Atmos. Chem. Phys. Discuss., 12, 5425–5485, 2012
www.atmos-chem-phys-discuss.net/12/5425/2012/
doi:10.5194/acpd-12-5425-2012

Atmospheric Chemistry and Physics Discussions

Modelling of organic aerosols over Europe (2002–2007) using a volatility basis set (VBS) framework with application of different assumptions regarding the formation of secondary organic aerosol

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Received: 3 January 2012 – Accepted: 6 February 2012 – Published: 20 February 2012

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

A new organic aerosol (OA) module has been implemented into the EMEP chemical transport model. Four different volatility basis set (VBS) schemes have been tested in long-term simulations for Europe, covering the six years 2002–2007. Different assumptions regarding partitioning of primary OA (POA) and aging of POA and secondary OA (SOA), have been explored. Model results are compared to filter measurements, AMS-data and source-apportionment studies, as well as to other model studies. The present study indicates that many different sources contribute significantly to OA in Europe. Fossil POA and oxidised POA, biogenic and anthropogenic SOA (BSOA and ASOA), residential burning of biomass fuels and wildfire emissions may all contribute more than 10 % each over substantial parts of Europe. Simple VBS based OA models can give reasonably good results for summer OA but more observational studies are needed to constrain the VBS parameterisations and to help improve emission inventories. The volatility distribution of primary emissions is an important issue for further work. This study shows smaller contributions from BSOA to OA in Europe than earlier work, but relatively greater ASOA. BVOC emissions are highly uncertain and need further validation. We can not reproduce winter levels of OA in Europe, and there are many indications that the present emission inventories substantially underestimate emissions from residential wood burning in large parts of Europe.

1 Introduction

During the last 10–15 yr carbonaceous aerosol has become one of the most intensively studied fields within the atmospheric sciences. This can be attributed to its postulated impacts on global climate (Novakov and Penner, 1993; Kanakidou et al., 2005), and on human health (McDonald et al., 2004).

Particulate carbonaceous matter (PCM) contributes around 10–40 % (mean 30 %) to total PM_{10} levels at rural and natural background sites in Europe (Yttri et al., 2007; Putaud et al., 2004). PCM consists largely of organic matter (OM, of which typically 40–80 % is OC: organic carbon (Turpin and Lim, 2001; El-Zanan et al., 2009), with the rest made up of associated oxygen, hydrogen, and other atoms) and so-called elemental or black carbon (EC or BC). The sum of EC and OC is referred to as total carbon (TC). OM is a very important fraction of sub-micron particles (PM_1) as well. In a recent aerosol mass spectrometry (AMS) study of non-refractive (NR) PM_1 in Central Europe Lanz et al. (2010) found that about 40–80 % of the NR-PM_1 was made up of OM.

The EMEP EC/OC model has previously been presented by Simpson et al. (2007); two versions of a gas-particle scheme for secondary organic aerosol (SOA) were used, Kam-2 from Andersson-Sköld and Simpson (2001), and a modification, Kam-2X, which use alternative "effective" vapour pressures, for the semi-volatile OA compounds, to increase partitioning to the particulate phase. Model results were compared with measurements from the EMEP EC/OC campaign (Yttri et al., 2007) and the EU CARBOSOL project (Legrand and Puxbaum, 2007). Comparisons were also made of the different components of TC, e.g. anthropogenic and biogenic secondary organic aerosols (ASOA, BSOA), against estimates of these compounds made by Gelencsér et al. (2007).

The study demonstrated that the Kam-2 and Kam-2X schemes were able to predict observed levels of OC in Northern Europe fairly well, but for southern Europe the model underestimated OC significantly. In wintertime, the under-prediction was shown to be caused by problems with wood-burning emissions (possibly local). In summer the problems were due to an under-prediction of the SOA components. The model results were very sensitive to assumptions concerning the vapour pressures of the model compounds.

As discussed in, e.g. Hallquist et al. (2009), the sources and formation mechanisms of SOA are still very uncertain, with many plausible pathways but still no reliable estimates of their relative importance. In such a situation one cannot expect a model to accurately reproduce measurements. Still, it is important to understand the extent to which models or parameterisations derived from smog-chambers can capture observed levels and variations in OC.

Donahue and co-workers introduced the use of a volatility basis set (VBS) to help models cope with the wide range of organic aerosol species and the oxidation of organics of different volatilities in the atmosphere (see, e.g. Donahue et al., 2006, 2009). This scheme is suitable for regional and global scale modelling of organic aerosol as it provides a convenient framework with the aerosol described by a physically plausible range of properties, and simple relationships governing partitioning and transformation of OA.

In this paper we explore the use of the VBS approach for modelling OA over Europe with the EMEP model (Simpson et al., 2007, 2012), and illustrate the sensitivity of the results to some key parameters. The model results are compared with PCM measurements of different types from a number of European campaigns from the years 2002–2007.

However, the large number of different components that contribute to PCM makes a simple comparison of modelled versus observed TC or OC potentially misleading. For example, OC from biomass-burning often contributes substantially to observed TC levels, but emission inventories may often miss the relevant sources.

Model-measurement discrepancies might easily be misinterpreted in terms of problems with, for example, the SOA components. In such situations additional components, such as levoglucosan, a well-known tracer for primary organic aerosol (POA) from wood burning, can provide valuable information on the reasons for model discrepancies. Indeed, levoglucosan comparisons could explain almost all of the wintertime discrepancies between modelled and observed data at two CARBOSOL sites, as shown in Simpson et al. (2007).

Thus, it is necessary to compare model results not only to measured OC, EC and TC but also to source-apportionment (S-A) studies that give information about the relative contributions from different sources to PCM (e.g. wood-burning, BSOA, etc.). Here we compare model results to S-A studies which have been analysed with approximately the same methodology: the 2-yr CARBOSOL campaign (Gelencsér et al., 2007) at sites in central Europe, the SORGA (Yttri et al., 2011) campaign in and close to Oslo in southern Norway, and the Göte-2005 campaign (Szidat et al., 2009) in and close to Gothenburg in southern Sweden. All of these campaigns made use of radiocarbon (^{14}C) data as well as of compounds that could be used as tracers for wood-burning and primary biological aerosol particles (PBAP).

A large number of new measurements has become available recently, e.g. through the EUCAARI (Kulmala et al., 2011) and other projects (e.g. Lanz et al., 2010). These data mainly consist of relatively short-term campaigns (typically 1 month), but with very high time resolution and multiple instruments. These will be analysed in a subsequent paper; the main focus of this paper is to provide an initial assessment of the different VBS schemes against long-term observations, and especially for sites where some source-apportionment results are already available.

2 The EMEP model

The EMEP MSC-W model is a development of the 3-D chemical transport model of Berge and Jakobsen (1998), extended with photo-oxidant and inorganic aerosol chemistry (Andersson-Sköld and Simpson, 1999; Simpson et al., 2003, 2012), and, in this work, organic aerosol modules.

The model domain used in this study covers all of Europe, and includes a large part of the North Atlantic and Arctic areas. A horizontal resolution of ca. $50 \times 50\,\text{km}^2$ is used. The model includes 20 vertical layers, using terrain-following coordinates; the lowest layer has a thickness of about 90 m.

The meteorological driver has changed recently. For the years up to 2005, we use PARLAM-PS – a dedicated version of the HIRLAM (HIgh Resolution Limited Area Model) numerical weather prediction model, with parallel architecture (Bjørge and

Skålin, 1995; Benedictow, 2003). For 2006 and later years, meteorological fields are derived from the European Centre for Medium Range Weather Forecasting Integrated Forecasting System (ECMWF-IFS) model (http://www.ecmwf.int/research/ifsdocs/). The performance of the EMEP model varies with the meteorological driver, but differences are modest for most pollutants. Tarrasón et al. (2008) discuss the differences in more detail.

The EMEP PCM model uses the same inorganic and VOC chemistry scheme, and deposition routines, as the standard EMEP model (Simpson et al., 2012), with the addition of SOA forming reactions. Dry deposition of semi-volatile organic vapours may be an important loss process for OA (Bessagnet et al., 2010). In this study we assume that the dry deposition velocities of the semi-volatile components in the gas phase are the same as for higher aldehydes (ALD, Simpson et al., 2012).

The PCM model uses the same basic gas/aerosol partitioning framework as in Simpson et al. (2007), but using the VBS approach rather than the earlier 2-parameter or gas/kinetics ("Kam-2(X)") schemes of Andersson-Sköld and Simpson (2001) or Simpson et al. (2007). The VBS approaches used in this paper will be described in Sect. 5.1.

3 Emissions

Two types of emissions are included in the model: anthropogenic and natural. Anthropogenic emissions are provided annually by all countries within EMEP, and gridded to the standard EMEP 50 × 50 km^2 emissions domain (http://www.emep.int/grid/). Non-methane volatile organic compounds (NMVOC) are speciated into 11 surrogate compounds, using emission-sector specific values as shown in Simpson et al. (2012). The anthropogenic emissions are adjusted with monthly/daily and day/night factors as described in Simpson et al. (2012).

3.1 Biogenic VOC emissions

Biogenic emissions of isoprene and monoterpenes are calculated in the model for every grid-cell, and at every model timestep, using near-surface air temperature and photosynthetically active radiation (Guenther et al., 1993; Simpson et al., 1999), together with maps of standardised emission factors.

As detailed in Simpson et al. (2012), the maps of standard emission factors have been extensively revised over the last year. The new procedures make use of updated emission rates together with maps of forest species from Köble and Seufert (2001). This work (also used by Karl et al., 2009 and Kesik et al., 2005) provided maps for 115 tree species in 30 European countries, based upon a compilation of data from the ICP-forest network (UN-ECE, 1998).

Sesquiterpene emissions are not included in the present model version, primarily because of major uncertainties regarding their emissions and the environmental factors controlling the emissions (Duhl et al., 2008).

3.2 Vegetation fire emissions

Emissions of gases and carbonaceous particles from vegetation fires are taken from the Global Fire Emission Database (GFEDv2, van der Werf et al., 2006, Giglio et al., 2003, Tsyro et al., 2007). The database provides emissions with $1^\circ \times 1^\circ$ spatial resolution and 8-days temporal resolution for the years 2002–2007.

We assume an initial OM/OC ratio of 1.7 for organic aerosol emissions from vegetation fires (based on AMS measurements presented by Aiken et al., 2008). The OM/OC ratio increases as the aerosol ages by OH-reactions in the atmosphere (see Sect. 5.1).

Emissions of volatile organic compounds (VOC) from vegetation fires (and residential wood burning) are included in the model but in the present model versions the formation of SOA from these VOCs is not separated from SOA from anthropogenic fossil VOC emissions. This may lead to a slight overestimation of the fossil OC in the model, and corresponding underestimation of modern OC, but in Europe the VOC emissions from forest fires are usually minor in comparison with anthropogenic fossil VOC emissions and Bessagnet et al. (2008) have shown that the SOA contribution from wildfires is small, even during a period of relatively intense fires in Europe.

3.3 EC and OC emissions

Carbonaceous aerosol emissions from anthropogenic sources are taken from the emission inventory by Denier van der Gon et al. (2009) (see Visschedijk et al., 2009 for details), prepared as part of the EUCAARI project (Kulmala et al., 2011). To make a carbonaceous aerosol inventory there are essentially two options:

1. to use direct EC and OC emission factors per unit of activity (e.g. g EC emitted per kg coal burned in a particular type of stove) or,
2. to establish the fraction EC and OC for PM_{10} and $PM_{2.5}$ emissions per unit of activity (e.g. EC = x % of $PM_{2.5}$ emitted per kg coal burned in a particular type of stove).

The EUCAARI EC and OC inventory follows the latter option. The motivation was that size-fractionated EC and OC emission factors (carbonaceous mass per unit of activity) are available only for a limited number of sources and technologies, and can vary widely due to different measurement protocols and analytical techniques (e.g. Watson et al., 2005). Therefore, although in principle a direct calculation of activity × EC or OC emission factor would be preferable, this would give widely varying, inconsistent and incomplete results.

Option 2 tackles this problem by starting from a size-fractionated particulate matter (PM_{10}/$PM_{2.5}$/PM_1) emission inventory followed by deriving and applying representative size-differentiated EC and OC fractions to obtain the EC and OC emissions in the size classes, <1 µm, 1–2.5 µm and 2.5–10 µm. The total EC and OC emission is then constrained by the amount of PM emitted. This limits uncertainty because extremes in the EC or OC emission factors measured can never generate more EC or OC than the total amount of PM in a particular size class.

The PM emission inventory needs to be consistent for all countries. It is based on previous particulate matter (PM) inventories, especially the PM module of the IIASA GAINS model (Kupiainen and Klimont, 2004, 2007). Representative elemental carbon (EC) and organic carbon (OC) fractions are selected from the literature and applied to ca. 200 individual GAINS PM source categories and separated in the three size classes.

Fuel wood is used extensively in Europe. Combustion of wood is a major source of EC and OC but reliable fuel wood statistics are difficult to obtain because fuel wood is often non-commercial and falls outside the economic administration. In this study the residential wood burning emissions from Visschedijk et al. (2009) are used. Visschedijk et al. (2009) updated and adjusted the residential wood use activity data per appliance type. This led to changes, compared to the GAINS activity data, to varying degrees for 17 UNECE countries in Europe. For the entire domain the estimated fuel wood use increased by 25 %, but this includes data from countries where no previous estimates were available.

Another important feature of the new inventory is its improved spatial resolution of $1/8^\circ \times 1/16^\circ$ lon-lat (or ∼ 7 km × 7 km) compared to previous inventories. The emissions are gridded using especially prepared distribution maps. Particular attention has been given to the spatial distribution of transport emission and emission due to residential combustion.

An example of the emission distribution pattern for $\mathrm{OC}_{\mathrm{PM}_{2.5}}$ (organic carbon in particles with diameter <2.5 µm) is presented in Fig. 1. The emissions are dominated by transport and residential combustion as can be seen by the highlighted urban centers, major road network and ship tracks.

Total carbonaceous aerosol emissions in $\mathrm{PM}_{2.5}$ are presented in Table 1. Total $\mathrm{PM}_{2.5}$ emissions in Europe amount to ∼3400 ktonnes and about half of the total $\mathrm{PM}_{2.5}$ emissions in Europe are carbonaceous aerosol, highlighting the importance of this fraction.

Elemental carbon emissions are dominated by road transport and residential combustion (each ~30 %; Table 1) but for OC residential combustion is clearly the dominant source, responsible for almost 50 % of the European emissions (Table 1).

Particle size distributions of EC and OC for mass show maxima in the range of 80 to 200 nm, thus being highly relevant for long range atmospheric transport. In the present EMEP PCM model only two size classes are used for the EC and OC emissions, PM-fine (up to 2.5 µm) and PM-coarse (2.5–10 µm), thus the PM_1 and $PM_{1-2.5}$ classes from the emission inventory are combined.

Emissions in the inventory are given in ktonnes(C) yr^{-1}. In the model this is converted to OM-emissions using the OM/OC ratios 1.25 for fossil fuel emissions and 1.7 for wood burning emissions, based on data from laboratory and field measurements (Aiken et al., 2008).

There are strong seasonal variations in EC and OC emissions. These are estimated from annual emissions according to SNAP-sector and country (Simpson et al., 2012). As an example, Fig. 2 provides an estimate of the monthly variation of OC emissions in 17 European countries. The seasonal variation is largest for the residential heating sector, with very low emissions during the summer months and large winter emissions.

4 Observations

The main focus of this paper is to provide an initial assessment of the different VBS schemes against long-term observations, including sites for which some source-apportionment (S-A) data are available.[1]

One important source of data is the CARBOSOL 2002–2004 campaign, which provided two years of measured data, together with source-apportionment for summer and winter seasons. These data and the S-A have been described in detail in: Legrand and Puxbaum (2007); Pio et al. (2007); Gelencsér et al. (2007); Simpson et al. (2007).

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[1] See Table A1 for information about the measurement sites and data sets used in this study.

Measurements were made at six sites in a transect across southern-central Europe. In this study we have excluded the remote Azores and the high-altitude station Sonnblick.

Other long-term data-sets consist of the EMEP EC/OC campaign 2002–2003 (Yttri et al., 2007), and the EMEP PM intensive campaign 2006–2007 (Yttri et al., 2008; Aas et al., 2012).

For source-apportionment data, we make use of three studies: the CARBOSOL campaign, the SORGA campaign in and near Oslo in southern Norway (Yttri et al., 2011), and the Göte-2005 campaign in and near Gothenburg in southern Sweden (Szidat et al., 2009). All of these campaigns made use of radiocarbon (^{14}C) data as well as of compounds that could be used as tracers for wood-burning and primary biological aerosol particles (PBAP). Further, these S-A studies were all conducted with different variants of the same methodology, using Latin-hypercube-sampling to allow for a wide range of uncertainties in the relations between tracers and their associated TC components.

Aerosol mass spectrometry (AMS) is becoming a very important technique for studying submicron particles (PM_1) at high time-resolution (e.g. Canagaratna et al., 2007). We plan a more extensive comparison with AMS data in a complementary study, here we compare model results to observations from one AMS-campaign, in Switzerland in June 2006 (Lanz et al., 2010).

5 EMEP VBS experiments

The VBS approach was introduced by Donahue and co-workers (Donahue et al., 2006, 2009), as a practical approach to dealing with the complexity of organics in the atmosphere.

The VBS consists of a group of lumped compounds with fixed saturation concentrations (C^*, µg m^{-3}), comprising a number of bins separated by one order of magnitude each in C^* at 298 K. Using the VBS, different SOA-forming reactions can be mapped onto the same set of bins over the range of organic aerosol mass concentration typical of ambient conditions (0.1–100 µg m^{-3}) while maintaining mass balance for more volatile co-products as well. Aging reactions can be added easily within the VBS if the kinetics and volatility distribution of the products can be measured or estimated.

A number of papers have illustrated the use of VBS-based models in North America (Robinson et al., 2007; Lane et al., 2008a,b; Shrivastava et al., 2008; Murphy and Pandis, 2009), and very recently in Europe (Fountoukis et al., 2011), and we build upon this work here.

In the EMEP models for particulate carbonaceous matter (EMEP-PCM) a four-bin VBS is used for the SOA components (saturation concentrations in the range 1–1000 µg m^{-3}) as in Lane et al. (2008b). A larger basis set, with nine bins, is used for the directly emitted organic aerosol components (of low to intermediate volatility, that is, in particulate as well as gaseous form) from fossil fuel use, biomass burning and vegetation fires, to cover the great range of different volatilities of these species (Shrivastava et al., 2008).

5.1 EMEP-VBS versions

Four versions of the EMEP model have been set up, introducing different aspects of the VBS approach in each version and testing various assumptions about aging reactions of OA-components in the gas phase. The model versions are summarised in Table 2.

In all model versions we assume a background concentration of 1.0 µg m^{-3} of organic particles (with an assumed OM/OC ratio of 2.0, i.e., background OC = 0.5 µg(C) m^{-3}) at the surface, decaying vertically with a scale height of 9 km. This background OA is assumed to be nonvolatile and represents, in a very simplified way, the sources of OA that are not included in the model, e.g. OA from oceanic sources and primary biological material. All of the background OA is considered as $PM_{2.5}$ in the model.

We assume that the semi-volatile OA only partitions to the $PM_{2.5}$ fraction of the organic material, that is, not to coarse particles or the elemental carbon (EC). In the real atmosphere some of the semi-volatile OA will adsorb to EC surfaces and some will possibly also be bound to coarse particles. Since we neglect these two processes we expect to underestimate the particulate OC concentrations somewhat.

The first model version, **VBS-NPNA** (**N**o **P**artitioning of primary emissions and **N**o **A**ging reactions included), is based on the SOA scheme of Lane et al. (2008a), for SOA formation from anthropogenic VOCs, isoprene, and terpene species[2]. The SOA yields are updated to take into account recent findings about higher yields from oxidation of aromatic VOCs (Hildebrandt et al., 2009; Ng et al., 2007; Tsimpidi et al., 2010). The SOA yields are summarised in Table 3.

The temperature dependence of the gas-particle partitioning is taken into account by using the Clausius-Clapeyron equation to calculate the saturation concentrations, along with the effective enthalpy of vaporization, ΔH. In principle, ΔH should vary across the VBS bins, with higher values for the lower C^* values (Epstein et al., 2010). However, the parameterisation of SOA partitioning from Pathak et al. (2007) used a constant *effective* $\Delta H = 30\,\mathrm{kJ\,mol^{-1}}$, for the entire basis set. This value was selected to reproduce the observed temperature dependence of the smog chamber aerosol yields and accounts for various temperature effects on the SOA yields. In addition, Fountoukis et al. (2011) have shown that model results are not very sensitive to assumptions concerning the ΔH value.

BSOA formation from terpenes is initiated by gas phase oxidation by O_3, OH or NO_3 in the model. For isoprene, only oxidation by OH leads to BSOA formation. Initial OM/OC ratios are assumed to be 1.7 for BSOA from terpenes and 2.0 for isoprene BSOA (based on Chhabra et al., 2010). For ASOA from alkanes and alkenes OM/OC = 1.7 is used and for ASOA from aromatic VOCs the ratio is 2.1 (Chhabra et al., 2010).

In the VBS-NPNA model version, primary organic aerosol (POA) emissions (including wood burning and vegetation fire OM emissions) are assumed non-volatile, taken directly from the carbonaceous aerosol emission data-sets.

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[2] Lane et al. (2008a) also included SOA formation from sesquiterpenes.

The **VBS-PAP** (**P**artitioning and atmospheric **A**ging of **P**OA emissions) model introduces three important changes to the treatment of the primary organic aerosol emissions and atmospheric chemistry, following suggestions of Shrivastava et al. (2008):

i. The emitted POA is distributed over different volatilities (9-bin VBS) and partitions between the gas and particulate phases. This allows a large fraction of the POA to evaporate.

ii. The POA emissions are assumed to be accompanied by emissions of low-vapour pressure (intermediate volatility OC, IVOC) gases, which are currently not captured in either the POA or the VOC inventories. Following Shrivastava et al. (2008) we assume that the total emissions of condensible material (including POA) amount to 2.5 times the POA inventory. This means that a VOC mass of 1.5 times the POA emissions is added to the total emission input in the model. We use the same emission split and enthalpies of vaporization as in Shrivastava et al. (2008) to calculate how much of this material is condensed at any moment.

iii. The POA compounds are allowed to react with OH in the gas phase, with each reaction resulting in a shift of the compound to the next lower volatility bin. The OH-reaction rate used in this study, 4.0×10^{-11} $cm^3 molecule^{-1} s^{-1}$, is taken from Robinson et al. (2007) and corresponds to the base case in Shrivastava et al. (2008). Like Robinson et al. (2007) and Shrivastava et al. (2008), we assume a small mass increase (7.5 %) with each aging reaction to account for added oxygen atoms.

In the **VBS-PAA** version (**P**artitioning of primary OA and **A**ging of **A**ll semivolatile OA components in the gas phase) aging reactions for SOA-components in the gas phase are also included with the same assumption of each reaction leading to a lowering of the volatilities of these species by a factor of ten. The OH-reaction rate for SOA-aging (4.0×10^{-12} $cm^3 molecule^{-1} s^{-1}$) is assumed to be an order of magnitude lower than for POA (as suggested by Lane et al., 2008b).

Lane et al. (2008b) showed that including aging reactions for SOA leads to serious overestimation of OC concentrations in rural areas in eastern USA. They suggest that although aging reactions for SOA components do occur, the effect may not be a net increase in particle mass since decomposition reactions may compete with substitution reactions.

Murphy and Pandis (2009) include aging reactions for POA and anthropogenic SOA but not for biogenic SOA. In this study we test this assumption in the **VBS-PAPA** version (**P**artitioning and **A**ging of **P**rimary OA and **A**nthropogenic SOA), using the aging rates suggested by Murphy and Pandis (2009), 4.0×10^{-11} $\mathrm{cm^3 molecule^{-1} s^{-1}}$ for POA and 1.0×10^{-11} $\mathrm{cm^3 molecule^{-1} s^{-1}}$ for ASOA.

6 Results and discussion

6.1 Total organic aerosol in $PM_{2.5}$

Figure 3 shows calculated total organic mass in $PM_{2.5}$ ($OM_{PM_{2.5}}$) concentrations with the four different model variants (six-year average for the whole period 2002–2007).

In the simplest model version (NPNA), with no aging of the aerosol, and the primary OA emissions treated as non-volatile, the calculated OM concentrations are low in large parts of Europe. The OM distribution reflects the emission inventory with the highest concentrations in France, Russia, Latvia and a region in Central Europe (the Czech Republic, Slovakia and southern Poland). A few other hotspots with high concentrations are also seen; most notably Oslo (Norway), Istanbul/Bosphorus Strait, northern Portugal and point sources in Ukraine.

When the primary emissions are treated in the VBS and are subject to evaporation and aging reactions (PAP) the picture changes and the concentrations are more homogeneous across Europe. OM concentrations in the hotspots are decreased (in spite of the increase in total POA emitted in the PAP version), due to evaporation of part of the POA emissions. The levels further away from the main emission areas are increased due to the aging reactions that decrease the volatility of the semi-volatile OC. Eastern and Central Europe, as well as parts of France, the Po Valley and the Oslo region, have the highest OM concentrations (above 3 $\mu g m^{-3}$).

Adding aging reactions also for the SOA (PAPA and PAA) increase the calculated OM concentrations further. In the model version including aging of BSOA (PAA) the model OM is above 3 $\mu g m^{-3}$ in large parts of Europe (the main exceptions are the British Isles and the northern part of Scandinavia and Russia that have low concentrations of organic aerosol). OM concentrations above the Mediterranean and Black Seas are elevated in the PAPA and PAA models. This accumulation over the sea areas is likely due to fairly high concentrations of OH in these regions, leading to high oxidation rates for the semi-volatile OA components in the gas phase, and little precipitation, which means small deposition losses.

6.2 Contributions from different sources to organic aerosol in Europe

In Fig. 4 (and Figs. A4–A6) the calculated relative contributions to $OM_{PM_{2.5}}$ from different sources are compared. Although it is not totally clear which model version gives the most realistic results we choose to show results for the PAA version here, since it gives the highest modelled $OM_{PM_{2.5}}$ and includes more atmospheric processing of the OA than the other versions.

Several different sources contribute significantly to the modelled $OM_{PM_{2.5}}$. Biogenic SOA is an important component; in parts of Finland and Spain and the Mediterranean region the BSOA contribution to $OM_{PM_{2.5}}$ is above 30 % in the PAA version, which has the highest BSOA levels, because of the aging reactions of semi-volatile BSOA. In model versions that do not include atmospheric aging of BSOA the importance of this source is much lower (below 20 % in most of Europe, see Figs. A4–6).

The importance of anthropogenic SOA in the model is very sensitive to assumptions regarding the aging of ASOA in the atmosphere. In the model versions that do not include aging of ASOA the contribution to $OM_{PM_{2.5}}$ is below 10 % in all of Europe. In the PAA scheme, with aging of both ASOA and BSOA, only the northernmost part of

Europe have less than 5 % contribution of ASOA to $OM_{PM_{2.5}}$. The 6-yr average ASOA concentrations are lower than the BSOA concentrations in all model version except the PAPA-model, that includes aging of ASOA (with a fairly high reaction rate) but not of BSOA. In the PAPA model (Fig. A6) ASOA is a substantial $OM_{PM_{2.5}}$ source (10–20 % in large parts of Europe, more in Italy and over the Mediterranean Sea).

For the period 2002–2007 wildfires seem to be a major source of $OM_{PM_{2.5}}$ in some parts of Europe, most notably Russia and Eastern Europe and Portugal and western Spain. In these regions more than 10 % of the long-term average $OM_{PM_{2.5}}$ may be due to vegetation fire emissions. However, if the wildfire OA emissions are treated as nonvolatile and not aging in the atmosphere the impacts are much more local (see Fig. A4).

In the PAA-model the primary fossil fuel OA (including the oxidised POA) contribution to $OM_{PM_{2.5}}$ is fairly homogeneous across Europe, between 10–20 % except in northern Europe, where it is lower, and in high emission areas (e.g. the Po Valley, the English channel, Paris, Holland, Ruhr), where the contribution is 20–30 %. The picture is rather different when the primary emissions are treated as nonvolatile (NPNA-version, Fig. A4); in this version there is no evaporation of the emitted POA in the emission regions, which leads to high contributions in the major source areas.

We find relatively large contributions of wood burning to $OM_{PM_{2.5}}$, above 10 % in large parts of Europe in all model versions.

6.3 OM/OC ratios

The ratio of total organic mass to organic carbon (the OM/OC-ratio) is an important property of the organic aerosol. The OM/OC-ratio is often used to estimate total OM in $PM_{2.5}$ from measured OC concentrations. A value of OM/OC = 1.4 has often been used, although Turpin and Lim (2001) showed that OM/OC ratios are usually higher than this.

OM/OC ratios vary with season and location (e.g. Simon et al., 2011). Urban aerosols, dominated by fresh POA emissions, usually have a relatively low OM/OC ratio (e.g. Turpin and Lim, 2001), which increase as the aerosol ages and oxygen is added. Secondary organic aerosol and biomass burning aerosol usually have higher OM/OC ratios than POA (Aiken et al., 2008).

We have calculated long term (2002–2007) average OM/OC ratios for Europe and examples of the results are shown in Fig. 5 (and Fig. A3). The ratio depends strongly on the assumptions whether the primary OA emissions are non-volatile and chemically inert or are subject to oxidation (aging) reactions in the atmosphere.

In the NPNA model (Fig. 5a), areas near high POA emissions have relatively low OM/OC ratios (<1.6) and in most of Europe the ratio is below 1.9. When chemical aging of POA and SOA is included (models PAPA and PAA, Figa. 5b and A3d) most of Europe has OM/OC ratios above 1.9; for the Mediterranean and parts of southern Europe even above 2.0; the OM/OC ratios are below 1.8 only in a few high emission areas. The model version with aging of only POA (PAP, Fig. A3b) gives ratios inbetween; most of central and northern Europe have OM/OC ratios in the 1.8–1.9 range with this model version, outside this region the range is 1.9–2.0, except in some urban hotspots where it is lower.

6.4 Comparison to other modelling studies

The model results in this study show some marked differences to the earlier EMEP EC/OC model (Simpson et al., 2007) (or those of Bessagnet et al., 2008). The geographical distribution of OC over Europe and the relative contributions from different sources to the organic aerosol differ significantly between the new model and the results in Simpson et al. (2007).

An obvious difference between the two studies is that the new model includes wildfire emissions of PCM, which the old model did not. This explains some of the changes in the modelled OC distribution (new areas with relatively high OC concentrations in eastern Europe) but there are several other important differences as well.

The most striking differences in the geographical distribution of modeled total OC is that the (Kam-2X) results in Simpson et al. (2007) show a large area with high OC concentrations in northern Europe and another high-concentration region in central Europe. In the present study we find none of these to have particularly high yearly average OC concentrations.

One reason for the much lower estimate of the BSOA in this study may be the new BVOC emission estimates used here. It is also possible that the use of low "effective" vapor pressures for the BSOA components in the Kam-2X model used by Simpson et al. (2007) led to much greater partitioning to the particle phase. Indeed, that study highlighted that the use of different vapour pressure assumptions (the Kam-2 versus Kam-2X schemes) dramatically alters SOA formation.

Another big difference between the two studies is that the calculated ASOA contribution to $OM_{PM_{2.5}}$ is much larger with the new model, especially if aging reactions are included for the semi-volatile ASOA components in the VBS-scheme (PAPA and PAA models). The reason for the small ASOA-contribution in Simpson et al. (2007) (and other studies) is likely the usage of older (lower) estimates of SOA formation from oxidation of aromatic compounds in that study; the yields from such compounds have been revised dramatically upwards in recent years (Ng et al., 2007; Hildebrandt et al., 2009; Hallquist et al., 2009).

Fountoukis et al. (2011) recently used the PMCAMx-2008 model for a study of PM_1 in Europe during the EUCAARI campaign in May 2008. PMCAMx-2008 includes an organic aerosol scheme, which is very similar to the VBS-PAPA version of this study, and it is interesting to compare the results of this study to Fountoukis et al. (2011). Since the present study does not include 2008, a direct comparison of the results is not possible but we have extracted model results for the six May months of 2002–2007 (see Figs. A8, A9) and compare these to the 2008 results in Fountoukis et al. (2011).

For most parts of Europe the calculated total organic aerosol in fine particles is lower in the study by Fountoukis et al. (2011) than the corresponding results (for 2002–2007) with the EMEP VBS-PAPA model. This is especially clear over southern Europe and the

Mediterranean and Black Seas. We also get higher concentrations in western Russia, Belarus and Ukraine (possibly due to some periods with high wildfire emissions in this region during the period 2002–2007).

Fountoukis et al. (2011) calculate higher OA concentrations over England, the English Channel, the North Sea and the Benelux countries, the south-eastern Baltic Sea, as well as over some urban hotspots, especially St. Petersburg. This seems mostly to be due to much higher "Fresh POA" concentrations in these regions in the PMCAMx-2008 model compared to the present study. The fresh POA in PMCAMx includes oceanic emissions (from sea spray) and this source of OA is not explicitly included in the present version of the EMEP model, which may explain some of the differences in and near sea areas. For many high-emission hotspots it seems that the PMCAMx emissions are much less dispersed (and/or evaporated) than in the EMEP model, which may indicate that some differences are due to model resolution and possibly boundary layer physics issues.

6.5 Comparison of model results to long-term measurements

6.5.1 Total Carbon (TC)

Model calculations are compared to observations from three different campaigns, the EMEP EC/OC campaign 2002–2003, the CARBOSOL project 2002–2004, and the EMEP PM intensive measurement periods in 2006–2007. The maps in Fig. 3 present average results for the whole 6-yr period (2002–2007), but there are important seasonal variations.

The results for the PM_{10} samples are summarised in the Tables 4, A3, and A4 and Figs. A1 and A2. Tables A2, A5, and A6 contain results for PCM in fine particles ($PM_{2.5}$ measurements). Since the dominant winter and summer sources of PCM are different we include some model evaluation data split into summer and winter half-years (here the summer period is defined as the months May–October).

Comparing the different model versions there is a clear increase in $TC_{PM_{10}}$ from the simplest model (NPNA) to the model that includes most aging reactions (PAA). For the long-term measurements, and the average of the summer data, the PAA model version is usually closest to the observed levels.

The mean absolute error (MAE) of the model results range from 56 % (PAA) to 61 % (NPNA) for $TC_{PM_{10}}$ (all data) and correlations are low, with the highest correlation coefficient (based on all 1356 daily data) of only 0.45 (for the NPNA model).

Summer results are slightly better with MAE ranging from 42 % (PAA) to 54 % (NPNA) and correlation coefficients from 0.66 (NPNA) to 0.58 (PAP).

Looking at only the winter results gives worse agreement, with MAE of 66 % for all model versions and the highest correlation coefficient at only 0.37 (again for the NPNA model).

Based on these comparisons it is not easy to pick a "best" model. Winter results are of too poor quality and the difference between the model versions are not very large. We believe that improvements in the emission estimates are needed in order to improve the model performance significantly for winter periods.

A careful check of the representativity of the measurement sites for the model (and emission inventory) resolution may also be needed. Some sites may be subject to large local emissions from, for example, residential biomass burning and some stations are located in urban areas and, for these, the regional scale model results are expected to underestimate the primary emission contributions.

A certain underestimation of PCM_{10} is to be expected also due to missing emissions of coarse primary biological particles (OC_{PBAP}) in the model. These may be an important fraction of $OC_{PM_{10}}$ (Winiwarter et al., 2009; Yttri et al., 2011). Local sources are likely to have a relatively large impact on OC_{PBAP}, which complicates the comparison of the regional scale model results to PCM_{10} measurements.

Model performance varies greatly between different sites. A number of stations (especially in the northern part of Europe) are relatively well modelled, with fair correlation between model and measured $TC_{PM_{10}}$, while some other sites are very poorly described by the model (especially Ispra and San Pietro Capofiume, in Italy, and Braganca in Portugal). For Ispra and Braganca the correlation between model and measured $TC_{PM_{10}}$ is close to zero.

For San Pietro Capofiume the correlation deteriorates when the primary OA emissions are treated as partly volatile within the VBS; this is likely a consequence of comparing urban background measurements to regional scale ($50 \times 50\,km^2$) model results. This effect is, however, not seen for the other urban site Gent; this could either be due to less evaporation of POA at lower temperatures or perhaps the measurement site being located further away from major local sources in this city.

There is much less data available for $TC_{PM_{2.5}}$ (Table A2) than for $TC_{PM_{10}}$. The conclusions from comparisons of measured and modelled $TC_{PM_{2.5}}$ are similar as for $TC_{PM_{10}}$. Model results for summer are much better than for winter and there is a tendency that the PAA model gives TC-concentrations in slightly better agreement with observations than the other model versions do.

For the Italian sites (Ispra and Montelibretti) the differences between summer and winter results for $TC_{PM_{2.5}}$ are huge. The PAA model gives reasonably good results for both sites for June 2006 (13 and 29 % underestimation and correlation coefficients of 0.61 and 0.69, respectively). For the winter period (January–February 2007) the observed $TC_{PM_{2.5}}$ of Ispra and Montelibretti were very high (ca. $20\,\mu g(C)m^{-3}$) and the PAA model results are an order of magnitude lower (the model $TC_{PM_{2.5}}$ for the summer period are actually much higher than for the winter period). Dispersion problems could explain some of the wintertime under-prediction, but comparisons for other pollutants (e.g. NO_2, not shown) at these sites show much better agreement than we find here for TC. Consistent with other studies (Simpson et al., 2007; Genberg et al., 2011; Denier van der Gon et al., 2012), this points to major problems in the emission inventory (likely the biomass burning component) for winter emissions in at least the areas around these sites.

6.5.2 Organic Carbon (OC)

Detailed model results for organic carbon for one year are illustrated in Fig. 6 for the site Aspvreten in eastern Sweden. Comparisons of the four different model versions against observed $OC_{PM_{10}}$ are shown. The model calculated $OC_{PM_{10}}$ are split into different source contributions.

Large wildfire contributions to OC are seen in August–September 2002. BSOA is important during summer (in the PAA version) and residential biomass burning during the winter and early spring.

Comparing the model calculated $OC_{PM_{10}}$ to the 48 measurements, during the EC/OC campaign, show that the model underpredicts $OC_{PM_{10}}$ but that there is a reasonably good correlation between modelled and observed concentrations. The PAA model gives the best results at this site with a mean bias of 4 % and a correlation coefficient of 0.78. The PAPA and PAP models also give good results for Aspvreten but NPNA underestimates $OC_{PM_{10}}$ by more than 40 %.

As will be discussed in more detail in Sect. 6.6, the PAA code predicts the highest BSOA levels, and has values of these lying closest to the observation-derived values (at least for summer periods). Figure 7a, b illustrates the results of this model version for a range of sites from the EMEP EC/OC 2002–2003 campaign.

The results shown in these plots and Tables A3 and A5 can be summarised as follows:

- including the VBS approach for primary emissions (and varying degrees of aging of the OA; PAP, PAPA, PAA) results in closer agreement between modelled and observed average OC concentrations than the model version with a traditional treatment of POA as completely non-volatile. However, the gap between observed and modelled concentrations remains substantial, especially for the winter periods.
- Summer levels are quite well captured by the PAA scheme, with the peaks nicely reproduced in many cases.

- Several different sources contribute significantly to $OC_{PM_{10}}$. The importance of the individual sources vary from site to site and is different in winter and summer. The "traditional" SOA components (BSOA and ASOA from VOCs) are most important during the summer months but other sources also contribute during these periods, especially fossil primary (POA + OPOA) OC is important at many locations. Vegetation fires are very important sources of $OC_{PM_{10}}$ during certain episodes. There were large emissions affecting many sites during August–September 2002 and somewhat smaller episodes in March, April and May 2003. For the urban background sites Gent and San Pietro Capofiume as well as for the rural site Penicuik (near Edinburgh) and the regional background site Kollumerwaard in the Netherlands, the fossil fuel OC is a dominant source of $OC_{PM_{10}}$ most of the time. Residential wood burning is an important source during winter at most sites.

- Observations at some sites that are occasionally subject to very clean air, such as the near coastal sites Mace Head (Ireland) and Birkenes (Norway), and Aspvreten (Sweden), Kollumerwaard (the Netherlands) and Penicuik (the UK), indicate that the background OC concentration used in the model ($0.5\,\mu g(C)\,m^{-3}$) is too high, at least during winter. About 10 % of the winter measurements and about 3 % of the summer measurements of TC in PM_{10} are lower than $0.5\,\mu g(C)\,m^{-3}$ (see Figs. 7a, b, A1 and A2). In the near future improvements of the model treatment of OA from the ocean is planned.

6.6 Source apportionment studies

Since the emission input is known by source sector, the model results can be compared to source apportionment (S-A) studies that give information about the relative contributions from different sources to PCM. This may give further indications of the performance of the SOA modules and/or shortcomings of the emission input.

Here we compare model results to three S-A studies which have been analysed with essentially the same methodology: the 2-yr CARBOSOL campaign at sites in central

Europe (Gelencsér et al., 2007), the SORGA campaign in the Oslo region in southern Norway (Yttri et al., 2011), and the Göte-2005 campaign in and close to Gothenburg in southern Sweden (Szidat et al., 2009).

The different studies have split the measured OC and EC into somewhat different components. Here we use the following notation:

Component	OC arising from:
OC_{bb}	wood-burning (residential combustion and vegetation fires)
OC_{onf}	the sum of all non-fossil organic carbon sources other than OC_{bb}, (e.g. biogenic SOA and primary biological particles)
OC_{POA}	fossil OC, from primary emissions
OC_{ASOA}	anthropogenic SOA
OC_{f}	fossil organic carbon, primary or secondary

These components and their derivation have been discussed in the three source-apportionment studies, most recently by Yttri et al. (2011). Some differences exist in the data available from each study, and in the ratios chosen to translate measurements of the tracer to associated OC amounts, but all used the same basic statistical approach initiated in Gelencsér et al. (2007). Instead of just providing one estimate for the relative contribution of different sources to total carbon, this S-A approach recognises uncertainties in the observed data themselves, and in the relationships between tracers and associated OC. Making use of Latin-hypercube-sampling (LHS) to explore the numerous possible uncertain relationships, a statistical distribution of possible solutions was obtained. We make use of the results as expressed through the percentiles (e.g. 5th, 50th, 95th) of these solutions.

Concerning the SORGA and Göte urban sites (Oslo and Gothenburg), it should be noted that in principle the model resolution is not well suited for urban measurements. Although these cities are relatively small (ca. 0.5 million inhabitants), some underestimation of especially the primary emission components should be expected.

The comparison of modelled versus observed components of PCM for summer is given in Table 5, and for winter in Table 6. In general, model results are better for the summer campaigns than for winter.

Model results are also very different for the different campaigns and it is interesting to compare the results for the two Scandinavian campaigns[3]. Norway and Sweden are neighbouring countries and the Oslo and Gothenburg regions are not very far apart. The cities are also of similar sizes.

TC is in good agreement with the observed level in Gothenburg for the two model versions that include aging reactions for SOA (PAPA and PAA) but, as already pointed out, an underestimation is expected within the city so the two model versions without aging of SOA may also be considered fairly good for TC. For the Norwegian sites the PAA model results are in good agreement with the measured TC but less good for the various OC and EC components.

For the summer measurements OC_f is underestimated in both cities, which is not surprising for a coarse resolution model. For Gothenburg the OC_{bb} is in good agreement with the observations but for Oslo the model underestimates the OC_{bb} unless the primary emissions are treated as completely non-volatile (NPNA model). Other non-fossil OC components (OC_{onf}) are underestimated at both sites unless aging reactions are included for BSOA in the model (PAA).

Modelled EC_{bb} is rather low in both cities but above the 10th percentile of the S-A analysis. EC_f is overestimated in Gothenburg, which is somewhat surprising and may indicate too high EC-emissions for this region in the used inventory.

For the rural station Hurdal (70 km NE of Oslo) the model overestimates OC_{bb} relatively much (but the levels are low during summer). OC_{onf} is underestimated even when aging of BSOA is included. OC_f is overestimated when aging reactions are

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[3] The S-A data from the SORGA measurements in Norway are from PM_1 measurements. The model results are for $PM_{2.5}$. Most of the $PM_{2.5}$ mass is expected to be found in PM_1 but, especially for aged aerosol particles, some overestimation can be expected when comparing the model results to the PM_1 measurements.

included for ASOA. Model POA is too high when it is treated as nonvolatile (NPNA). Model errors for the different source categories compensate so that the modelled TC is in good agreement with the observed concentration for the PAPA and PAA model versions.

For the winter campaigns model results are remarkably different for the Norwegian and Swedish studies. For the Swedish Göte campaign the model underestimates OC_{bb} severely but does a good job for the OC_{onf}. Fossil OC and EC are underestimated (as expected). The EC_{bb} is well modelled in contrast to the underestimation of OC_{bb}. The model results for the rural station Råö are good for TC but the individual components are not so well reproduced, with large underestimations of OC_{bb} and OC_f and too high estimates of OC_{onf} and EC_f.

The model results for the SORGA campaign are very different and do not agree well with the winter data from this campaign. Both the biomass burning and other non-fossil contributions are greatly overestimated. EC_f is overestimated as well. At the rural Hurdal station the total fossil OC contribution is in good agreement with the S-A analysis but the fraction of ASOA is greatly underestimated and the primary OA is overestimated. TC is strongly overestimated even for Oslo where an underestimation would be expected with the coarse model resolution used.

The combined results from the SORGA and Göte campaigns point to a too high contribution from background OC in the model during winter. Of the four sites only Gothenburg has OC_{onf} concentrations close to or above the model background OC of $0.5\,\mu g(C)m^{-3}$. This is consistent with the results discussed in Sect. 6.5.

For the CARBOSOL sites (Aveiro in Portugal and K-Puszta in Hungary) the model overestimates summer levels of OC_{bb}. Other non-fossil OC contributions are underestimated. OC_f is rather well captured at K-Puszta but underestimated at Aveiro. For both sites EC_{bb} and EC_f are reasonably well modelled. The TC concentrations are underestimated.

Wintertime OC_{bb} at the CARBOSOL sites are underestimated by more than a factor of ten. Similar results were found by Simpson et al. (2007). That study showed that much higher emissions from wood-burning were required in order to explain the observed levoglucosan levels, and accounting for this would also explain almost all of the discrepancy between modelled and observed TC.

For Aveiro OC_f is also severely underestimated compared to the measurements, much more so than in Simpson et al. (2007), presumably as a result of the different emission inventories in use. Results for K-Puszta are only marginally better, the OC_f is underestimated by a factor of five. EC concentrations are slightly better modelled, being within the 5th-95th percentile for K-Puszta. For Aveiro the EC_{bb} is far below the 5th percentile of the S-A estimate.

Observation-derived BSOA in summertime tends to be higher than produced by most of the VBS schemes, although VBS-PAA comes closest to capturing the observed levels. This should not be taken as proof that the PAA scheme is fundamentally better, as different combinations of BVOC emissions and VBS schemes might well have given similar or even greater levels of BSOA, as we will illustrate in Sect. 6.8. There is a great need to constrain/validate the model BVOC emissions to be able to better constrain the VBS-schemes for BSOA.

6.7 Residential biomass burning emissions

Residential burning of biomass fuels (e.g. wood) is a major source of organic aerosol in Europe but the emission estimates are, along with those of BVOC, among the most uncertain. The comparison of model results to both long-term measurements of OC and source-apportionment data indicate that the wood burning emissions may be underestimated in large parts of Europe in the emission inventory used in this study.

The model results are in general in much poorer agreement with observations for winter than for summer periods. Although the model resolution used in this study cannot capture very local phenomena, such as nearby residential wood burning, under-prediction of wintertime TC seems rather common when multiple sites are studied. Local dispersion in winter conditions (e.g. inversions) is also difficult to treat accurately in a regional scale model, but, as noted in Sect. 6.5, model results for pollutants such as NO_2 are usually much better. As discussed also in

Simpson et al. (2007); Genberg et al. (2011); Gilardoni et al. (2011), the main reason for this winter problem is likely underestimation of emissions from residential biomass burning in some areas of Europe.

The more detailed results from the Scandinavian S-A studies (Sect. 6.6) also indicate that the biomass burning emissions in the Gothenburg region in Sweden were severely underestimated during winter while the opposite was found in the Oslo region in Norway, where the emissions used in the model seem to be heavily overestimated during the winter period. A recent study by Genberg et al. (2011) has also shown much larger contributions of biomass burning to OC in southern Sweden than model estimates using the same emission inventory as in the present study.

To investigate this further we compared the activity data and related PM and OC emissions from residential wood combustion in Norway and Sweden. Total wood use in Sweden is about 60 % higher than in Norway, however, the estimated OC emission for Sweden for this sector is a factor of 14 lower than for Norway!

The difference can be traced back to the reported PM emissions by country for residential combustion. Denier van der Gon et al. (2009) applied specific fractions for EC and OC to PM emissions derived from the IIASA GAINS model. The IIASA GAINS model determines PM emissions bottom-up but then goes through specific country consultation sessions to optimise the use of national data. In this case the Norwegian $PM_{2.5}$ emissions according to GAINS is about a factor of ten higher than the Swedish $PM_{2.5}$ emission for the same source sector. Since EC and OC were estimated as a fraction of PM, also the EC and OC emissions differ dramatically. This discrepancy explains why the comparison between measured and modelled concentrations can be dramatically different for two neighbouring countries.

In a follow-up study (Denier van der Gon et al., 2012), we will present results from an alternative EC and OC emission inventory for residential combustion by using consistent direct emission factors per unit of activity for all European countries.

6.8 Comparison to AMS measurements

Model calculated OM concentrations are compared to AMS measurements from Payerne in Switzerland for the period 31 May to 3 July 2006. These measurements were part of the EMEP intensive measurement period in 2006 and were performed by PSI (Lanz et al., 2010). Examples of results are presented in Fig. 8 and Table 7. All model versions underestimate the observed OM-concentrations. Differences are large between the different versions. When primary emissions are treated as nonvolatile and no aging reactions are included for the SOA (NPNA) the model $OM_{PM_{2.5}}$ is a factor of three lower than the observed AMS OM-concentrations. Model results improve when aging reactions are included for both the primary emissions and SOA. With the PAA version the model concentration is on the average 27 % lower than the AMS measurements.

Since the biogenic SOA is very important during summer, and the BVOC-emissions are highly uncertain, a sensitivity test was performed, with the PAA model version, with three times larger emissions of terpene and isoprene. This gives an indication of the level of uncertainty that the BVOC-emissions introduce in the model results. The higher BVOC-emissions lead to higher $OM_{PM_{2.5}}$ concentrations at Payerne and for the first half of the measurement campaign the agreement with AMS measurements is much better than with standard emissions. However, for the last week of the campaign the model now overshoots the observed concentrations dramatically and for the period as a whole there is no clear improvement when BVOC emissions are tripled.

A detailed modelling study covering the Payerne AMS measurements has been performed by Aksoyoglu et al. (2011). They used the CAMx model with 1-way nesting from the European scale down to a $3 \times 3\,\mathrm{km}^2$ resolution grid covering Switzerland. The model included ASOA formation from aromatics and BSOA from isoprene, terpenes and sesquiterpenes; oligomerisation reactions were also included in a simplified way. POA emissions were treated as non-volatile. In spite of the coarser model resolution, the EMEP VBS-PAA model gives OM results of similar quality (or even slightly better) than the CAMx model results in Aksoyoglu et al. (2011) for the June measurements at Payerne (see Table 7).

Factor analysis of the AMS-data indicate that about 6 % of the OA is primary OA (Lanz et al., 2010; Aksoyoglu et al., 2011). When primary emissions are treated as non-volatile (traditional approach) the POA-fraction is overestimated (the NPNA model gives 23 % POA, similar to the 26 % calculated by Aksoyoglu et al., 2011). The model versions that treat the primary emissions within the VBS-system (PAP, PAPA, PAA) seem to give more realistic fractions of fresh POA at Payerne during summer (ca. 3–4 %). These results support the idea that models (and emission inventories) need to take into account the volatility distribution and atmospheric aging of primary OA for a realistic description of the properties of the organic aerosol.

7 Conclusions

The EMEP chemical transport model for Europe has been extended with a new scheme for treatment of organic aerosol by the volatility basis set (VBS) approach. Different assumptions regarding the primary OA emissions and aging of POA and SOA have been tested in long-term model simulations for the years 2002–2007. The main conclusions from these simulations and comparisons to observations are as follows:

- compared to earlier studies of organic aerosol in Europe with the EMEP model the new model versions indicate that several different sources contribute significantly to OA. The relative importance of BSOA (from terpenes and isoprene) is much lower than in the previous model versions and, on an annual average basis, fossil sources are found to be of similar importance as BSOA with the new model.
- Summertime OA is dominated by BSOA, although with important contributions from wildfires. Wintertime OA has important contributions from biomass-burning, as well as fossil sources. Since there are large sources of non-fossil OM at all times of year (BSOA, biomass burning, wildfires, background OM) the total OC in the model is dominated by modern carbon.

- Vegetation fire emissions contributed significantly to average concentrations of $OM_{PM_{2.5}}$ in large parts of Europe, especially the eastern part of Europe and the western part of the Iberian peninsula.
- The model/emission combinations tested in this study are not able to reproduce winter time levels of particulate carbonaceous matter in Europe. The problems may to a large extent be due to known problems with the emission estimates for wood-burning. A new bottom-up emission inventory for emissions from residential heating by biomass combustion is likely to improve winter results substantially for the organic part of the PCM.
- The differences in results shown here between model versions treating primary OA emissions as either non-volatile or of variable volatility (and subject to atmospheric aging) indicate that it is very important to determine the volatility distribution of primary OA emissions, and the atmospheric reactivity of the POA, to be able to model long-range transport in a realistic way. If a large part of the primary emissions are in the intermediate volatility range (and thus in the gas phase at the emission) and then age in the atmosphere to condense at a later time, long range transport will be much more important than what is found when the traditional assumptions regarding the emissions are used.
- Some of the VBS schemes used here produce summertime results for OA that are in fair agreement with observed values. Model schemes that allow aging of SOA appear to perform somewhat better than those with limited or no aging.
- For summer periods, major model uncertainties are related to the assumed BVOC emissions. This means that there is a great need to validate BVOC emission schemes against observational data.
- Further work is also needed to better estimate background/boundary concentrations of organic aerosol (due to oceanic (sea-spray) sources) and primary biological OA.

Future plans involve further work investigating alternative (bottom-up) emission estimates for residential wood burning in Europe, and further detailed comparison of the model with newly available filter and AMS data. Major data-sets involve the EMEP intensive of 2008–2009 and data from the EU EUSAAR (e.g. Laj et al., 2009) and EUCAARI projects (Kulmala et al., 2011).

In addition, the use of more complex representations of OA needs to be considered. For example the 2-D VBS scheme (Jimenez et al., 2009; Donahue et al., 2011) offers more realism in the oxidation and fragmentation pathways. It is an open question at this stage, especially considering the uncertainty in emissions, whether such schemes will improve our ability to simulate ambient OA concentrations.

Further development work is also planned on the model description for the boundary/background OA from oceanic (sea-spray) sources.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/12/5425/2012/ acpd-12-5425-2012-supplement.pdf.

Acknowledgements. This work was funded by the Swedish Clean Air Research Programme (SCARP), the EU FP6 EUCAARI project (No. 34684), the Norwegian SORGA project, as well as by EMEP under UNECE.

References

Aas, W., Tsyro, S., Bieber, E., Bergström, R., Ceburnis, D., Ellermann, T., Fagerli, H., Frölich, M., Gehrig, R., Makkonen, U., Nemitz, E., Otjes, R., Perez, N., Perrino, C., Prévôt, A. S. H., Putaud, J.-P., Simpson, D., Spindler, G., Vana, M., and Yttri, K. E.: Lessons learnt from the first EMEP intensive measurement periods, Atmos. Chem. Phys. Discuss., 12, 3731–3780, doi:10.5194/acpd-12-3731-2012, 2012. 5436

Aiken, A. C., Decarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prévôt, A. S. H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J. L.: O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry, Environ. Sci. Technol., 42, 4478–4485, doi:10.1021/es703009q, 2008. 5432, 5435, 5443

Aksoyoglu, S., Keller, J., Barmpadimos, I., Oderbolz, D., Lanz, V. A., Prévôt, A. S. H., and Baltensperger, U.: Aerosol modelling in Europe with a focus on Switzerland during summer and winter episodes, Atmos. Chem. Phys., 11, 7355–7373, doi:10.5194/acp-11-7355-2011, 2011. 5455, 5456, 5476

Andersson-Sköld, Y. and Simpson, D.: Comparison of the chemical schemes of the EMEP MSC-W and the IVL photochemical trajectory models, Atmos. Environ., 33, 1111–1129, 1999. 5430

Andersson-Sköld, Y. and Simpson, D.: Secondary organic aerosol formation in Northern Europe: a model study, J. Geophys. Res., 106, 7357–7374, 2001. 5428, 5431

Benedictow, A.: Documentation and verification of the 1999 PARLAM-PS meteorological fields used as input for Eulerian EMEP model, Tech. Rep., The Norwegian Meteorological Institute, Oslo, Norway, research Note no. 111., (Reports also available for 1980,1985,1995,1999, 2000 and 2001, see www.emep.int), 2003. 5431

Berge, E. and Jakobsen, H. A.: A regional scale multi-layer model for the calculation of long-term transport and deposition of air pollution in Europe, Tellus, 50, 205–223, 1998. 5430

Bessagnet, B., Menut, L., Curci, G., Hodzic, A., Guillaume, B., Liousse, C., Moukhtar, S., Pun, B., Seigneur, C., and Schulz, M.: Regional modeling of carbonaceous aerosols over Europe-focus on secondary organic aerosols, J. Atmos. Chem., 61, 175–202, doi:10.1007/s10874-009-9129-2, 2008. 5433, 5443

Bessagnet, B., Seigneur, C., and Menut, L.: Impact of dry deposition of semi-volatile organic compounds on secondary organic aerosols, Atmos. Environ., 44, 1781–1787, doi:10.1016/j.atmosenv.2010.01.027, 2010. 5431

Bjørge, D. and Skålin, R.: PARLAM – the parallel HIRLAM version at DNMI, Research Report 27, The Norwegian Meteorological Institute, Oslo, Norway, 1995. 5430

Canagaratna, M. R., Jayne, J. T., Jimenez, J. L., Allan, J. D., Alfarra, M. R., Zhang, Q., Onasch, T., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L. R., Trimborn, A. M., Northway, M. J., DeCarlo, P. F., Kolb, C. E. Davidovits, P., and Worsnop, D. R.: Chemical and microphysical characterization of ambient aerosols with the aerosol mass spectrometer, Mass

Spectrom. Rev., 26, 185–222, 2007. 5436

Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.: Elemental analysis of chamber organic aerosol using an aerodyne high-resolution aerosol mass spectrometer, Atmos. Chem. Phys., 10, 4111–4131, doi:10.5194/acp-10-4111-2010, 2010. 5438

Denier van der Gon, H., Visschedijk, A., Droge, R., Mulder, M., Johansson, C., and Klimont, Z.: A high resolution emission inventory of particulate elemental carbon and organic carbon for Europe in 2005, paper presented at 7th International Conference on Air Quality – Science and Application (Air Quality 2009), Istanbul, 24–27 March 2009, 2009. 5433, 5454

Denier van der Gon, H., Visschedijk, A., Pandis, S., Fountoukis, C., Bergström, R., Simpson, D., and Johansson, C.: Particulate emissions from residential wood combustion in Europe – revised estimates and an evaluation, in prep., 2012. 5447, 5454

Donahue, N. M., Robinson, A. L., Stanier, C. O., and Pandis, S. N.: Coupled Partitioning, Dilution, and Chemical Aging of Semivolatile Organics, Environ. Sci. Technol., 40, 2635–2643, doi:10.1021/es052297c, 2006. 5429, 5436

Donahue, N. M., Robinson, A. L., and Pandis, S. N.: Atmospheric organic particulate matter: From smoke to secondary organic aerosol, Atmos. Environ., 43, 94–106, doi:10.1016/j.atmosenv.2008.09.055, 2009. 5429, 5436

Donahue, N. M., Epstein, S. A., Pandis, S. N., and Robinson, A. L.: A two-dimensional volatility basis set: 1. organic-aerosol mixing thermodynamics, Atmos. Chem. Phys., 11, 3303–3318, doi:10.5194/acp-11-3303-2011, 2011. 5458

Duhl, T. R., Helmig, D., and Guenther, A.: Sesquiterpene emissions from vegetation: a review, Biogeosciences, 5, 761–777, doi:10.5194/bg-5-761-2008, 2008. 5432

El-Zanan, H. S., Zielinska, B., Mazzoleni, L. R., and Hansen, D. A.: Analytical Determination of the Aerosol Organic Mass-to-Organic Carbon Ratio, J. Air Waste Manag. Assoc., 59, 58–69, 2009. 5428

Epstein, S. A., Riipinen, I., and Donahue, N. M.: A Semiempirical Correlation between Enthalpy of Vaporization and Saturation Concentration for Organic Aerosol, Environ. Sci. Technol., 44, 743–748, doi:10.1021/es902497z, 2010. 5438

Fountoukis, C., Racherla, P. N., Denier van der Gon, H. A. C., Polymeneas, P., Charalampidis, P. E., Pilinis, C., Wiedensohler, A., Dall'Osto, M., O'Dowd, C., and Pandis, S. N.: Evaluation of a three-dimensional chemical transport model (PMCAMx) in the European domain during the EUCAARI May 2008 campaign, Atmos. Chem. Phys., 11, 10331–10347, doi:10.5194/acp-11-10331-2011, 2011. 5437, 5438, 5444, 5445

Gelencsér, A., May, B., Simpson, D., Sánchez-Ochoa, A., Kasper-Giebl, A., Puxbaum, H., Caseiro, A., Pio, C., and Legrand, M.: Source apportionment of $PM_{2.5}$ organic aerosol over Europe: primary/secondary, natural/anthropogenic, fossil/biogenic origin, J. Geophys. Res., 112, D23S04, doi:10.1029/2006JD008094, 2007. 5428, 5430, 5435, 5450, 5473

Genberg, J., Hyder, M., Stenström, K., Bergström, R., Simpson, D., Fors, E. O., Jönsson, J. Å., and Swietlicki, E.: Source apportionment of carbonaceous aerosol in southern Sweden, Atmos. Chem. Phys., 11, 11387–11400, doi:10.5194/acp-11-11387-2011, 2011. 5447, 5454

Giglio, L., Descloitres, J., Justice, C., and Kaufman, Y.: An enhanced contextual fire detection algorithm for MODIS, Remote Sens. Environ., 87, 273–282, doi:10.1016/S0034-4257(03)00184-6, 2003. 5432

Gilardoni, S., Vignati, E., Cavalli, F., Putaud, J. P., Larsen, B. R., Karl, M., Stenström, K., Genberg, J., Henne, S., and Dentener, F.: Better constraints on sources of carbonaceous aerosols using a combined ^{14}C – macro tracer analysis in a European rural background site, Atmos. Chem. Phys., 11, 5685–5700, doi:10.5194/acp-11-5685-2011, 2011. 5454

Guenther, A., Zimmerman, P., Harley, P., Monson, R., and Fall, R.: Isoprene and monoterpene rate variability: model evaluations and sensitivity analyses, J. Geophys. Res., 98, 12609–12617, 1993. 5432

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155–5236, doi:10.5194/acp-9-5155-2009, 2009. 5428, 5444

Hildebrandt, L., Donahue, N. M., and Pandis, S. N.: High formation of secondary organic aerosol from the photo-oxidation of toluene, Atmos. Chem. Phys., 9, 2973–2986, doi:10.5194/acp-9-2973-2009, 2009. 5438, 5444

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prévôt, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of Organic Aerosols in the Atmosphere, Science, 326, 1525–1529, doi:10.1126/science.1180353, 2009. 5458

Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, Atmos. Chem. Phys., 5, 1053–1123, doi:10.5194/acp-5-1053-2005, 2005. 5427

Karl, M., Guenther, A., Köble, R., Leip, A., and Seufert, G.: A new European plant-specific emission inventory of biogenic volatile organic compounds for use in atmospheric transport models, Biogeosciences, 6, 1059–1087, doi:10.5194/bg-6-1059-2009, 2009. 5432

Kesik, M., Ambus, P., Baritz, R., Brüggemann, N., Butterbach-Bahl, K., Damm, M., Duyzer, J., Horváth, L., Kiese, R., Kitzler, B., Leip, A., Li, C., Pihlatie, M., Pilegaard, K., Seufert, S., Simpson, D., Skiba, U., Smiatek, G., Vesala, T., and Zechmeister-Boltenstern, S.: Inventories of N_2O and NO emissions from European forest soils, Biogeosciences, 2, 353–375, doi:10.5194/bg-2-353-2005, 2005. 5432

Köble, R. and Seufert, G.: Novel Maps for Forest Tree Species in Europe., in: A Changing Atmosphere, 8th European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants, Torino, Italy, 17–20 September 2001., available at: http://ies.jrc.ec.europa.eu/Units/cc/events/torino2001/torinocd/Documents/Terrestrial/TP35.htm, 2012-02-15, 2001. 5432

Kulmala, M., Asmi, A., Lappalainen, H. K., Baltensperger, U., Brenguier, J.-L., Facchini, M. C., Hansson, H.-C., Hov, Ø., O'Dowd, C. D., Pöschl, U., Wiedensohler, A., Boers, R., Boucher, O., de Leeuw, G., Denier van der Gon, H. A. C., Feichter, J., Krejci, R., Laj, P., Lihavainen, H., Lohmann, U., McFiggans, G., Mentel, T., Pilinis, C., Riipinen, I., Schulz, M., Stohl, A., Swietlicki, E., Vignati, E., Alves, C., Amann, M., Ammann, M., Arabas, S., Artaxo, P., Baars, H., Beddows, D. C. S., Bergström, R., Beukes, J. P., Bilde, M., Burkhart, J. F., Canonaco, F., Clegg, S. L., Coe, H., Crumeyrolle, S., D'Anna, B., Decesari, S., Gilardoni, S., Fischer, M., Fjaeraa, A. M., Fountoukis, C., George, C., Gomes, L., Halloran, P., Hamburger, T., Harrison, R. M., Herrmann, H., Hoffmann, T., Hoose, C., Hu, M., Hyvärinen, A., Hõrrak, U., Iinuma, Y., Iversen, T., Josipovic, M., Kanakidou, M., Kiendler-Scharr, A., Kirkevåg, A., Kiss, G., Klimont, Z., Kolmonen, P., Komppula, M., Kristjánsson, J.-E., Laakso, L., Laaksonen, A., Labonnote, L., Lanz, V. A., Lehtinen, K. E. J., Rizzo, L. V., Makkonen, R., Manninen, H. E., McMeeking, G., Merikanto, J., Minikin, A., Mirme, S., Morgan, W. T., Nemitz, E., O'Donnell, D., Panwar, T. S., Pawlowska, H., Petzold, A., Pienaar, J. J., Pio, C., Plass-Duelmer, C., Prévôt, A. S. H., Pryor, S., Reddington, C. L., Roberts, G., Rosenfeld, D., Schwarz, J., Seland, Ø., Sellegri, K., Shen, X. J., Shiraiwa, M., Siebert, H., Sierau, B., Simpson, D., Sun, J. Y., Topping, D., Tunved, P., Vaattovaara, P., Vakkari, V., Veefkind, J. P., Visschedijk, A., Vuollekoski, H., Vuolo, R., Wehner, B., Wildt, J., Woodward, S., Worsnop, D. R., van Zadelhoff, G.-J., Zardini, A. A., Zhang, K., van Zyl, P. G., Kerminen, V.-M., S Carslaw, K., and Pandis, S. N.: General overview: European Integrated project on Aerosol Cloud Climate and Air Quality interactions (EUCAARI) – integrating aerosol research from nano to global scales, Atmos. Chem. Phys., 11, 13061–13143, doi:10.5194/acp-11-13061-2011, 2011. 5430, 5433, 5458

Kupiainen, K. and Klimont, Z.: Primary emissions of submicron and carbonaceous particles and the potential for their control., IIASA IR-04-079, International Institute for Applied Systems Analysis (IIASA), 2004. 5434

Kupiainen, K. and Klimont, Z.: Primary emissions of fine carbonaceous particles in Europe, Atmos. Environ., 41, 2156–2170, doi:10.1016/j.atmosenv.2006.10.066, 2007. 5434

Laj, P., Klausen, J., Bilde, M., Plaß-Duelmer, C., Pappalardo, G., Clerbaux, C., Baltensperger, U., Hjorth, J., Simpson, D., Reimann, S., Coheur, P.-F., Richter, A., Mazière, M. D., Rudich, Y., McFiggans, G., Torseth, K., Wiedensohler, A., Morin, S., Schulz, M., Allan, J., Attié, J.-L., Barnes, I., Birmilli, W., Cammas, P., Dommen, J., Dorn, H.-P., Fowler, D., Fuzzi, J.-S., Glasius, M., Granier, C., Hermann, M., Isaksen, I., Kinne, S., Koren, I., Madonna, F., Maione, M., Massling, A., Moehler, O., Mona, L., Monks, P., Müller, D., Müller, T., Orphal, J., Peuch, V.-H., Stratmann, F., Tanré, D., Tyndall, G., Riziq, A., Roozendael, M. V., Villani, P., Wehner, B., Wex, H., and Zardini, A.: Measuring Atmospheric Composition Change, Atmos. Environ., 43, 5351–5414, doi:10.1016/j.atmosenv.2009.08.020, 2009. 5458

Lane, T. E., Donahue, N. M., and Pandis, S. N.: Effect of NO_x on secondary organic aerosol concentrations, Environ. Sci. Technol., 42, 6022–6027, doi:10.1021/es703225a, 2008a. 5437, 5438, 5469

Lane, T. E., Donahue, N. M., and Pandis, S. N.: Simulating secondary organic aerosol formation using the volatility basis-set approach in a chemical transport model, Atmos. Environ., 42, 7439–7451, doi:10.1016/j.atmosenv.2008.06.026, 2008b. 5437, 5439, 5469

Lanz, V. A., Prévôt, A. S. H., Alfarra, M. R., Weimer, S., Mohr, C., DeCarlo, P. F., Gianini, M.

F. D., Hueglin, C., Schneider, J., Favez, O., D'Anna, B., George, C., and Baltensperger, U.: Characterization of aerosol chemical composition with aerosol mass spectrometry in Central Europe: an overview, Atmos. Chem. Phys., 10, 10453–10471, doi:10.5194/acp-10-10453-2010, 2010. 5428, 5430, 5436, 5455, 5456, 5476

Legrand, M. and Puxbaum, H.: Summary of the CARBOSOL project: Present and retrospective state of organic versus inorganic aerosol over Europe, J. Geophys. Res., 112, D23S01, doi:10.1029/2006JD008271, 2007. 5428, 5435

McDonald, J. D., Eide, I., Seagrave, J., Zielinska, B., Whitney, K., Lawson, D. R., and Mauderly, J. L.: Relationship between Composition and Toxicity of Motor Vehicle Emission Samples, Environ. Health Persp., 112, 1527–1538, 2004. 5427

Murphy, B. N. and Pandis, S. N.: Simulating the Formation of Semivolatile Primary and Secondary Organic Aerosol in a Regional Chemical Transport Model, Environ. Sci. Technol., 43, 4722–4728, doi:10.1021/es803168a, 2009. 5437, 5440, 5469

Ng, N. L., Kroll, J. H., Chan, A. W. H., Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from *m*-xylene, toluene, and benzene, Atmos. Chem. Phys., 7, 3909–3922, doi:10.5194/acp-7-3909-2007, 2007. 5438, 5444

Novakov, T. and Penner, J.: Large contribution of organic aerosols to cloud condensation nuclei concentrations, Nature, 365, 823–826, 1993. 5427

Pathak, R. K., Presto, A. A., Lane, T. E., Stanier, C. O., Donahue, N. M., and Pandis, S. N.: Ozonolysis of α-pinene: parameterization of secondary organic aerosol mass fraction, Atmos. Chem. Phys., 7, 3811–3821, doi:10.5194/acp-7-3811-2007, 2007. 5438

Pio, C. A., Legrand, M., Oliveira, T., Afonso, J., Santos, C., Caseiro, A., Fialho, P., Barata, F., Puxbaum, H., Sanchez-Ochoa, A., Kasper-Giebl, A., Gelencser, A., Preunkert, S., and Schock, M.: Climatology of aerosol composition (organic versus inorganic) at nonurban sites on a west-east transect across Europe, J. Geophys. Res., 112, D23S02, doi:10.1029/2006JD008038, 2007. 5435

Putaud, J.-P., Raes, F., Van Dingenen, R., Bruggemann, E., Facchini, M. C., Decesari, S., Fuzzi, S., Gehrig, R., Huglin, C., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Muller, K., Querol, X., Rodriguez, S., Schneider, J., Spindler, G., Brink, H. t., Torseth, K., and Wiedensohler, A.: A European aerosol phenomenology-2: chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe, Atmos. Environ., 38, 2579–2595, 2004. 5428

Robinson, A. L., Donahue, N. M., Shrivastava, M. K., Weitkamp, E. A., Sage, A. M., Grieshop, A. P., Lane, T. E., Pierce, J. R., and Pandis, S. N.: Rethinking Organic Aerosols: Semivolatile Emissions and Photochemical Aging, Science, 315, 1259–1262, doi:10.1126/science.1133061, 2007. 5437, 5439

Shrivastava, M. K., Lane, T. E., Donahue, N. M., Pandis, S. N., and Robinson, A. L.: Effects of gas particle partitioning and aging of primary emissions on urban and regional organic aerosol concentrations, J. Geophys. Res., 113, D18301, doi:10.1029/2007JD009735, 2008. 5437, 5439, 5469

Simon, H., Bhave, P. V., Swall, J. L., Frank, N. H., and Malm, W. C.: Determining the spatial and seasonal variability in OM/OC ratios across the US using multiple regression, Atmos. Chem. Phys., 11, 2933–2949, doi:10.5194/acp-11-2933-2011, 2011. 5442

Simpson, D., Winiwarter, W., Börjesson, G., Cinderby, S., Ferreiro, A., Guenther, A., Hewitt, C. N., Janson, R., Khalil, M. A. K., Owen, S., Pierce, T. E., Puxbaum, H., Shearer, M., Skiba, U., Steinbrecher, R., Tarrasón, L., and Öquist, M. G.: Inventorying emissions from Nature in Europe, J. Geophys. Res., 104, 8113–8152, 1999. 5432

Simpson, D., Fagerli, H., Jonson, J., Tsyro, S., Wind, P., and Tuovinen, J.-P.: The EMEP Unified Eulerian Model. Model Description, EMEP MSC-W Report 1/2003, The Norwegian Meteorological Institute, Oslo, Norway, 2003. 5430

Simpson, D., Yttri, K., Klimont, Z., Kupiainen, K., Caseiro, A., Gelencsér, A., Pio, C., and Legrand, M.: Modeling Carbonaceous Aerosol over Europe. Analysis of the CARBOSOL and EMEP EC/OC campaigns, J. Geophys. Res., 112, D23S14, doi:10.1029/2006JD008158, 2007. 5428, 5429, 5431, 5435, 5443, 5444, 5447, 5452, 5453, 5454

Simpson, D., Benedictow, A., Berge, H., Bergström, R., Emberson, L. D., Fagerli, H., Hayman, G. D., Gauss, M., Jonson, J. E., Jenkin, M. E., Nyíri, A., Richter, C., Semeena, V. S., Tsyro, S., Tuovinen, J.-P., Valdebenito, Á., and Wind, P.: The EMEP MSC-W chemical transport model – Part 1: Model description, Atmos. Chem. Phys. Discuss., 12, 3781–3874, doi:10.5194/acpd-12-3781-2012, 2012. 5429, 5430, 5431, 5432, 5435

Szidat, S., Ruff, M., Perron, N., Wacker, L., Synal, H.-A., Hallquist, M., Shannigrahi, A. S., Yttri, K. E., Dye, C., and Simpson, D.: Fossil and non-fossil sources of organic carbon (OC) and elemental carbon (EC) in Göteborg, Sweden, Atmos. Chem. Phys., 9, 1521–1535, doi:10.5194/acp-9-1521-2009, 2009. 5430, 5436, 5450

Tarrasón, L., Fagerli, H., Gauss, M., Nyíri, A., Simpson, D., Tsyro, S., and Aas, W.: S, N and O_3 in EECCA countries, in: Transboundary Acidification, Eutrophication and Ground Level Ozone in Europe in 2006. EMEP Status Report 1/2008, 67–86, The Norwegian Meteorological Institute, Oslo, Norway, 2008. 5431

Tsimpidi, A. P., Karydis, V. A., Zavala, M., Lei, W., Molina, L., Ulbrich, I. M., Jimenez, J. L., and Pandis, S. N.: Evaluation of the volatility basis-set approach for the simulation of organic aerosol formation in the Mexico City metropolitan area, Atmos. Chem. Phys., 10, 525–546, doi:10.5194/acp-10-525-2010, 2010. 5438, 5469

Tsyro, S., Simpson, D., Tarrasón, L., Kupiainen, K., Klimont, Z., Yttri, K., and Pio, C.: Modelling of black carbon over Europe, J. Geophys. Res., 112, D23S19, doi:10.1029/2006JD008164, 2007. 5432

Turpin, B. J. and Lim, H. J.: Species contributions to $PM_{2.5}$ mass concentrations: Revisiting common assumptions for estimating organic mass, Aerosol Sci. Technol., 35, 602–610, 2001. 5428, 5442, 5443

UN-ECE: International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests. Manual on methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests, updated version available at: (http://icp-forests.net), 2012-02-15, 1998. 5432

van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Kasibhatla, P. S., and Arellano Jr., A. F.: Interannual variability in global biomass burning emissions from 1997 to 2004, Atmos. Chem. Phys., 6, 3423–3441, doi:10.5194/acp-6-3423-2006, 2006. 5432

Visschedijk, A. J. H., Denier van der Gon, H. A. C., Dröge, R., and Van der Brugh, H.: A European high resolution and size-differentiated emission inventory for elemental and organic carbon for the year 2005, TNO TNO-034-UT-2009-00688_PT-ML, TNO, Utrecht, The Netherlands, 2009. 5433, 5434

Watson, J., Chow, J., and Chen, L.-W.: Summary of organic and elemental carbon/black carbon analysis methods and intercomparisons, Aerosol Air Qual. Res., 5, 65–102, http://www.aaqr.org, 2005. 5433

Winiwarter, W., Bauer, H., Caseiro, A., and Puxbaum, H.: Quantifying emissions of primary biological aerosol particle mass in Europe, Atmos. Environ., 43, 1403–1409, doi:10.1016/j.atmosenv.2008.01.037, 2009. 5446

Yttri, K. E., Aas, W., Bjerke, A., Cape, J. N., Cavalli, F., Ceburnis, D., Dye, C., Emblico, L., Facchini, M. C., Forster, C., Hanssen, J. E., Hansson, H. C., Jennings, S. G., Maenhaut, W., Putaud, J. P., and Trseth, K.: Elemental and organic carbon in PM_{10}: a one year measurement campaign within the European Monitoring and Evaluation Programme EMEP, Atmos. Chem. Phys., 7, 5711–5725, doi:10.5194/acp-7-5711-2007, 2007. 5428, 5436

Yttri, K., Aas, W., Tørseth, K., Stebel, K., Nyíri, A., Tsyro, S., Merckova, K., Wankmüller, R., Winiwarter, W., Bauer, H., Caseiro, A., Puxbaum, H., Holzer-Popp, T., and Schroedter-Homscheidt, M.: Transboundary particulate matter in Europe – Status report 2008, EMEP Status Report 4/2008, NILU, available at: http://www.emep.int, 2012-02-15, 2008. 5436

Yttri, K. E., Simpson, D., Stenström, K., Puxbaum, H., and Svendby, T.: Source apportionment of the carbonaceous aerosol in Norway – quantitative estimates based on 14C, thermal-optical and organic tracer analysis, Atmos. Chem. Phys., 11, 9375–9394, doi:10.5194/acp-11-9375-2011, 2011. 5430, 5436, 5446, 5450

Table 1. Estimated EC and OC emissions (<2.5 µm) for UNECE Europe in 2005 by source sector (ktonnes(C) yr^{-1}).

SNAP Description	EC kt yr^{-1}	%	OC kt yr^{-1}	%
1. Combustion in energy industries	20	3	11	1
2. Residential and non-industrial combustion	186	30	395	47
3. Combustion in manufacturing industry	6	1	9	1
4. Production processes	36	6	81	10
5. Extraction and distribution of fossil fuels	4	1	1	0
6. Solvent use	0	0	0	0
7. Road transport	201	32	104	12
8. Other mobile sources and machinery	95	15	71	8
9. Waste treatment and disposal	37	6	63	7
10. Agriculture	36	6	112	13
Total excluding international shipping	623	100	848	100
International shipping	124		84	

Table 2. Summary of the four EMEP VBS versions used in this study.

Version	Volatility distributed POA?	POA/SOA aging reactions	References
VBS-NPNA	No, POA nonvolatile	None	Lane et al. (2008a) Tsimpidi et al. (2010)
VBS-PAP	Yes	POA (4.0×10^{-11} cm^{3}molecule^{-1}s^{-1})	Shrivastava et al. (2008)
VBS-PAPA	Yes	POA (4.0×10^{-11} cm^{3}molecule^{-1}s^{-1}), ASOA (1.0×10^{-11} cm^{3}molecule^{-1}s^{-1})	Murphy and Pandis (2009)
VBS-PAA	Yes	POA (4.0×10^{-11} cm^{3}molecule^{-1}s^{-1}), ASOA & BSOA (4.0×10^{-12} cm^{3}molecule^{-1}s^{-1})	Lane et al. (2008b)

Table 3. Mass yields of the semi-volatile surrogate species, with 298 K saturation concentrations of 1, 10, 100 and 1000 µg m^{-3}, for the EMEP model SOA precursors, for the high- and low-NO$_x$ cases (corresponding to peroxy radical reaction with NO and HO$_2$, respectively).

Precursor	α-values (mass based stoichiometric yields)							
	High-NO$_x$ Case				Low-NO$_x$ Case			
	1	10	100	1000	1	10	100	1000
Alkanes	0	0.038	0	0	0	0.075	0	0
Alkenes	0.001	0.005	0.038	0.15	0.005	0.009	0.060	0.225
Aromatics	0.002	0.195	0.3	0.435	0.075	0.3	0.375	0.525
Isoprene	0.001	0.023	0.015	0	0.009	0.03	0.015	0
Terpenes	0.012	0.122	0.201	0.5	0.107	0.092	0.359	0.608

Notes: Alkanes (excluding C_2H_6), alkenes (excluding C_2H_4) and aromatics are represented by the surrogates n-butane, propene, o-xylene in the EMEP chemistry.

Table 4. Filter measurements of Total Carbon (TC) in PM_{10}. Comparison of model results (four different model versions, see text) to data from field campaigns in 2002–2007. Unit: $\mu g(C) m^{-3}$.

	N	Observed	VBS-NPNA	VBS-PAP	VBS-PAPA	VBS-PAA
CARBOSOL (October 2002–June 2004):						
Schauinsland	104	2.69	2.11	2.21	2.42	2.67
Puy de Dome	86	1.74	1.80	1.85	1.99	2.16
EMEP EC/OC (July 2002–June 2003):						
Virolahti	51	2.44	1.71	2.16	2.25	2.51
Aspvreten	48	2.41	1.63	2.13	2.25	2.48
Birkenes(2002–2004)	267	1.19	1.28	1.45	1.53	1.65
Penicuik	50	2.04	1.54	1.58	1.67	1.74
Kollumerwaard	50	3.22	2.30	2.44	2.60	2.78
Gent	52	5.92	3.81	3.53	3.69	3.82
Mace Head	50	1.39	0.86	0.98	1.04	1.10
Langenbrügge	50	4.93	1.99	2.27	2.44	2.68
Kosetice	38	5.59	2.46	2.56	2.70	2.80
Stara Lesna	52	5.12	2.20	2.68	2.86	3.17
Illmitz	50	6.51	2.36	2.67	2.88	3.20
Ispra	45	9.62	2.75	2.71	3.07	3.31
Braganca	50	4.89	1.31	1.53	1.61	1.72
San Pietro Capofiume	50	7.35	2.45	2.64	2.95	3.36
EMEP intensive PM measurement period summer 2006:						
Birkenes	30	1.15	0.90	1.07	1.18	1.35
Harwell	17	1.33	1.58	1.61	1.86	1.97
Melpitz	31	4.38	1.49	1.65	1.92	2.49
Kosetice	21	2.81	1.50	1.68	1.97	2.66
Montelibretti	31	5.43	1.69	1.84	2.26	3.27
Montseny	2	3.04	2.43	2.97	3.58	4.70
EMEP intensive PM measurement period winter 2007:						
Birkenes	34	0.66	0.78	0.80	0.80	0.80
Melpitz	33	2.36	1.29	1.21	1.21	1.21
Kosetice	29	2.39	1.76	1.59	1.59	1.59
Montelibretti	31	16.8	2.02	1.85	1.89	1.89
Montseny	4	1.54	3.23	2.97	3.09	3.10
All Data	1356	3.57	1.80	1.94	2.08	2.29
correlation coeff. (r)			0.45	0.38	0.39	0.38
mean absolute error			2.16	2.12	2.05	1.97
Summer Data (May–Oct)	662	3.20	1.61	1.86	2.08	2.47
correlation coeff. (r)			0.65	0.57	0.60	0.63
mean absolute error			1.73	1.65	1.52	1.35
Winter Data (Nov–Apr)	694	3.92	1.98	2.02	2.09	2.11
correlation coeff. (r)			0.38	0.33	0.32	0.32
mean absolute error			2.57	2.57	2.56	2.57

Notes: for one station (Harwell) hourly observation data were available. Here these were averaged to daily means.

Table 5. Source apportionment studies, summer. Comparison of model results to observation-derived values for TC and different source categories of OC and EC (units µg(C)m^{-3}). The observed values are based on a statistical approach (Latin-hypercube sampling) and given as 5-95th (CARBOSOL) or 10-90th (SORGA and Göte) percentiles where this range is available from the publications.

		Observed	VBS-NPNA	VBS-PAP	VBS-PAPA	VBS-PAA
Hurdal (SORGA) (Rural, PM_1, model $PM_{2.5}$)	TC	1.67	1.27	1.32	1.46	1.83
	OC_{bb}	0.06–0.09	0.20	0.19	0.19	0.20
	OC_{onf}	1.14–1.27	0.66	0.67	0.68	1.08
	OC_f	0.11–0.26	0.19	0.24	0.37	0.33
	OC_{POA}	0.04–0.14	0.16	0.037/0.20	0.038/0.20	0.041/0.21
	OC_{ASOA}	0.01–0.18	0.032	0.036/0.20	0.16/0.33	0.13/0.29
	EC_{bb}	0.02–0.04	0.049			
	EC_f	0.11–0.24	0.18			
Oslo (SORGA) (Urban, PM_1, model, $PM_{2.5}$)	TC	2.23	1.58	1.46	1.61	2.00
	OC_{bb}	0.23–0.38	0.27	0.20	0.21	0.21
	OC_{onf}	0.79–1.04	0.66	0.67	0.68	1.11
	OC_f	0.46–0.74	0.31	0.26	0.39	0.36
	OC_{POA}	0.07–0.35	0.28	0.050/0.22	0.052/0.22	0.055/0.23
	OC_{ASOA}	0.16–0.65	0.034	0.036/0.21	0.17/0.34	0.13/0.30
	EC_{bb}	0.09–0.16	0.095			
	EC_f	0.14–0.40	0.23			
Gothenburg (Göte) (Urban, $PM_{2.5}$)	TC	2.7 ± 0.4	2.13	2.15	2.37	2.81
	OC_{bb}	0.13–0.28	0.13	0.24	0.24	0.24
	OC_{onf}	0.99–1.36	0.62	0.63	0.65	1.14
	OC_f	0.65–1.02	0.59	0.50	0.69	0.64
	EC_{bb}	0.02–0.07	0.029			
	EC_f	0.31–0.47	0.75			

Table 5. Continued.

		Observed	VBS-NPNA	VBS-PAP	VBS-PAPA	VBS-PAA
Aveiro (CARBOSOL)	TC	4.0	2.40	2.48	2.67	3.02
(Rural, $PM_{2.5}$)	OC_{bb}	0.23–0.44	0.76	0.82	0.83	0.83
	OC_{onf}	~2.1–2.7	0.72	0.74	0.75	1.14
	OC_f	~0.7	0.35	0.35	0.51	0.47
	OC_{POA}	0.19–0.55	0.29	0.056/0.28	0.057/0.28	0.060/0.28
	OC_{ASOA}	0.07–0.77	0.057	0.068/0.29	0.23/0.46	0.19/0.41
	EC_{bb}	0.02–0.20	0.14			
	EC_f	0.32–0.65	0.44			
K-Puszta (CARBOSOL)	TC	5.0	1.89	2.61	2.98	3.74
(Rural, $PM_{2.5}$)	OC_{bb}	0.27–0.52	0.34	0.84	0.84	0.85
	OC_{onf}	~2.7–4.0	0.77	0.83	0.87	1.71
	OC_f	~0.62	0.33	0.49	0.81	0.73
	OC_{POA}	0.15–0.49	0.26	0.063/0.40	0.067/0.40	0.071/0.41
	OC_{ASOA}	0.05–0.77	0.072	0.093/0.43	0.41/0.75	0.33/0.66
	EC_{bb}	0.02–0.24	0.052			
	EC_f	0.25–0.55	0.40			

Notes: since it is not obvious if the oxidised POA would be considered as POA or ASOA in the S-A analysis, model values for OC_{POA} and OC_{ASOA} are given as $OC_{POA}/(OC_{POA} + OC_{OPOA})$ and $OC_{ASOA}/(OC_{ASOA} + OC_{OPOA})$, respectively. Observed single values preceded by ~ are "best estimates" from the respective publication and OC_{onf} ranges preceded by ~ are estimated 5-95th percentiles based on the corresponding values for OC_{BSOA} and OC_{PBAP} from the references. For SORGA and Göte the comparisons are for the actual time periods for which measurements were performed. For CARBOSOL model results for the complete months given in Gelencsér et al. (2007) were used, due to lack of information of exact measurement periods.

Table 6. Source apportionment studies, winter. For notation, see Table 5.

		Observed	VBS-NPNA	VBS-PAP	VBS-PAPA	VBS-PAA
Hurdal (SORGA) (Rural, PM$_1$, model PM$_{2.5}$)	TC	1.05	2.74	2.84	2.84	2.85
	OC$_{bb}$	0.29–0.44	1.03	1.01	1.01	1.01
	OC$_{onf}$	0.05–0.27	0.68	0.69	0.69	0.69
	OC$_f$	0.20–0.36	0.14	0.25	0.25	0.25
	OC$_{POA}$	0.01–0.13	0.11	0.19/0.22	0.19/0.23	0.19/0.23
	OC$_{ASOA}$	0.09–0.34	0.022	0.021/0.053	0.024/0.057	0.023/0.055
	EC$_{bb}$	0.11–0.18	0.54			
	EC$_f$	0.02–0.17	0.36			
Oslo (SORGA) (Urban, PM$_1$, model PM$_{2.5}$)	TC	2.63	7.96	6.87	6.88	6.89
	OC$_{bb}$	0.28–0.44	4.29	3.27	3.27	3.27
	OC$_{onf}$	0.06–0.51	0.81	0.77	0.77	0.79
	OC$_f$	0.53–1.01	0.52	0.50	0.50	0.50
	OC$_{POA}$	0.05–0.42	0.48	0.41/0.46	0.41/0.46	0.41/0.46
	OC$_{ASOA}$	0.17–0.94	0.044	0.037/0.086	0.040/0.089	0.039/0.088
	EC$_{bb}$	0.28–0.44	1.75			
	EC$_f$	0.10–0.57	0.59			
Gothenburg (Göte) (Urban, PM$_{10}$)	TC	3.0 ± 0.7	1.40	1.35	1.36	1.37
	OC$_{bb}$	0.42–0.75	0.20	0.18	0.18	0.18
	OC$_{onf}$	0.36–0.91	0.55	0.55	0.55	0.57
	OC$_f$	0.67–1.01	0.22	0.18	0.20	0.19
	EC$_{bb}$	0.06–0.12	0.11			
	EC$_f$	0.63–0.97	0.32			

Table 6. Continued.

		Observed	VBS-NPNA	VBS-PAP	VBS-PAPA	VBS-PAA
Råö (Göte) (Rural, $PM_{2.5}$)	TC	1.8 ± 0.1	1.57	1.59	1.62	1.63
	OC_{bb}	0.34–0.77	0.22	0.24	0.24	0.24
	OC_{onf}	0.07–0.55	0.59	0.59	0.59	0.62
	OC_f	0.41–0.63	0.24	0.24	0.26	0.25
	EC_{bb}	0.10–0.18	0.13			
	EC_f	0.23–0.35	0.39			
Aveiro (CARBOSOL) (Rural, $PM_{2.5}$)	TC	14.1	1.92	1.41	1.42	1.42
	OC_{bb}	7.4–9.8	0.66	0.24	0.24	0.24
	OC_{onf}	~0.2–3.5	0.55	0.54	0.54	0.54
	OC_f	~2.4	0.19	0.11	0.12	0.12
	OC_{POA}	0.09–1.1	0.17	0.056/0.093	0.056/0.094	0.056/0.094
	OC_{ASOA}	0.2–2.8	0.017	0.016/0.053	0.031/0.069	0.023/0.060
	EC_{bb}	0.56–1.69	0.23			
	EC_f	0.14–1.41	0.29			
K-Puszta (CARBOSOL) (Rural, $PM_{2.5}$)	TC	10.7	2.62	2.32	2.37	2.39
	OC_{bb}	3.6–5.9	0.73	0.45	0.45	0.45
	OC_{onf}	~0.3–3.6	0.58	0.58	0.58	0.62
	OC_f	~2.2	0.43	0.42	0.46	0.44
	OC_{POA}	0.2–1.3	0.38	0.22/0.36	0.22/0.36	0.22/0.36
	OC_{ASOA}	0.3–3.0	0.052	0.055/0.19	0.098/0.24	0.077/0.22
	EC_{bb}	0.29–1.39	0.29			
	EC_f	0.28–1.71	0.59			

Table 7. Organic aerosol in fine particles at Payerne (Switzerland) for the period 31 May to 3 July 2006. Comparison of EMEP PCM model results to AMS measurements and a high-resolution model study (Lanz et al., 2010; Aksoyoglu et al., 2011). Statistics for 665 hourly measurements for the organic mass and monthly average Fresh POA and other (oxidised) OA fractions.

	Observed	VBS-NPNA	VBS-PAP	VBS-PAPA	VBS-PAA	VBS-PAA (BVOCx3)	Aksoyoglu et al. (2011)
Organic Mass ($\mu g m^{-3}$)	6.1	2.0	2.6	3.4	4.5	7.7	
Mean Fractional Bias		−86 %	−68 %	−47 %	−25 %	+20 %	−35 %
Mean Fractional Error		87 %	70 %	52 %	38 %	39 %	50 %
Correlation coeff. (*r*)		0.58	0.60	0.58	0.60	0.58	
(Fresh) POA-fraction	6 %	23 %	4.4 %	3.7 %	3.0 %	2.1 %	26 %
Other OA-fraction	94 %	77 %	96 %	96 %	97 %	98 %	74 %

Notes: the Observed Fresh POA and Other OA-fractions are based on factor analysis of AMS-data and are taken from Aksoyoglu et al. (2011). The POA fraction from Aksoyoglu et al. (2011) is interpreted as Fresh POA (including both fossil and biomass burning sources) and the Other OA-fraction ("SOA" in Aksoyoglu et al., 2011) includes all other OA, i.e. traditional SOA as well as aged POA from different sources.

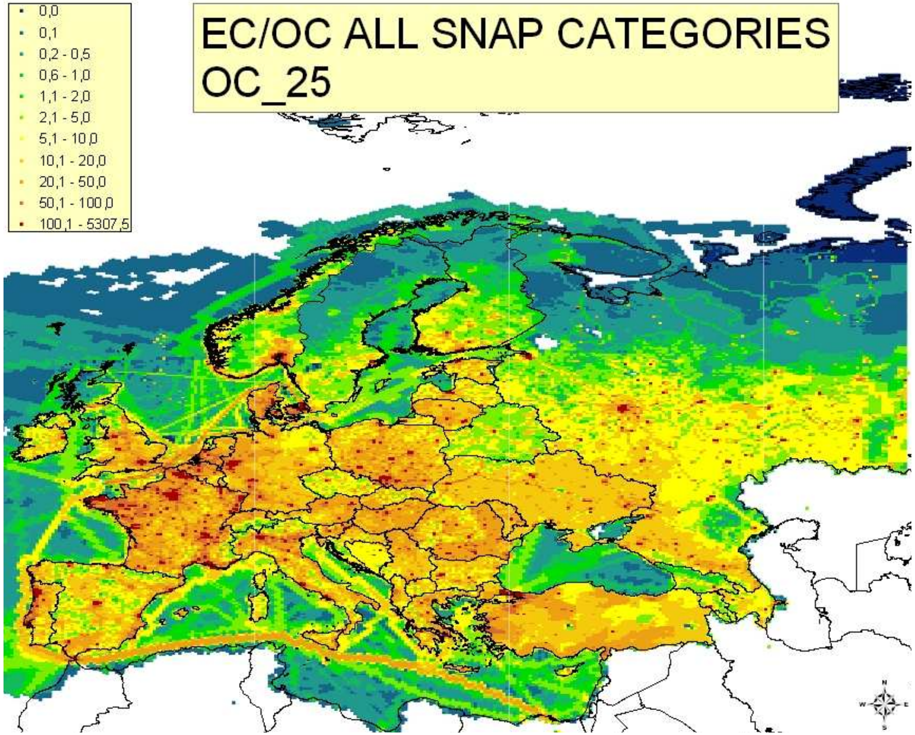


Fig. 1. Emission intensity pattern of OC in $PM_{2.5}$ over Europe (low to high: blue, green, yellow, orange, red). Unit: tonnes gridcell^{-1} yr^{-1}.

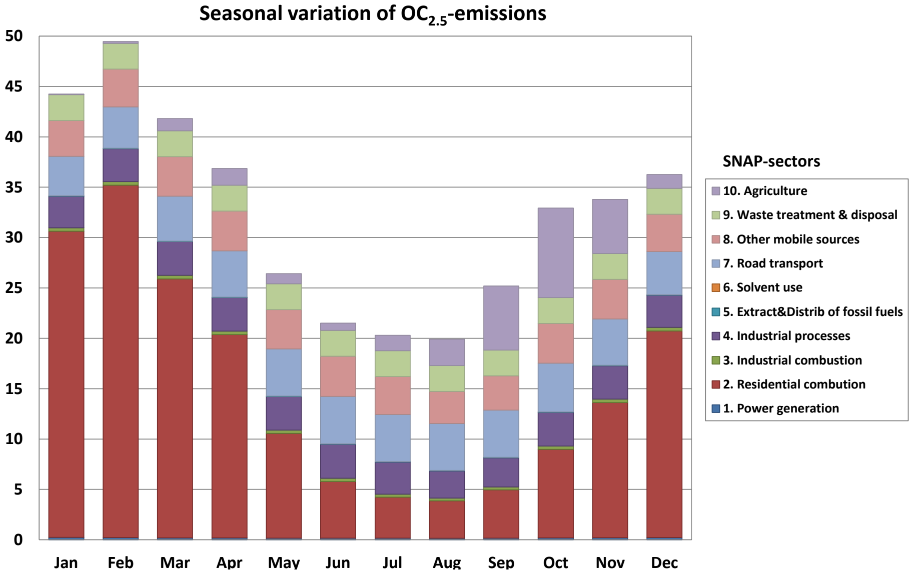
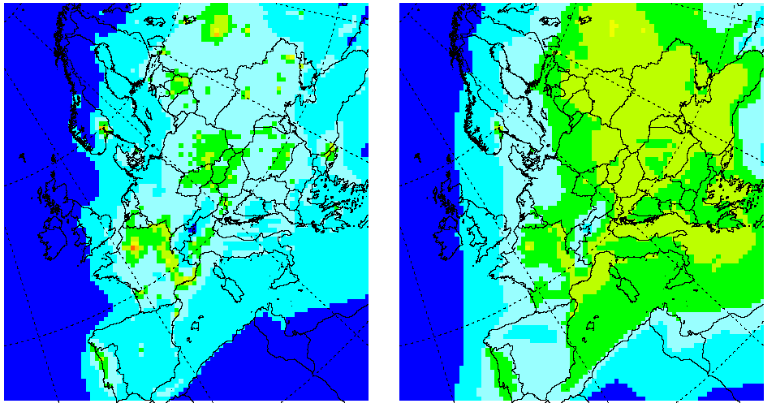
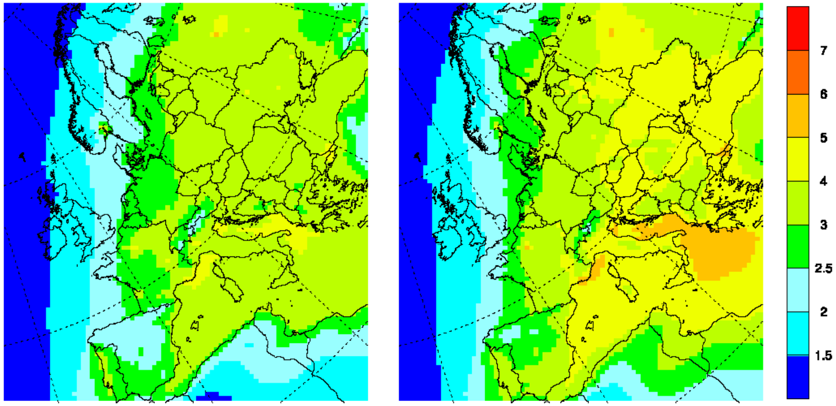


Fig. 2. Monthly variation of anthropogenic primary OC emissions (<2.5 µm) in 17 European countries (EU15 + Norway and Switzerland), specified by source-sector. Unit: ktonnes(C) month^{-1}.



(a) VBS-NPNA

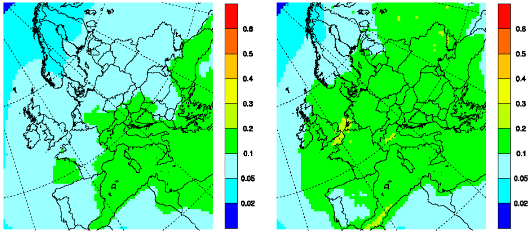
(b) VBS-PAP



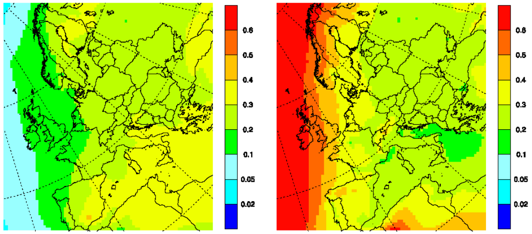
(c) VBS-PAP

(d) VBS-PAA

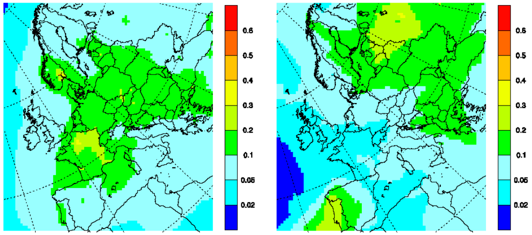
Fig. 3. Total Organic Matter (OM) in $PM_{2.5}$. 6-yr average concentration (for the period 2002–2007) calculated with the EMEP-PCM model. Comparison between four different model versions (see text). Unit: $\mu g m^{-3}$.



(a) ASOA (b) Fossil POA+OPOA

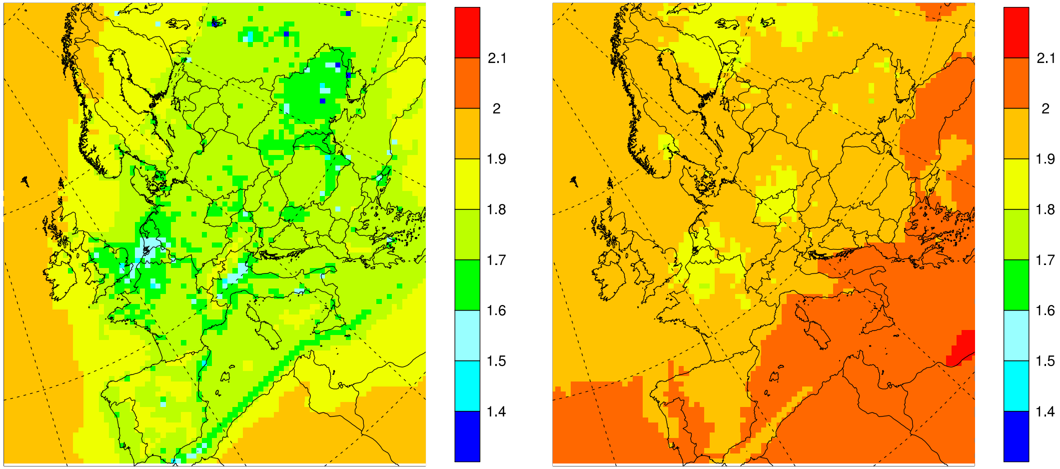


(c) BSOA (d) Background OA



(e) Residential Wood Burning OA (f) Wildfire OA

Fig. 4. Calculated relative contribution to particulate organic matter (OM) in $PM_{2.5}$ from different sources, using the model version VBS-PAA. Fraction of $OM_{PM_{2.5}}$ from **(a)** anthropogenic SOA, **(b)** fossil fuel primary OA (POA) and oxidised POA, **(c)** biogenic SOA, **(d)** background organic aerosol (from sources not explicitly included in the model), **(e)** residential biomass burning, **(f)** vegetation (wild) fires. Average for the 6-yr period 2002–2007.



(a) VBS-NPNA (b) VBS-PAPA

Fig. 5. Model calculated OM/OC ratio in $PM_{2.5}$ with two of the model versions, NPNA giving the lowest ratios and PAPA giving the highest. Average OM/OC for the whole 6-yr period 2002–2007.

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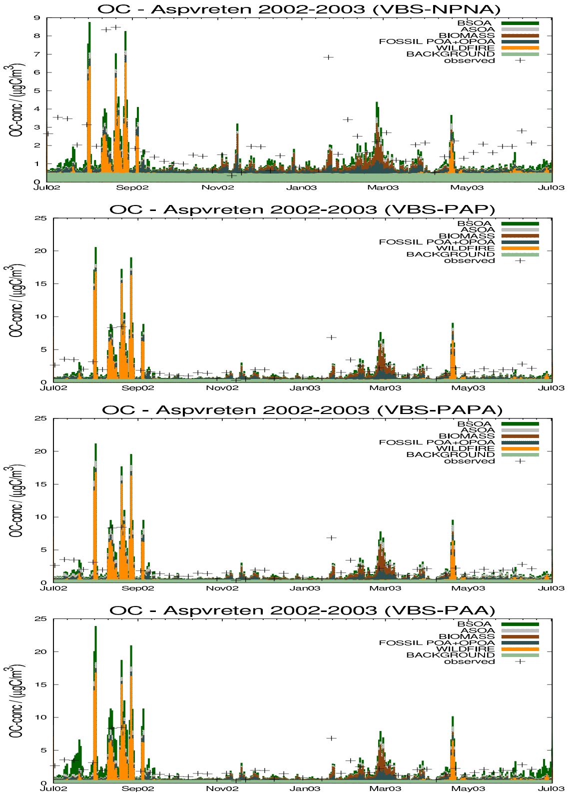

Fig. 6. Calculated OC concentrations, at Aspvreten (Sweden), with four different model versions (see text). The modelled OC components are: BSOA, ASOA – biogenic and anthropogenic SOA from VOC-emissions; BIOMASS – OC from domestic/residential biomass-burning; FOSSIL POA + OPOA – OC from fossil (anthropogenic) sources (primary OC and oxidised POC, i.e. all fossil OC except the ASOA from VOC); WILDFIRE – OC from wildfire emissions; and, BACKGROUND – background OC. Measured total OC-concentrations are indicated with +. Units: µg(C)m^{-3}.

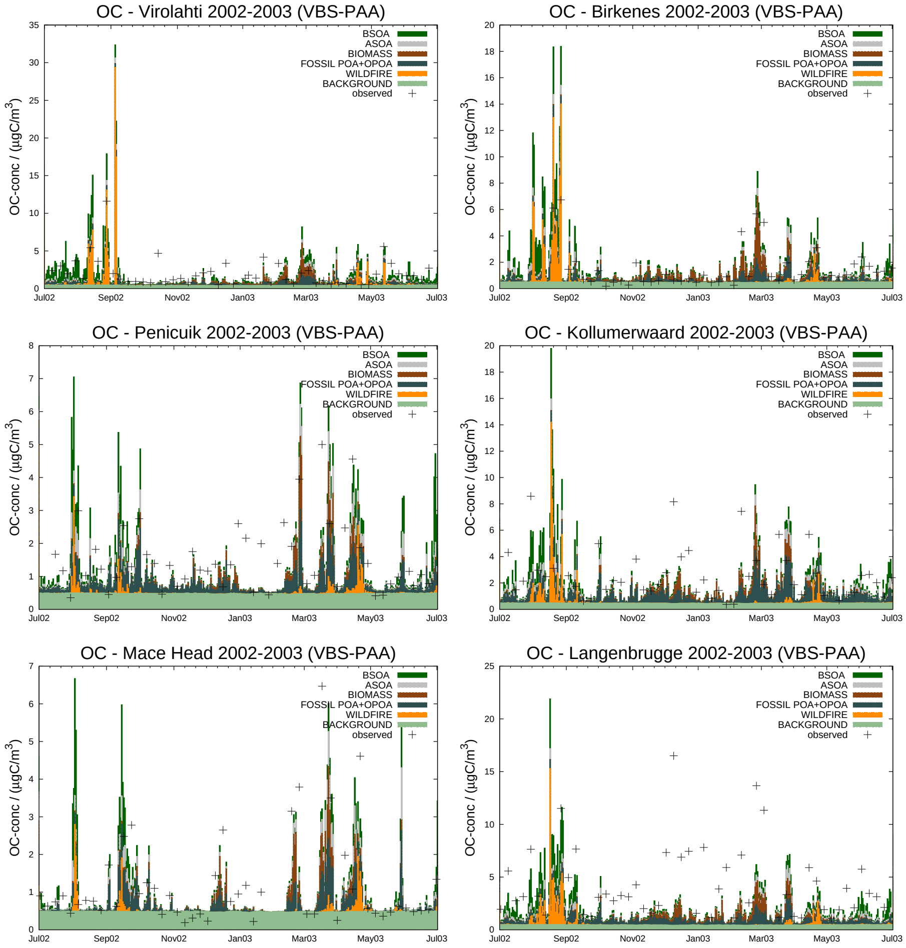

Fig. 7. (a) Modelled versus observed OC at selected sites, ranging from northern to southern Europe. Continued with Fig. 7b. Colours and symbols as in Fig. 6.

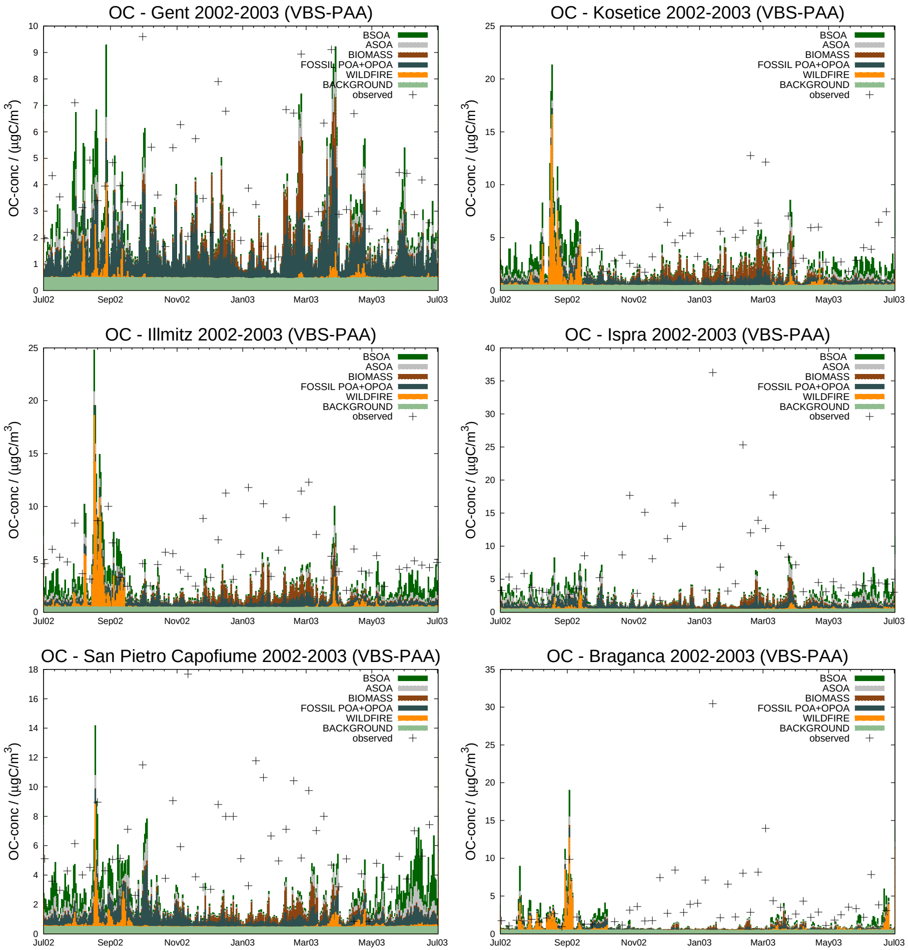

Fig. 7. (b) Continued from Fig. 7a.

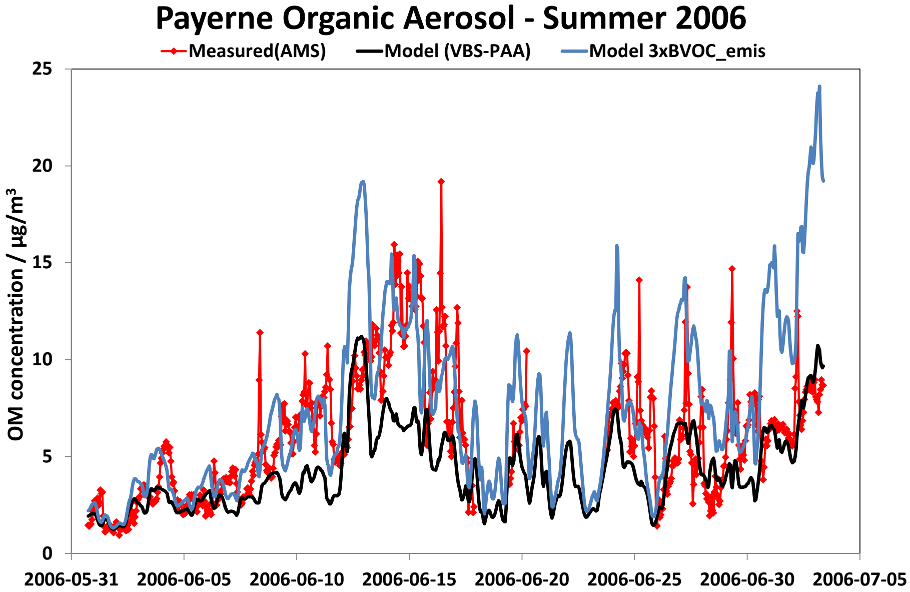

Fig. 8. Total organic mass in fine particles at Payerne, Switzerland (AMS measurements OM in PM_1 (red curve), and model calculated OM in $PM_{2.5}$ with the VBS-PAA model version (black curve: standard BVOC emissions, blue curve: sensitivity test with BVOC emissions tripled)). Unit: $\mu g m^{-3}$.