., 1989
Paris	2.2	48.5	Year	2.04	4.6	Ruellan and Cahier, 2001
Aveiro	-8.4	40.4	Year	0.32	11.8	Nunes and Pio, 1993
Lisbon	-9.2	38.4	Jun	0.36	2.1	Alves et al., 2002
Barcelona	2.0	41.2	Year	1.76	3.0	Rodriguez et al., 2002

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