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Modeling carbonaceous aerosol over Europe: Analysis of the CARBOSOL and EMEP EC/OC campaigns

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[1] In this paper the European Monitoring and Evaluation Programme (EMEP) MSC-W model is used to assess our understanding of the sources of carbonaceous aerosol in Europe (organic carbon (OC), elemental carbon (EC), or their sum, total carbon (TC)). The modeling work makes use of new data from two extensive measurement campaigns in Europe, those of the CARBOSOL project and of the EMEP EC/OC campaign. As well as EC and OC measurements, we are able to compare with levoglucosan, a tracer of wood-burning emissions, and with the source apportionment (SA) analysis of Gelencsér et al. (2007), which apportioned TC into primary versus secondary and fossil fuel versus biogenic origin. The model results suggest that emissions of primary EC and OC from fossil fuel sources are probably captured to better than a factor of two at most sites. Discrepancies for wintertime OC at some sites can likely be accounted for in terms of missing wood-burning contributions. Two schemes for secondary organic aerosol (SOA) contribution are included in the model, and we show that model results for TC are very sensitive to the choice of scheme. In northern Europe the model seems to capture TC levels rather well with either SOA scheme, but in southern Europe the model strongly underpredicts TC. Comparison against the SA results shows severe underprediction of the SOA components. This modeling work confirms the difficulties of modeling SOA in Europe, but shows that primary emissions constitute a significant fraction of ambient TC.

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1. Introduction

[2] Carbonaceous matter is believed to contribute to around 10–40% (mean 30%) of PM₁₀ levels at rural and natural background sites in Europe [Yttri et al., 2007; Putaud et al., 2004]. This particulate carbonaceous matter (PCM) consists largely of organic matter (OM, of which typically 50–80% is OC: organic carbon, with the rest made up of associated

oxygen, hydrogen, and other atoms [e.g., Turpin et al., 2000]) and so-called elemental or black carbon (EC or BC). The sum of EC and OC is referred to as total carbon, or TC.

[3] Understanding of the sources of PCM has been severely limited, not just in Europe but throughout the world [Gelencsér, 2004; Turpin et al., 2000]. The chemical composition is largely unknown, with less than 20% typically identifiable using GC/MS methodology [Turpin et al., 2000]. There have been very few direct measurements which allow a determination of how much of PCM is from anthropogenic versus biogenic sources, or from primary emissions versus from secondary organic aerosol (SOA) formation. Recent reviews have highlighted the complexity of carbonaceous aerosol both in terms of known composition and formation mechanisms [Baltensperger et al., 2005; Donahue et al., 2005; Fuzzi et al., 2006; Gelencsér, 2004; Kanakidou et al., 2005; Pöschl, 2005].

[4] However, over the last few years some measurement results have become available which have started to shed light on the important sources of PCM in Europe. For example, Szidat et al. [2006] used ¹⁴C analysis to attribute the sources of aerosol in Zurich, Switzerland to either “fossil” carbon (from coal, oil) or “modern” carbon (from recent vegetation, either by combustion or emissions). They found that fossil fuel combustion accounts for only ~30% of OC throughout the year, even in the city center. Biomass

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burning in wintertime and SOA in summertime seem to account for the majority of the remaining OC. Using a network of Nordic sites measuring number distributions, combined with extensive trajectory analysis, *Tunved et al.* [2006] has shown a very good relationship between accumulated terpene emissions and particle mass changes, suggesting that in clean air conditions at least the buildup of PM can be interpreted almost entirely in terms of biogenic precursors.

[5] During 2002–2004 two measurement campaigns were conducted in Europe, in order to provide a better characterization and understanding of PCM. The EU CARBOSOL Project (Carbonaceous Aerosols over Europe [e.g., *Legrand and Puxbaum*, 2007]), combined weekly measurements of EC, OC, inorganic ions, elemental composition, levoglucosan and radioactive tracers across a network of six sites in southern-central Europe. The European Monitoring and Evaluation Programme (EMEP) EC/OC campaign measured EC, OC, TC and PM₁₀ at 14 sites, and many of these sites have complementary measurements of other species [*Yttri et al.*, 2007]. In addition, some of the samples from the EMEP campaign have been analyzed for levoglucosan. Analysis of the CARBOSOL measurements has given rather similar conclusions to those found by *Szidat et al.* [2006], namely that in wintertime residential wood burning is a significant contributor to measured PCM levels, whereas in summertime another modern C source, likely SOA, is the dominant contributor [*Gelencsér et al.*, 2007].

[6] Previous modeling studies in Europe [*Andersson-Sköld and Simpson*, 2001; *Schell et al.*, 2001; *Tsigaridis and Kanakidou*, 2003] have suggested that biogenic SOA is the major source of PCM in many parts of Europe. A problem with all of these studies, though, is that measurement data with which these predictions could be validated was simply lacking. The new measurements described above now allow us to make a much better comparison of model results with observations than has hitherto been possible in Europe, and this comparison is the subject of this paper.

[7] The modeling of SOA formation is particularly problematic for the simple reason that so far we are not sure which processes control SOA formation in the atmosphere. Most studies have focused on formation through gas phase chemistry followed by condensation of the semivolatile products formed (the so-called gas/particle partitioning methods, hereinafter G/P methods), following the principles discussed by *Pankow* [1994a, 1994b], *Odum et al.* [1997] and *Bowman et al.* [1997]. Some problems of the G/P methods have been discussed in several papers [*Andersson-Sköld and Simpson*, 2001; *Chung and Seinfeld*, 2002; *Tsigaridis and Kanakidou*, 2003], and *Donahue et al.* [2005] have provided a recent summary of many of the critical parameters which we lack in attempting to parameterize SOA yields from terpenes in this way. Many different pathways to SOA formation have also been presented, usually involving some heterogeneous reactions [*Ervens et al.*, 2004; *Gelencsér*, 2004; *Jang et al.*, 2002; *Limbeck et al.*, 2003; *Kalberer et al.*, 2004]. Modeling systems to explore the latter pathways are even further from validation than those for the gas phase.

[8] Further, one can note that it is not generally considered good practice in any field of science to extrapolate results outside the range of the experiments upon which the

parameterization is based. In the field of SOA modeling, it has become standard practice to take parameters obtained at ppm levels of terpene oxidation and apply these to ambient conditions where terpene levels are often in the sub-ppb range. However, until better alternatives become available, such methods would seem to provide our only practical approach to estimating SOA formation in the atmosphere. The philosophy adopted in this paper is to use such approaches as a first attempt to model SOA, and to see how far the results correlate with observations. In such knowledge-poor conditions, pragmatic application of tentative methods may still provide insights into atmospheric processes, as long as we have sufficient experimental data.

[9] Because of the great complexity of carbonaceous aerosol, and the very different mechanisms which lead to measured PCM, we present this work in two papers. In the present paper, we present the results of a base case simulation of the model, with main focus on model performance for organic and total carbon, and on the role of SOA versus primary emission sources. *Tsyro et al.* [2007] focus on elemental carbon, and in particular on how uncertainties in scavenging processes, the inventory and measurements affect our interpretation of the model performance for this hard-to-define compound.

2. Terminology

[10] As well as the definitions given above for EC, OC, OM and PCM, the terminology used for the various fractions and sources of carbonaceous aerosol is given here for reference. These fractions are further discussed in section 4:

VOC	volatile organic compounds;
SVOC	semivolatile organic compounds, the subset of VOC which has sufficiently low vapor pressure that a significant fraction may partition to the particle phase;
EC	primary elemental carbon emissions (also loosely referred as BC; the distinction is difficult [e.g., <i>Gelencsér</i> , 2004]) (in this study all sources of EC are anthropogenic, but natural sources are possible, e.g., forest fires);
POA	primary organic aerosol, here from anthropogenic emissions (see <i>Fuzzi et al.</i> [2006] for discussion of some biogenic POA components);
SOA	secondary organic aerosol, the condensed, aerosol, fraction of reaction products (SVOC) from atmospheric chemistry of VOC;
ASOA	anthropogenic SOA (here, from aromatics);
BSOA	biogenic SOA (here, from terpenes);
BGND	background OC, see section 4;
PM _f	fine aerosol, sometimes used loosely, but meaning either PM ₁ or PM _{2.5} ;
PM _c	coarse aerosol (2.5 < d < 10 μm).

3. Measurements

[11] We make use of measurements from two independent campaigns: (1) the EU CARBOSOL project, October 2002 to July 2004, and (2) the EMEP EC/OC campaign, July 2002 to July 2003. The CARBOSOL project provides a

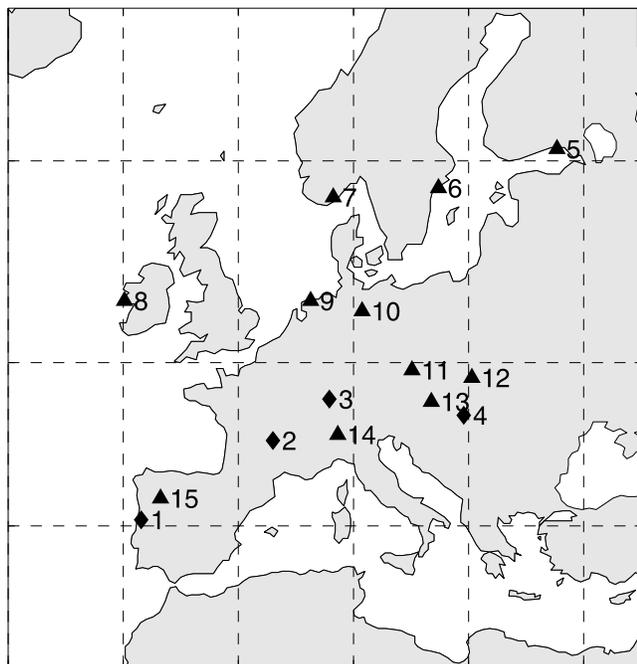


Figure 1. Location of CARBOSOL (diamonds) and EMEP (triangles) sites used in this study (CARBOSOL sites numbered west to east, EMEP numbered north to south).

greater number of components but from a limited number of sites. The EMEP campaign provides fewer data per site, but covers a wider geographical area. For this study we have included only those sites situated in rural/background areas on the European mainland, excluding some urban sites from the EMEP campaign and the very remote Azores and Sonnblick sites from CARBOSOL. Figure 1 illustrates the location of the sites used, and Table 1 provides details of

location and altitude. The compatibility of the measurements of these two networks are discussed in section 3.3.

3.1. CARBOSOL Measurements

[12] Weekly (7-day) $PM_{2.5}$ aerosol samples were collected at six sites along a west–east transect in Europe between October 2002 and July 2004. The detailed description of the sampling sites, sampling and analyses can be found elsewhere [Pio *et al.*, 2007]. Briefly, the samples were collected on preheated quartz fibre filters, and stored in the refrigerator until analysis. OC/EC analysis was performed at the University of Aveiro using a thermo-optical method similar to that in use in the IMPROVE network [Chow *et al.*, 1993]. However, even methods which use charring control by transmittance can produce quite different results, depending mainly on the maximum temperature of the heating step under the inert atmosphere [Chow *et al.*, 2001]. The methodology used in CARBOSOL was intercompared with other methods, revealing, in general, values of EC lying between those obtained with the IMPROVE and NIOSH protocols [Schmid *et al.*, 2001]. The analyses of levoglucosan were performed at the Vienna University of Technology, using gradient-HPLC with electrochemical detection [Puxbaum *et al.*, 2007]. Levoglucosan analysis was performed on samples of approximately one month duration for each site.

[13] Two of the CARBOSOL sites used here (PDD and SIL) were mountain sites, which lie above the boundary layer in wintertime, and where concentrations can be influenced by upslope convection in summertime. The behavior of pollutants at such mountain sites can be difficult to capture with a large-scale model such as EMEP. One specific problem is knowing which vertical level of the model is most appropriate for comparison purposes. As the EMEP model has been extensively evaluated against sulphate measurements, and this pollutant is well characterized, we have examined the EMEP model’s sulphate predictions from various vertical levels against the observed values, and chosen the model level for which the seasonal

Table 1. Sampling Sites of the CARBOSOL and EMEP EC/OC Campaign Used in This Study

Site Number	Country	Site	Code	Category ^a	Location		
					Longitude, °E	Latitude, °N	Height asl, m
<i>CARBOSOL</i>							
1	Portugal	Aveiro	AVE	R	−8.63	40.57	48
2	France	Puy de Dome	PDD	RB	3.00	45.45	1450
3	Germany	Schauinsland	SIL	RB	7.90	47.92	1205
4	Hungary	K-Pusztá	KPZ	R	19.58	46.97	125
<i>EMEP</i>							
5	Finland	Virolahti	FI17	RB	27.68	60.52	4
6	Sweden	Aspvreten	SE12	RB	17.38	58.8	20
7	Norway	Birkenes	NO01	RB	8.25	58.38	190
8	Ireland	Mace Head	IE31	RB	−9.9	53.33	25
9	Netherlands	Kollumerwaard	NL09	RB	6.28	53.33	0
10	Germany	Langenbrügge	DE02	RB	10.75	52.8	74
11	Czech Rep.	Koštice	CZ03	RB	15.08	49.58	534
12	Slovakia	Stara Lesna	SK04	RB	20.28	49.15	808
13	Austria	Illmitz	AT02	RB	16.77	47.77	117
14	Italy	Ispira	IT04	NC	8.63	45.8	209
15	Portugal	Braganca	PT01	RB	−6.77	41.82	691

^aR, rural; RB, rural background; NC, near city.

cycles of SO_4^{2-} were captured best [see also *Fagerli et al.*, 2007]. Although results from these mountain sites are interesting, it is clear that the surface sites (KPZ, AVE) are subject to the greatest pollution loadings, and thus most clearly reflect boundary layer sources of both inorganic and organic pollutants.

3.2. EMEP Measurements

[14] During the EMEP EC/OC campaign, 1 July 2002 to 1 July 2003, 24h samples were collected once per week (starting Tuesday mornings) at 14 sites. Aerosol sampling was performed using CEN (European Committee for Standardisation) approved or equivalent PM_{10} samplers. Samples were collected on prebaked quartz fibre filters. Analyses were performed using the thermal optical transmission (TOT) instrument from Sunset Lab Inc., using a NIOSH-derived temperature programme (quartz.par). The instrument corrects for charring that might take place during analysis. Details of this campaign, and of the filters content of PM_{10} , elemental carbon, organic carbon and total carbon are reported elsewhere [*Yttri et al.*, 2007].

[15] Ten samples from each of the 14 sites included in the campaign were analyzed for levoglucosan. Four of the samples were picked from summer months (April–September), whereas the other six samples were picked from winter months (October–March). The 140 samples selected for analysis were collected on the same ten dates in order to ease the comparison and to get a snapshot of the impact from wood burning emissions on these days. Levoglucosan was quantified using high-performance liquid chromatography in combination with a high-resolution mass spectrometry based on a time-of-flight principle [*Dye and Yttri*, 2005]. Here we use data from 11 sites, which were located in rural/background areas (including Ispra which, although lying within 50 km of Milan, is in many respects a rural site).

3.3. Comparability

[16] Unfortunately, the CARBOSOL and NILU networks were run independently, and no cross validation is available between the two data sets. This may lead to some difficulties for the comparisons of EC and OC, as these components are subject to significant methodological problems, with different analysis methods often producing different EC/OC splits for the same sample [*Schmid et al.*, 2001]. Further, these splits also vary with sampling procedure [*ten Brink et al.*, 2004]. However, it is much easier to determine the sum of EC + OC than their individual amounts, so total carbon ($\text{TC} = \text{EC} + \text{OC}$) is typically a fairly robust parameter from measurements [*Schmid et al.*, 2001; *ten Brink et al.*, 2004]. Within each network, consistency for any given component was assured since only one laboratory/Institute was responsible for the analysis from all sites of that network.

[17] The issue of artefacts within each network is also important, but difficult to deal with. It has long been recognized that both positive and negative artefacts can be introduced during continued sampling of particulate OC [*McDow and Huntzicker*, 1990], significantly biasing the particulate OC loading of the sample. Estimates of artefact contribution to measured particulate organic carbon concentrations range from -80 to $+100\%$, but there is no consensus on which artefacts dominate. Further, there are

indications that both types of artefact are more pronounced in rural areas than in urban areas. Various approaches exist that are supposed to account for the sampling artefacts of OC [*Mader et al.*, 2003; *Novakov et al.*, 2005], but the performance of these approaches is unclear. Neither the EMEP EC/OC campaign nor the CARBOSOL study accounts for the positive and the negative sampling artefact of OC. However, the thermal-programmed analysis of OC fractions on CARBOSOL experiments indicate that only a small fraction of OC is volatile at temperatures lower than 150°C [see *Pio et al.*, 2007]. Chemical transformation of filter-deposited particulate organics during long-term sampling poses another difficulty. Long-term sampling is more problematic for less chemically stable (more reactive) organic species. As a compensating phenomenon it can be said that long-term sampling reduces the importance of filter adsorption interferences as result of saturation of active sites on filter fibres.

4. EMEP Model

[18] The standard EMEP MSC-W 3-D Photo-oxidant model is a development from previous EMEP modeling activities [*Berge and Jakobsen*, 1998; *Jonson et al.*, 1999; *Simpson*, 1995] and the current standard version is fully documented by *Simpson et al.* [2003] and *Fagerli et al.* [2004]. Briefly, the model domain is centered over Europe but also includes most of the North Atlantic and the north polar regions. The model has 20 vertical layers in σ -coordinates below 100 hPa. It is primarily intended for use with a horizontal resolution of $\sim 50 \text{ km} \times 50 \text{ km}$ (at 60°N) in the EMEP polar stereographic grid. The chemical scheme uses about 140 reactions between 70 species [*Andersson-Sköld and Simpson*, 1999], and makes use of the EQSAM module detailed by *Metzger et al.* [2002a, 2002b] for the partitioning of inorganic species between the gas and aerosol phase.

[19] The standard EMEP model distinguishes two size modes for aerosols, fine aerosol ($\text{PM}_{2.5}$), and coarse aerosol (PMc , $2.5 < d < 10 \mu\text{m}$). Dry deposition of particles follows standard resistance formulations, accounting for diffusion, impaction, and sedimentation. Dry deposition of fine-mode particles is very slow, however, and the lifetime of these compounds is usually limited by wet-scavenging processes. Wet scavenging is treated with simple scavenging ratios, taking into account in-cloud and subcloud processes. The in-cloud scavenging ratio for EC is set to 0.2×10^6 , and for other carbonaceous aerosol to 0.5×10^6 , based upon measurements conducted in the CARBOSOL project to estimate scavenging ratios for groups of compounds [*Legrand and Puxbaum*, 2007]. The sensitivity of the model results for EC to this ratio is discussed by *Tsyro et al.* [2007]. The subcloud scavenging efficiency for carbonaceous particles is the same as for other fine particles.

[20] The OC/SOA model used here extends the chemical mechanism of the standard EMEP model with the inclusion of emissions of biogenic terpene emissions and a module for secondary organic aerosol formation, following on from the work of *Andersson-Sköld and Simpson* [2001] and *Simpson and Makar* [2004]. The extended model has a number of semivolatile organic gases which are assumed to be able to condense onto (or evaporate from) aerosol phase OC using

Table 2. Comparison of Theoretical and Experimental (Effective) Vapor Pressures (Pa)^a

	p_L^0 , KJ01 Theory	p_L^0 , P01 Theory	p_L^* , KJ01 exp.	p_L^* , P01 exp.
Pinic acid	1.73×10^{-3}	2.80×10^{-4}	N/A	3.98×10^{-4}
Norpinic acid	N/A	1.00×10^{-3}	N/A	6.80×10^{-4}
Pinonic acid	6.67×10^{-2}	2.96×10^{-4}	1.60×10^{-2}	5.98×10^{-4}
Norpinonic acid	N/A	1.09×10^{-3}	N/A	1.49×10^{-3}
Oxy pinononic acids	1.29×10^{-3}	2.71×10^{-4}	N/A	3.17×10^{-4}
Pinonaldehyde	5.47	6.17	3.73×10^{-1}	1.85×10^{-2}
Norpinonaldehyde	N/A	23.2	N/A	6.33×10^{-3}
Oxypinonaldehydes	1.73×10^{-1}	3.05×10^{-2}	5.20×10^{-3}	1.73×10^{-3}

^aKJ01 refers to *Kamens and Jaoui* [2001], and P01 refers to *Pankow et al.* [2001]. p_L^0 refers to pure-component vapor pressure, and p_L^* refers to effective vapor pressure; see text. p_L values are given at 307 K for KJ01 and 308 K for P01. The “exp”. p_L^* values for P01 were derived by multiplying the theoretical p_L values by the ratio of the predicted to measured yield percentages from three experiments. N/A, not available.

the gas/particle partitioning ideas developed by *Pankow* [1994a, 1994b] and *Odum et al.* [1997]. The partitioning is described by:

$$\frac{A_i}{G_i} = K_i. M_0 = 10^{-6} \frac{RT}{m_w \zeta_i p_{L,i}^0} \cdot M_0 \quad (1)$$

where A_i , G_i are aerosol and gas phase concentrations of semivolatile species i (in $\mu\text{g m}^{-3}$), K_i ($\text{m}^3 \mu\text{g}^{-1}$) is a partitioning coefficient, M_0 ($\mu\text{g m}^{-3}$) is mass of existing absorbing organic aerosol (including water), ζ_i is the activity coefficient, m_w (g mol^{-1}) is the average molecular weight of the liquid phase into which OC is assumed to partition and $p_{L,i}^0$ (Pa) is the vapor pressure of the liquid compound, subcooled if necessary. M_0 includes both BGND-OC and POA (both assumed to be absorbing, but nonvolatile), as well as the condensed part of SVOC. SVOC may condense or evaporate from aerosols, in order to fulfil the equilibrium assumption of equation (1). R is the gas-constant ($8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is temperature (K). The factor 10^{-6} is required for the above units.

[21] The estimation of $p_{L,i}^0$ (or, equivalently, K) and its temperature variation is one of the key problems associated with the practical application of gas/particle partitioning [*Andersson-Sköld and Simpson*, 2001; *Asher et al.*, 2002; *Tsigaridis and Kanakidou*, 2003]. For example, Table 2 shows estimates of vapor pressure as reported by *Kamens and Jaoui* [2001, hereinafter referred to as KJ01] and by *Pankow et al.* [2001, hereinafter referred to as P01], derived both theoretically and from smog chamber studies of α -pinene and other species. Comparing the theoretical values, we see that p_L^0 estimates are very close for pinonaldehyde, within a factor of five for most species, and different by a factor of 200 for pinonic acid.

[22] Both KJ01 and P01 compared yield estimates as observed in the chambers with those predicted using theory, and from this “experimental” vapor pressures p_L^* can be derived. It should be noted that we are here using vapor pressure in a pragmatic sense; any reactions in the particle phase do not really alter the pure-component p_L^0 values, but just result in a greater partitioning to the aerosol phase, so that $p_L^* \leq p_L^0$. In some cases the theoretical and experimental p_L vapor pressure agree very well, but in other cases the experimental vapor pressures are much lower than the theoretical values. As noted in KJ01 this likely reflects a possible reaction in the particle phase, and seems to have most importance for aldehydes. The uncertainties caused by such differences in vapor-pressure estimates will be explored

for BSOA formation through the use of two model versions with differing parameters (section 4.2).

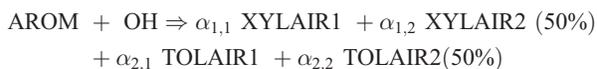
[23] The mean molecular weight (m_w) from equation (1) is also a difficult parameter for ambient conditions. Ideally one could calculate m_w through a knowledge of the components of the absorbing PM. However, we do not know this information except in controlled experimental conditions. Most modeling approaches have assumed SVOCs from biogenic precursors (mostly monoterpenes) to be responsible for SOA, but this would suggest low-molecular-weight compounds with 9 or 10 carbon atoms. Experimental evidence suggests that the water soluble (HULIS) component of OM has a mean MW of around 250 Da [*Kiss et al.*, 2003; *Samburova et al.*, 2005], although such studies have high uncertainty [*Graber and Rudich*, 2006]. The increasing evidence of oligomer/polymer formation [e.g., *Baltensperger et al.*, 2005] provides one explanation for the increase in molecular weight relative to precursors, but the true values of m_w for ambient aerosol are clearly very uncertain. The values assigned to m_w are discussed below for each class of PCM below.

[24] A further complication is uptake of water to the organic phase, since even a small mass uptake of water can reduce the mean m_w of this phase. However, we have conducted modeling studies with the inclusion of water uptake, and found that this does not appreciably alter the model predictions as presented here. Studies conducted by *Griffin et al.* [2003] and *Ansari and Pandis* [2000] also showed only modest effects on SOA if water uptake was included.

[25] Finally, the activity coefficient term in equation (1) presents one of the most formidable challenges in implementing these gas/particle partitioning ideas. It is possible to estimate ζ with methods such as UNIFAC [e.g., *Sandler*, 1998], and indeed such methods have been implemented in earlier versions of the EMEP SOA model. However, such calculations are extremely time-consuming and uncertain, and we have found that they make little difference to predictions of total PCM. For simplicity we therefore simply assume $\zeta = 1$ for all compounds.

4.1. Anthropogenic SOA, ASOA

[26] For anthropogenic compounds we use just four species, similar to those used by *Pun et al.* [2003] for their so-called Odum/Griffin (O/G) model:



where AROM represents the EMEP model's aromatic species, which is assumed to generate the same products as a 50% toluene, 50% xylene mixture of the O/G model. For each of these species, the stoichiometric coefficients (α) and partitioning coefficients (K) were as given by *Pun et al.* [2003]. The temperature dependence of K was calculated using the Clausius-Clapeyron equation and enthalpy values of $\Delta H/RT = 5000 K$ [cf. *Chung and Seinfeld*, 2002].

4.2. Biogenic SOA, BSOA

[27] In this study, all terpenes are assumed to be represented by the gas α -pinene, and we make use of two variations of the detailed "Kam-2" gas/particle scheme of *Andersson-Sköld and Simpson* [2001, hereinafter referred to as AS01]. This scheme, an extension of that presented by *Kamens et al.* [1999], included 30 reactions between α -pinene and 17 products species. The products include surrogates for species such as pinonaldehyde, pinonic acid, and a nonvolatile dimer species formed from pinic and nor-pinic acid.

[28] A disadvantage of the AS01 scheme is that it is based upon only one monoterpene species, and indeed α -pinene seems to yield only moderate SOA in smog chamber experiments compared to other terpenes [*Griffin et al.*, 1999a]. On the other hand, this schemes offer a chemical system with multiple products, based upon real chemical species and following kinetic principles. Most importantly, the Kam-2 scheme has been found to perform very well when compared to smog chamber data over a very wide range of concentrations and temperatures. It can be noted that we have also performed parallel studies with monoterpene schemes for four species, largely based upon *Chung and Seinfeld* [2002]. The results of these latter studies will not be reported here, but for now we can note that the use of the *Chung and Seinfeld* [2002] scheme results in rather similar OC values to those presented here for the Kam-2 scheme.

[29] As noted above, the choice of K or p_L values is fraught with serious uncertainties. We have chosen to adopt two alternative schemes in order to illustrate the importance of such uncertainties, which we will refer to as Kam-2 and Kam-2X:

4.2.1. Kam-2 Scheme

[30] The original Kam-2 developed by AS01 used the K values suggested by *Kamens et al.* [1999] as far as possible. An updated set of K values was presented in the KJ01 paper, with this set adjusted to fit experimental gas and particle phase product data. These new K values differ substantially for some species from those of KJ01, especially for pinonaldehyde and oxy-pinonaldehyde. At the same time, the gas-particle kinetic models was also updated by KJ01, with some different stoichiometrics for product formation to that suggested by *Kamens et al.* [1999].

[31] We have elected to keep the original Kam-2 scheme as our basic model, for two main reasons. Firstly, the scheme is somewhat simpler and hence computationally more efficient than that presented in KJ01. Secondly, and more importantly, the Kam-2 scheme was evaluated against a wide range of smog chamber experiments, covering α -pinene concentrations from 900 ppb to 20 ppb, NO_x from 240 ppb to 0 ppb, and temperatures from 49°C to 11°C. We know of no other gas/particle scheme which has been shown to demonstrate good agreement with aerosol yields over such a wide range of conditions.

[32] The only modifications made for this work are to adopt the new rates for the PAN-like species (α -P-PAN in AS01, pinald-PAN in KJ01), and the nitrate species (nitracid in AS01, OH-apNO₃ in KJ01), since these rates were the least well founded in AS01. This change has little consequence for the validity of the AS01 results however.

4.2.2. Kam-2X Model

[33] The Kam-2X model uses the same gas/particle chemical scheme as Kam-2, but with increased partitioning coefficients, making use of the experimentally derived "effective" vapor pressures from Table 2. Since the observed apparent p_L values in Table 2 are lower in the P01 data set than in the KJ01 data, we have chosen to use these as the basis for our modification. In model version Kam-2X, all p_L values are scaled so that at 308 K they match those of the P01 experiments. A slight complication is that the EMEP model's species are surrogates representing two or more real species, as discussed by *Kamens et al.* [1999] and AS01. Based upon the values given in Table 2, and measured partitioning and stoichiometric values from KJ01 and P01, we have assumed p_L values at 308 K for the model species to be (in Pa): 4.0×10^{-4} for DIACID (pinic acid); 6.8×10^{-4} for DIACID2 (norpinic acid); 1.7×10^{-2} for PINALD (pinonaldehyde + norpinonaldehyde); 1.7×10^{-3} for OXYPINALD (hydroxy and aldehyde substituted pinonaldehyde); 1.2×10^{-3} for PINACID (pinonic + norpinonic acid); and 3.2×10^{-4} for OXYPINACID (hydroxy and aldehyde substituted pinonic acids).

4.3. POA: Primary Organic Aerosol

[34] Primary organic aerosol emissions in the model are divided into two major groups, fossil fuel sources (FFUEL), and biomass burning (WOOD), which mainly consists of domestic wood combustion. All POA emissions are assumed to be nonvolatile.

4.3.1. FFUEL

[35] POA emissions from fossil fuel sources are mainly associated with diesel emissions. Only a minor fraction of these emissions has been resolved, however (e.g., 10% [*Rogge et al.*, 1993]). Of the resolved organics, the data of *Rogge et al.* [1993] and *Jang et al.* [1997] suggest a mean molecular weight of around 240 Da. Ninety percent of the elutable organic matter from heavy-duty vehicles was so-called unresolved complex mixture (UCM), said to consist mainly of branched and cyclic hydrocarbons. *Pun et al.* [2002] represented POA using eight species, with molecular weights (MW) of between 118 for diacids to 408 for n-alkanes, and suggesting MW = 390 for UCM. As we require only one compound to represent POA in this work, but have no specific information on the mean MW of European POA, we assume a mean MW values which lies between the estimates given above, 340 Da.

4.3.2. WOOD

[36] Wood combustion is estimated to be responsible for more than 30% of the annual PCM emissions in Europe (section 5). The surrogates used to represent emissions from wood combustion in this work include the very low vapor pressure compound levoglucosan and a generic WOOD-OC compound with MW 256 (for a C16 compound), loosely based upon the detailed data presented by, e.g., *Schauer et al.* [2001].

Table 3. Emissions of Submicron EC, OM, and PCM (=EC + OM) in Europe, Year 2000

SNAP Code	Sources	Emissions, Gg/yr			Fraction of Total PCM, %
		EC	OM	PCM	
1	combustion in energy and transformation industries	3.5	3.6	7.1	(0.4)
2a ^a	nonindustrial combustion plants	89.8	140.1	229.9	(12.5)
2b ^a	residential/commercial wood burning	165.1	456.4	621.5	(33.7)
3	combustion in manufacturing industry	3.8	10.3	14.1	(0.8)
4	production processes	34.8	23.6	58.4	(3.2)
5	extraction and distribution of fossil fuels and geothermal energy	13.3	2.7	16.0	(0.9)
7	road transport	212.8	147.2	359.9	(19.5)
8	other mobile sources and machinery	205.6	148.3	353.9	(19.2)
9	waste treatment and disposal	14.9	41.6	56.4	(3.1)
10	agriculture	30.1	94.9	125.0	(6.8)
Sum		773.6	1068.6	1842.1	(100.0)

^aSNAP-2 divisions (2a and 2b) are not part of the official SNAP nomenclature, but serve here to distinguish wood burning from other fuels.

4.4. BGND-OC: Background OC

[37] Background OC concentrations are introduced into the model in order to allow for the incoming air masses, and also to account in an approximate way for the contributions of the numerous OC sources which are not otherwise included, for example those of primary biogenic organic material [e.g., *Matthias-Maser and Jaenicke, 1994; Matthias-Maser et al., 1995; Puxbaum and Tenze-Kunit, 2003*], or of forest fires. Background levels of EC are assumed to be zero for this work, consistent with the very low levels ($\sim 50 \text{ ng m}^{-3}$) observed at Mace Head, west coast of Ireland, and Azores [*Cavalli et al., 2004; Kleefeld et al., 2002; Pio et al., 2007*].

[38] These BGND-OC are treated as “reservoir” species, with a constant surface concentration of $0.5 \mu\text{g m}^{-3}$ all year around. A scale height in the vertical of 9 km is imposed, based upon *Warneck [1988]*. BGND-OC is not subject to deposition processes or evaporation, since it is assumed that sources which are not included in our model contribute on a more or less continuous basis. Although this assumption is clearly highly simplified, the level of $0.5 \mu\text{g m}^{-3}$ is consistent with measurements made at Mace Head [*Cavalli et al., 2004; Kleefeld et al., 2002*], for the CARBOSOL background site in the Azores ($0.33 \mu\text{g m}^{-3}$ annual average [*Pio et al., 2007*]), as well as with data from remote regions [*Heintzenberg, 1989*].

[39] This assumption of a constant background level of OC also enables an important simplification in this work. This BGND-OC ensures the term M_0 in equation (1) is nonzero everywhere, and thus partitioning of SVOC to the particle phase can occur without the need for any compound first exceeding its saturation vapor pressure [see, e.g., *Bowman et al., 1997; Seinfeld and Pandis, 1998*].

[40] The mean MW of this BGND-OC is 240, derived assuming a mixture of approximately 25% levoglucosan, 25% palmitic acid, and 50% of a humic-like substance with a composition similar to fulvic-acid, but a MW of 326 to better reflect observed MWs of these substances [*Kiss et al., 2003; Samburova et al., 2005*].

5. Emissions

[41] The main emission sources to the EMEP model comprise annual data on SO_2 , NO_x , NMVOC, CO, NH_3 , $\text{PM}_{2.5}$ and PM_{10} from fossil fuel combustion and other anthropogenic sources. These data are generally taken as far

as possible from nationally submitted official submissions, otherwise from estimates within EMEP MSC-W [*Vestreng et al., 2004*]. Disaggregation to hourly values is done using procedures detailed by *Simpson et al. [2003]*.

[42] For particulate matter emissions of EC and OC, we have used a new inventory for annual national emissions of submicron particles developed by *Kupiainen and Klimont [2007]*. These emissions are believed to represent the most comprehensive evaluation to date of European sources of PCM. Strictly, this inventory was developed for submicron particles, rather than for $\text{PM}_{2.5}$ as measured in CARBOSOL, however, the difference between emissions in these size ranges is believed to be less than $\sim 10\%$ for the major sources of EC and OC [*Bond et al., 2004*]. This is well within the uncertainties of EC/OC modeling, so we simply use the emissions unchanged.

[43] Table 3 summarizes the emissions of EC, OM, and PCM used in this study, with emissions classified according to the so-called SNAP (source-nomenclature for Air Pollution [*Richardson, 1999*]) emission categories. Residential wood burning, a subcategory of SNAP-2, is specified separately in view of the importance of this source to this paper.

[44] For the coarse fraction of particulate matter (PMc), no detailed EC or OC inventory is available, but for each country and emission sector we do have the total PMc emissions. As PMc emissions are smaller than $\text{PM}_{2.5}$ emissions, and non-C compounds relatively more important in coarse compared to fine aerosol, simple assumptions for the shares of EC and OC in PMc should suffice. For residential combustion (SNAP-2, both FFUEL and WOOD), we assume zero EC emissions in PMc, and OM is 50% of PMc. For mobile source emissions (SNAP-7,8), we have made use of road tunnel measurements reviewed by *M. Handler et al.* (Size and composition of particulate emissions from motor vehicles in the Kaisermühlen-Tunnel, Vienna, submitted to Atmospheric Environment, 2006), which includes new data from Austria. Most studies suggested that OC made up between 25 and 40% of PMc, or about 30–50% as OM. EC emissions were much more variable, accounting for between 4 and 18%. There is little material with which to distinguish gasoline from diesel emissions, and much of the OM is expected to come from brakes, tyres and road abrasion, so we use the same factors for all mobile sources, namely that EC is 10% PMc, and OM is 40% PMc. For agriculture (SNAP-10), PMc emis-

sions are dominated by poultry and pig farms, and much of this material may be assumed to be organic. We thus assume that PMc consists of 0% EC, 70% OM, and 30% other compounds. For other SNAP sectors we assume zero EC and OM emissions in PMc.

5.1. Wood Burning and Levoglucosan

[45] As shown in Table 3, residential and commercial wood burning is estimated to account for more than 30% of PCM emissions, and most of this emission occurs in the winter months. As well as being a large source of emissions, it is also likely the source with the biggest uncertainty. Emissions are highly technology-dependent, and depend strongly on operating practice, load, fuel type and quality, and the nature of the appliances [e.g., *Fine et al.*, 2001, 2002; *Schauer et al.*, 2001; *Yttri et al.*, 2005; *Kupiainen and Klimont*, 2007; *Puxbaum et al.*, 2007]. Even national average emission factors vary widely from country to country, with, e.g., PM emission factors reported as 150 mg/MJ in Denmark and 1932 mg/MJ in Norway [*Sternhufved et al.*, 2004]. For the *Kupiainen and Klimont* [2007] inventory used here, country-specific statistics on operating practice, fuel properties, and the specific mix of combustion installations were used, but it is difficult to assign a level of accuracy to such a difficult source category.

[46] Levoglucosan is typically the single compound emitted in greatest quantities from wood burning, and indeed is usually the single compound showing the highest concentration which can be identified in ambient air samples [*Fine et al.*, 2002; *Schauer et al.*, 2001; *Simoneit*, 2002]. Units of emission are somewhat confusing, with levoglucosan (MW 162) emissions usually given in mg compound, whereas the reference OC emissions are per carbon atom (g C). For wood typical of the southern US, *Fine et al.* [2002] found that levoglucosan accounted for an average of 13.6% and 4.2% of fine-particle OC emissions from hardwoods and softwoods respectively, with on average 100 mg levoglucosan/g OC. *Schauer et al.* [2001] found a levoglucosan/OC ratio of 18% for pine combustion in fireplaces. Test burns of beech and spruce in tile ovens in Austria gave a levoglucosan/OC fraction of 14% [*Puxbaum et al.*, 2007]. Summarizing a number of such studies, *Puxbaum et al.* [2007] suggested an overall ratio of 136 mg levoglucosan/g OC. In test burns on eight wood boilers in Sweden, *Hedberg et al.* [2006] found an average emission ratio, levoglucosan/PM_{2.5}, of 7.2% ($\pm 6.9\%$). Assuming that the PM_{2.5} emission were essentially all OM, and an OM:OC ratio of 2.2–2.6 [*Turpin et al.*, 2000], would suggest an emission fraction of 160–190 mg levoglucosan/g OC. Lower levoglucosan/OC ratios [e.g., *Andreae and Merlet*, 2001] are probably more typical of open fires (forest and agricultural fires).

[47] Studies made in ambient air in Europe add useful information concerning emissions factors from wood burning and the contribution of levoglucosan. In Norway, *Yttri et al.* [2005] measured levoglucosan in PM₁₀ in the town Elverum in winter, where wood-burning emissions are believed to dominate the ambient aerosol. The correlation between PM₁₀ and levoglucosan in Elverum during the winter gave a slope of 0.038 and correlation of $r^2 = 0.86$. Measurements of levoglucosan in the PM₁₀ fraction, and OC in both PM_{2.5} and PM₁₀ samples suggest levoglucosan/OC values in fine-aerosol of around 7–10% (K. E. Yttri et

al., Ambient aerosol concentrations of elemental carbon, organic carbon, water-insoluble carbon and water-soluble carbon at three different sites in Norway, submitted to Atmospheric Environment, 2006).

[48] In the study of *Hedberg et al.* [2006], detailed emission inventories were built up and tested for Lycksele in northern Sweden, where wood burning makes a significant contribution to the energy supply in wintertime. Concurrent analysis of levoglucosan, PM_{2.5}, and trace elements in the ambient air allowed the construction of a source-receptor model, which showed a very linear relationship ($r^2 = 0.80$) between levoglucosan and fine PM from wood combustion. This relationship suggested a levoglucosan:PM-wood ratio of 18.4% ($\pm 13\%$). Assuming similar factors for OM:OC as above would suggest a levoglucosan/OC ratio of 40–48%. This ratio is much higher than those found elsewhere in the literature, and higher than *Hedberg et al.* [2006] found in the test burns mentioned above. However, the source-receptor model only accounted for 61% of the observed PM_{2.5} mass. If some of this missing mass is associated with wood combustion the levoglucosan/OC estimate from this work would be lowered somewhat. It is not clear why the Norwegian and Swedish estimates should be so different. One possible reason though could be very different technology levels for wood-burning appliances used in the different areas.

[49] Thus, although emission ratios seem to vary, most studies show a levoglucosan/OC ratio of around 10–20%. Lower ratios are possible, but higher ratios unlikely, which allows us to use levoglucosan as an invaluable tracer which can set lower limits at least on the contribution of OC derived from wood burning to OC measured at a site.

[50] For simplicity, we have used a ratio of levoglucosan/OM of 10% in the model, but will present results within a factor of two of this, i.e., with ratios of 5, 10 and 20%. Since our emission inventory assumes an OM:OC ratio of 1.3 for all sources this corresponds to levoglucosan/OC of 13%, with a range from 6.5% to 26%. This range should span the likely possible range of emission ratios over most of Europe, although does not capture the extreme values found in northern Sweden.

5.2. Biogenic Emissions

[51] Additionally, hourly biogenic emissions of NMVOC arising from forests are calculated by the model using the emissions algorithms of *Guenther et al.* [1995], combined with emission factors developed for European species [*Simpson et al.*, 1999, 2003]. The calculations of monoterpene emissions have been updated in this study (as compared to *Andersson-Sköld and Simpson* [2001]), with respect to forest maps, biomass density and emission factors. For most of Europe, species-specific maps from *Köble and Seufert* [2005] were used, enabling the identification of 116 different species across 30 countries. Emission factors for each species were based largely upon *Simpson et al.* [1999], with some updates for Mediterranean species from the University of Lancaster database of BVOC emissions factors [*Stewart et al.*, 2003]. Additionally, for Norway spruce (*Picea abies*) the light-dependent emissions were ignored, and the temperature-only “standard” (30°C and full sunlight) emission factor set to 3.0 $\mu\text{g g}^{-1}\text{h}^{-1}$. Uncertainties in these factors are discussed in section 8.4.

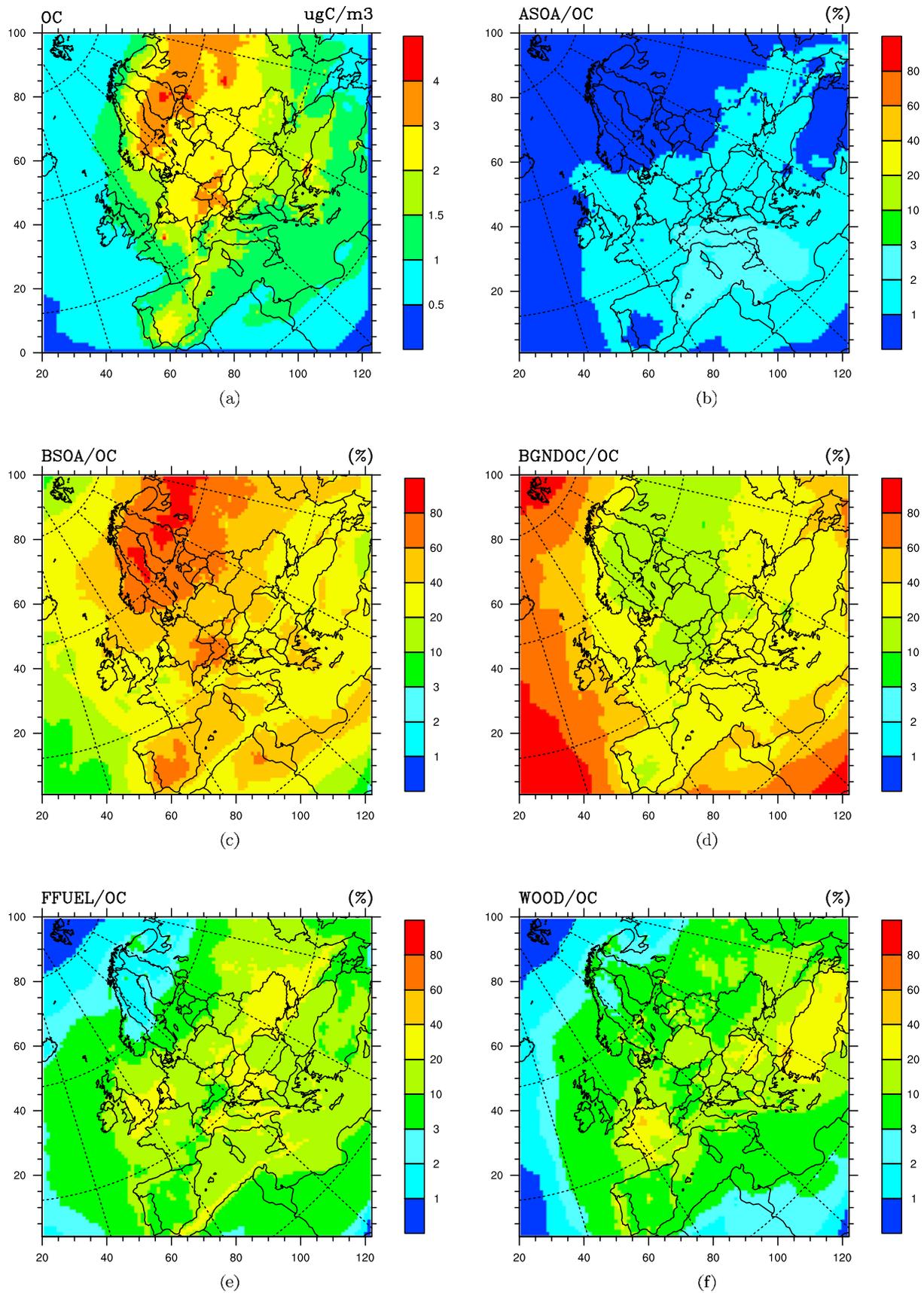


Figure 2. Results: Modeled OC results for 2002, scheme Kam-2X. (a) Concentrations ($\mu\text{g C m}^{-3}$) and percentage contributions to total OC from (b) ASOA, (c) BSOA, (d) background, (e) fossil fuel, and (f) wood combustion.

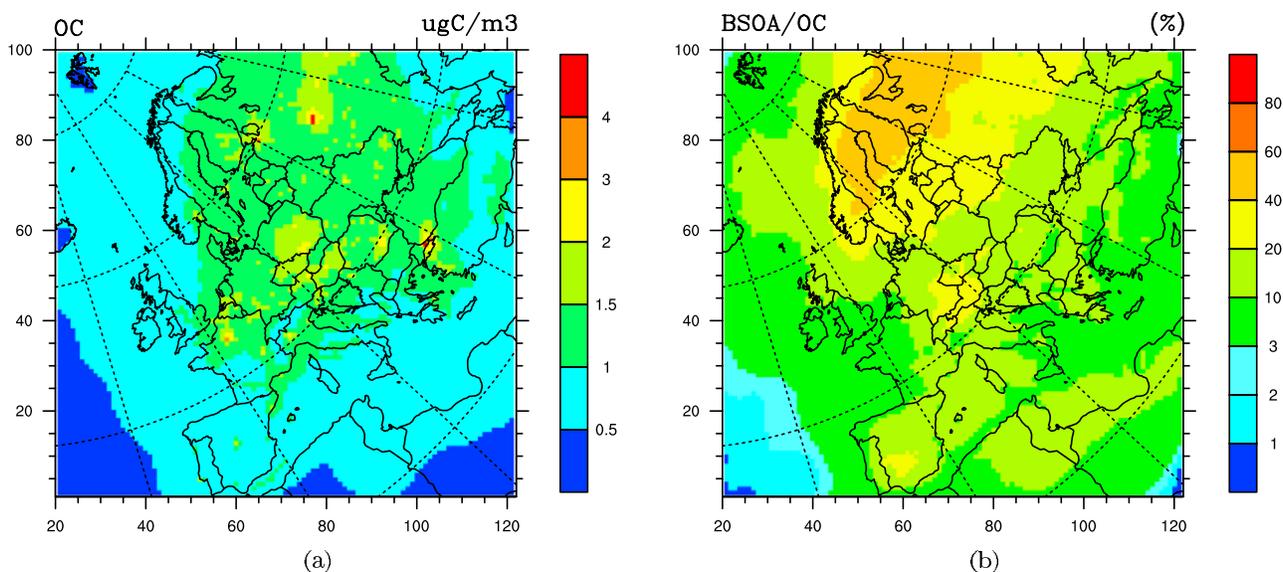


Figure 3. Results: Modeled OC results for 2002, scheme Kam-2. (a) Concentrations ($\mu\text{g C m}^{-3}$) and (b) percentage contributions to total OC from BSOA.

[52] Foliar biomass densities (D) for spruce and other coniferous forest were assumed to follow the latitudinal relationships specified in Lindfors *et al.* [1999], although limited to the range $600 \text{ g m}^{-2} < D < 1400 \text{ g m}^{-2}$ for spruce, and $200 \text{ g m}^{-2} < D < 700 \text{ g m}^{-2}$ for other coniferous species.

6. Base Case Results

[53] Figure 2 shows the modeled annual average OC concentration, obtained for the year 2002, using the Kam-2X BSOA scheme. This scheme clearly shows a broad maxima of OC in northern and eastern Europe and particularly for Finland and Russia, although urban areas in Paris, Milan and Istanbul are also visible. Figures 2b–2f show the percentage contributions of the different components to this total, and illustrate how the relative contributions vary markedly across Europe. For example, BSOA shows a maximum contribution in northern and eastern Europe. The background OC levels (BGND-OC) also contribute significantly to the total OC levels, amounting to over 40% in Scotland and Ireland, and even 20% over much of Spain. Primary fossil fuel emissions (FFUEL) account for typically 3–20% of calculated OC. Wood burning also accounts for similar levels of OC. In contrast, Figure 3b shows that the anthropogenic contributions from ASOA are very small everywhere (<3%) compared to other sources.

[54] Figure 3a shows the modeled OC concentration obtained using the Kam-2 scheme for BSOA. Figure 3b shows the percentage contribution of BSOA. The results of the Kam2 scheme show a relatively flat field of OC across Europe, with most areas experiencing between 1 to $2 \mu\text{g m}^{-3}$ OC. A few major urban areas show levels of OC exceeding $4 \mu\text{g m}^{-3}$, notably Paris, Istanbul and Moscow. The contribution of BSOA is much less than for the Kam-2x scheme, but still exceeds 40% in northern Europe. The difference between Figures 2a and 3a is dramatic, and gives some indication of the uncertainty associated with SOA modeling.

[55] These results are illustrated as time series plots in Figure 4, for both the Kam-2 and Kam-2X schemes. Consistent with the maps discussed above, the Kam-2X shows significantly greater BSOA formation than Kam-2. Interestingly, the BSOA contribution is seen to be as high in winter as in summer at some sites, especially with the Kam-2X scheme. This result shows that the effect of increased condensation due to lower temperatures can easily outweigh the effect of much lower terpene emissions in wintertime. The contribution of the WOOD sources is also very significant in the winter months at all sites (throughout the year at Aveiro). Primary FFUEL contributions are relatively low at the Nordic sites, but significant elsewhere. For all sites, and with both schemes, the contribution of ASOA is insignificant compared to BSOA and/or POA sources.

[56] A clear conclusion from the results shown in Figure 4 is that the BSOA formation is very sensitive to the choice of partitioning coefficients.

7. Comparison With Measurements

[57] Figures 5–12 show comparisons of the modeled versus measured values of some aerosol components made at selected CARBOSOL and EMEP sites. Tables 4–6 summarize the results for levoglucosan and TC at all sites. For TC we present results from both the Kam-2 (Table 5) and Kam-2X (Table 6) schemes. The time series plots for levoglucosan include a factor of two range of uncertainty in order to reflect the discussions presented in section 5.1. For the CARBOSOL sites, SO_4^{2-} serves as a useful marker of model performance for a compound where the emissions and chemistry are known reasonably well. EC serves as a marker of primary anthropogenic sources. (EC is included here in order to aid the interpretation of the TC results, but is discussed in much more detail by Tsyro *et al.* [2007]).

[58] For the CARBOSOL sites (Figures 5–7) the EMEP model captures observed SO_4^{2-} levels very well. Annual correlation coefficients were $r = 0.84, 0.61$ and 0.65 for AVE, KPZ and PDD, respectively. The good agreement for

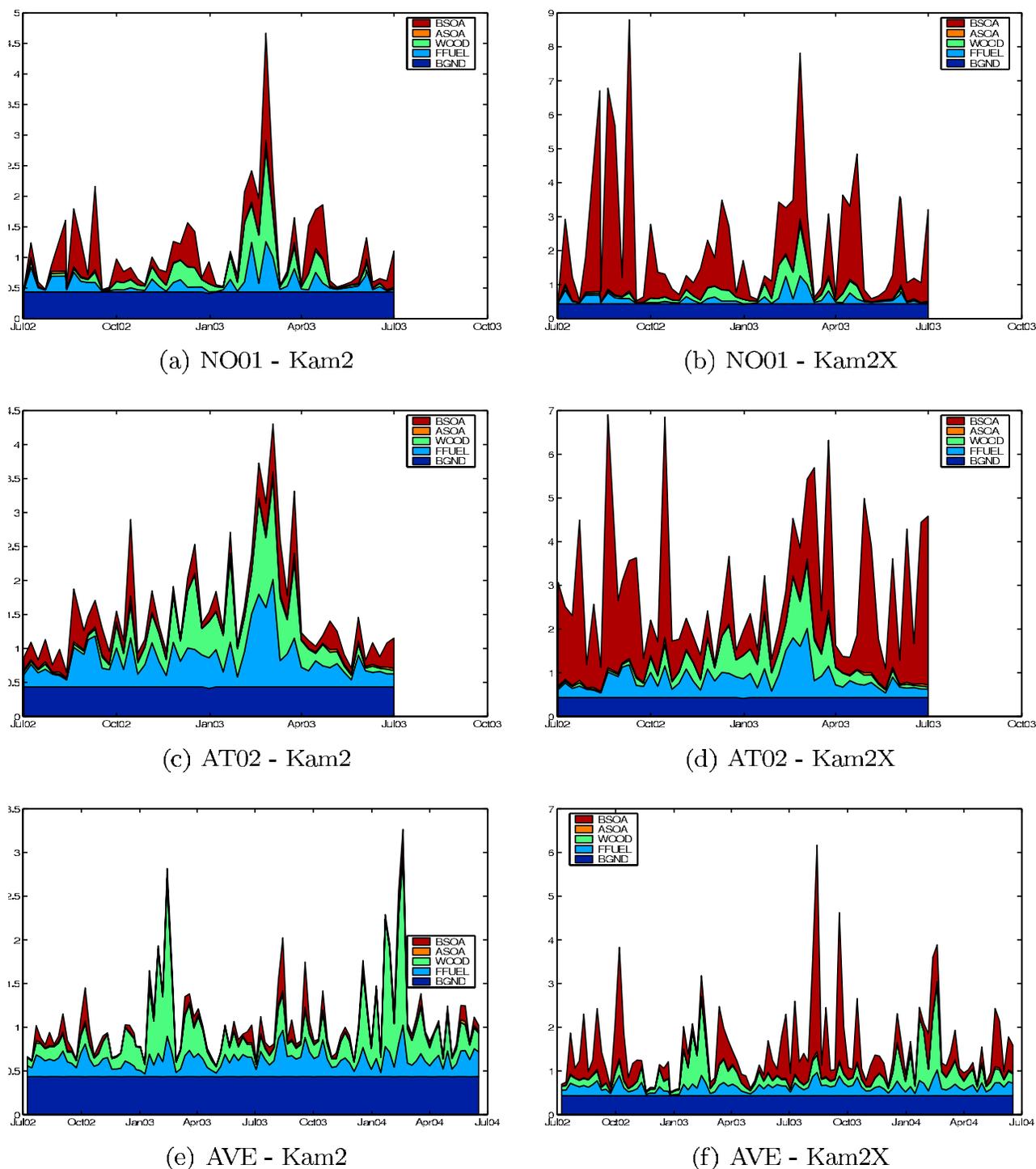


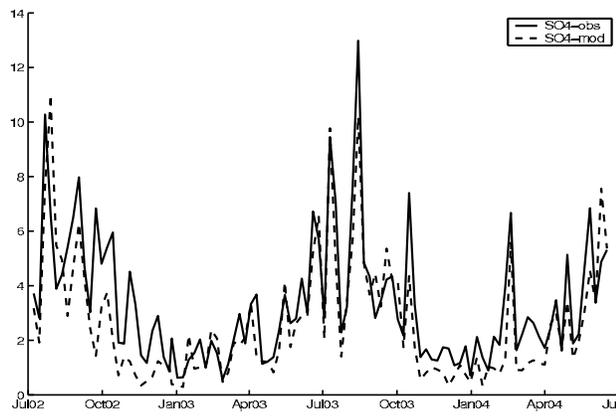
Figure 4. Contributions of BSOA, ASOA, WOOD, FFUEL and BGND components to modeled OC, using either the (left) Kam2 or (right) Kam2X model. Sites are (a and b) Birkenes, Norway (NO01); (c and d) Illmitz, Austria (AT02); and (e and f) Aveiro, Portugal (AVE).

sulphate suggests that the model itself performs well in terms of advection and dispersion for pollutants where the emissions are well known. Much more extensive evaluations for sulphate and other inorganic species have been presented elsewhere [e.g., Fagerli *et al.*, 2003], and confirm this conclusion.

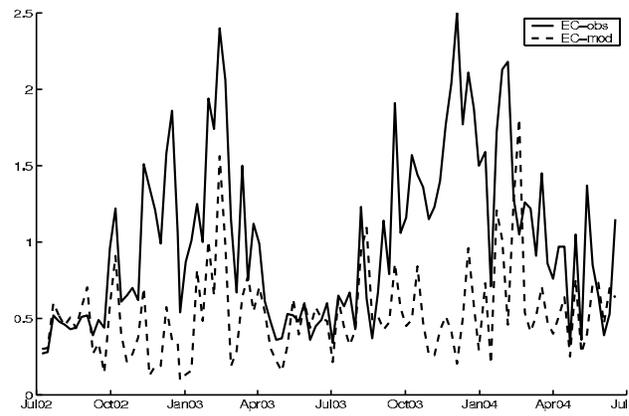
[59] Model results for EC are worse than for SO_4^{2-} in wintertime, with significant underpredictions at all sites

(giving lower annual correlation coefficients, $r = 0.40, 0.64, 0.31$ for AVE, KPZ, PDD). Summertime EC levels are captured fairly well however, which might suggest that the major source of EC in summertime, mobile sources, is captured satisfactorily.

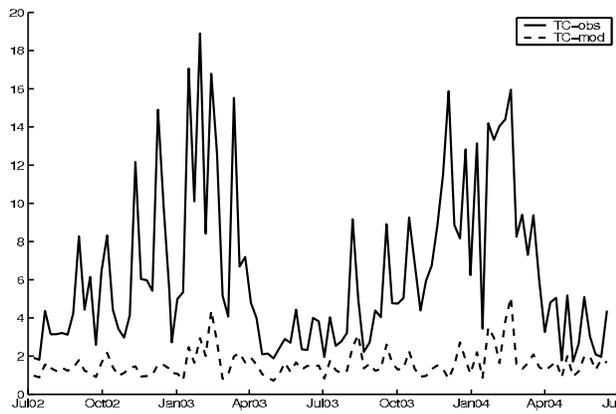
[60] For the two surface sites (AVE, KPZ), both model versions (Kam-2 and Kam-2X) significantly underpredict observed TC levels. The Kam-2X results are somewhat



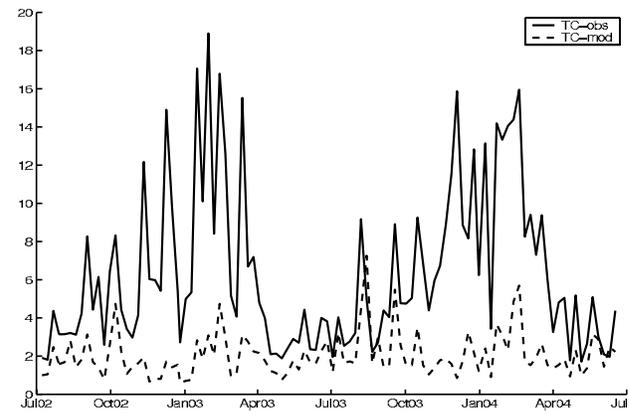
(a) SO_4^{2-}



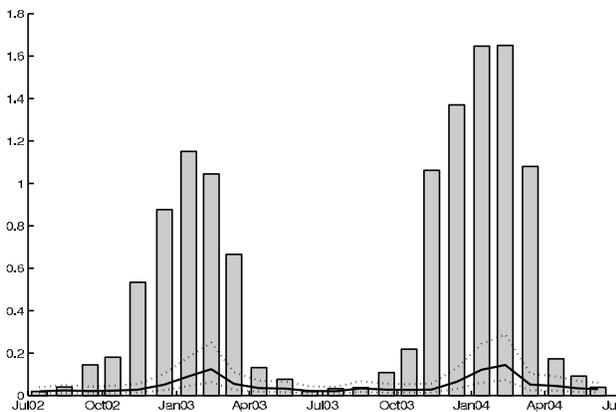
(b) EC



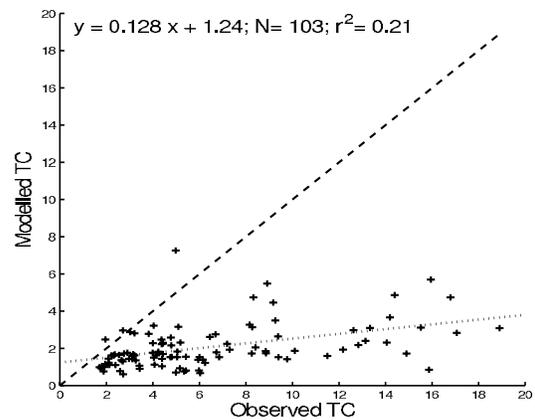
(c) TC - Kam2



(d) TC - Kam2X



(e) Levoglucosan



(f) Scatter-plot, Kam2X

Figure 5. Modeled and observed results for Aveiro (AVE), Portugal. Units are $\mu\text{g C m}^{-3}$ for TC and EC and $\mu\text{g m}^{-3}$ for SO_4^{2-} and levoglucosan. For levoglucosan, bars indicate observations, the solid line indicates the central value of model results, and dotted lines indicate the factor of two range about this central value. For the scatterplot the dashed line gives the 1:1 correspondence, and the dotted line is the regression line. For other plots the observations are given as solid lines, and the modeled results are given as dashed lines.

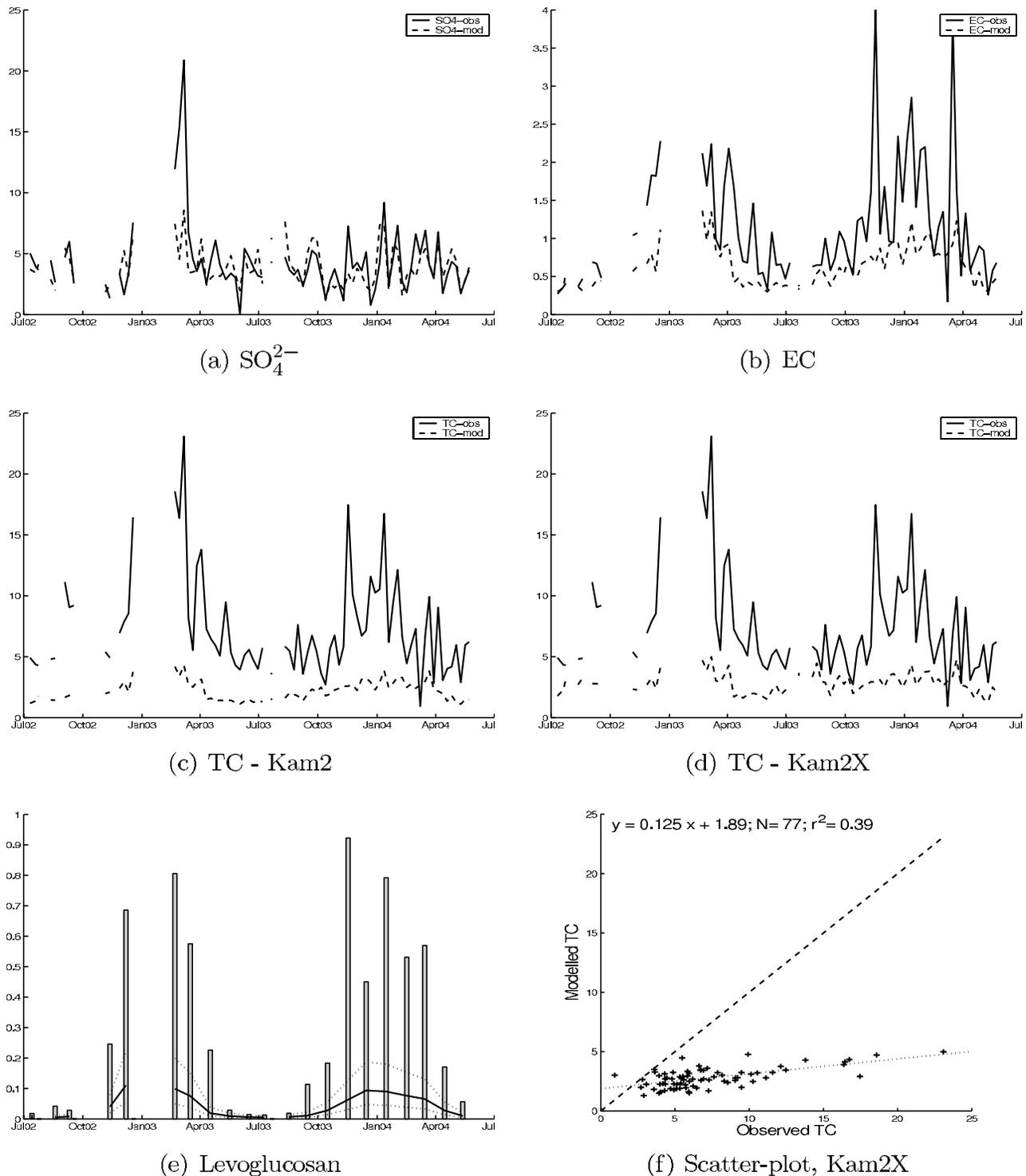


Figure 6. Modeled and observed results for K-Puszt (KPZ), Hungary. Units and setup are as for Figure 5.

better, but both summertime and wintertime TC are underestimated by factors of 3–5. TC levels at the mountain site PDD are reproduced rather well with the Kam-2X scheme, however, with the seasonal cycle here showing a distinct summer maxima.

[61] The failure of either model scheme to reproduce TC levels, despite good agreement for SO_4^{2-} and reasonable summertime agreement for EC, must result from either an

underestimate of POA emissions, or an underestimate of SOA formation. In summertime we have insufficient information from these data alone to allow us to distinguish between these possibilities (see section 7.1), but in wintertime the levoglucosan results yield valuable clues. For Aveiro and K-Puszt the modeled levoglucosan values significantly underpredict the observed winter values, by a factor of almost eight at KPZ, or over 14 at AVE. As noted in section

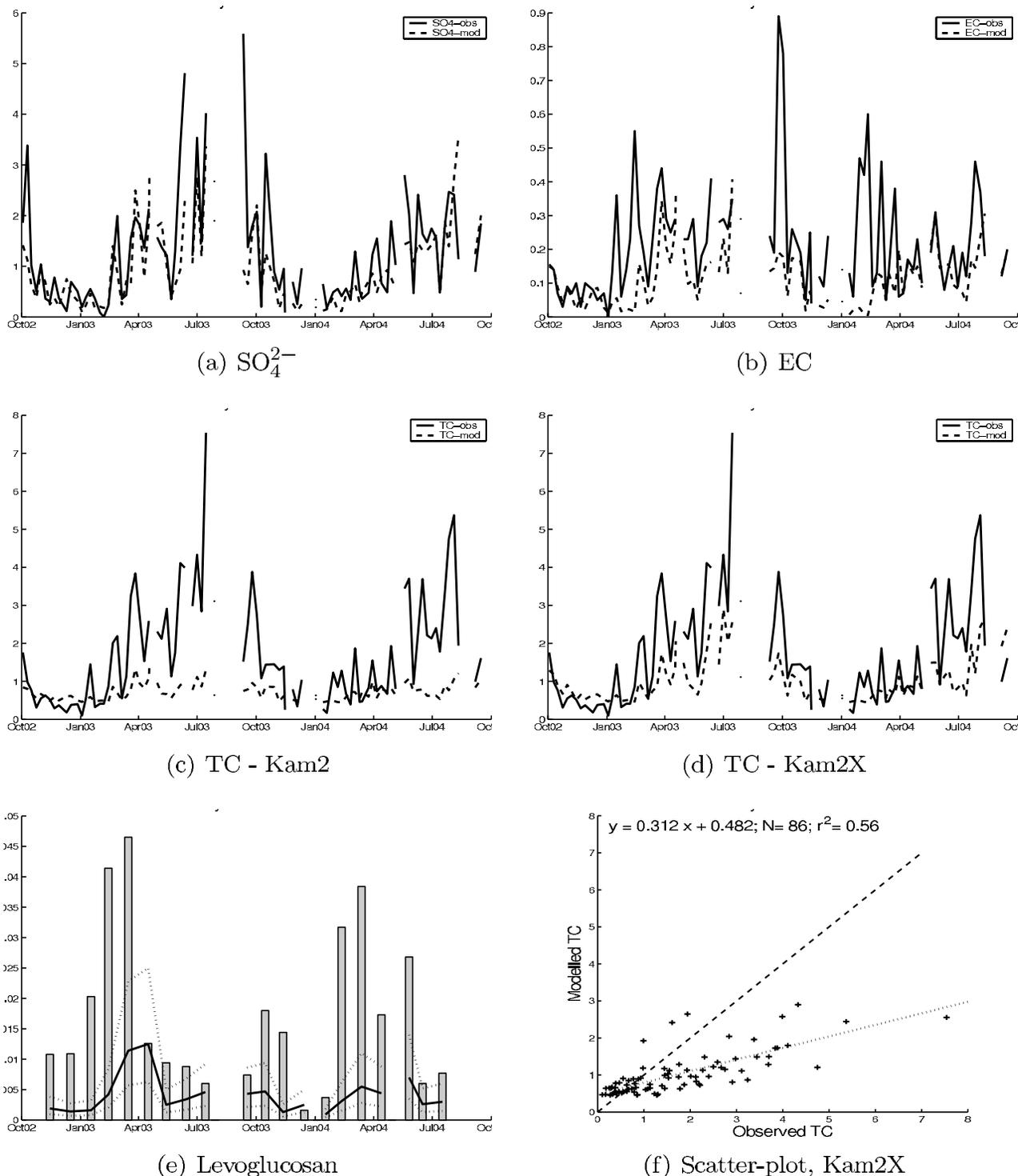


Figure 7. Modeled and observed results for Puy du Dome (PDD), France. Units and setup are as for Figure 5.

5.1, the base model setup assumes a levoglucosan/OM ratio of 10%. It is unlikely that this ratio could be much above 20%, so these results demonstrate that the measured TC at these sites must have a much larger contribution from wood-burning sources than is captured in the model. At Aveiro for example, if we assume that the levoglucosan/OC ratio in sources influencing the site is around 13%, the measured $0.96 \mu\text{g m}^{-3}$ levoglucosan (wintertime) would be associated

with an OC concentration of around $7 \mu\text{g C m}^{-3}$ OM, which alone (and accounting for uncertainties in the levoglucosan/OC ratio) could account for almost all of the measured wintertime TC, $8.9 \mu\text{g C m}^{-3}$ (or OC, $7.6 \mu\text{g C m}^{-3}$).

[62] At PDD the levoglucosan is also significantly under-predicted (factor 6), but concentration levels are so low ($0.03 \mu\text{g m}^{-3}$ STP in wintertime) that this underprediction has less consequence for the TC comparison. Interestingly,

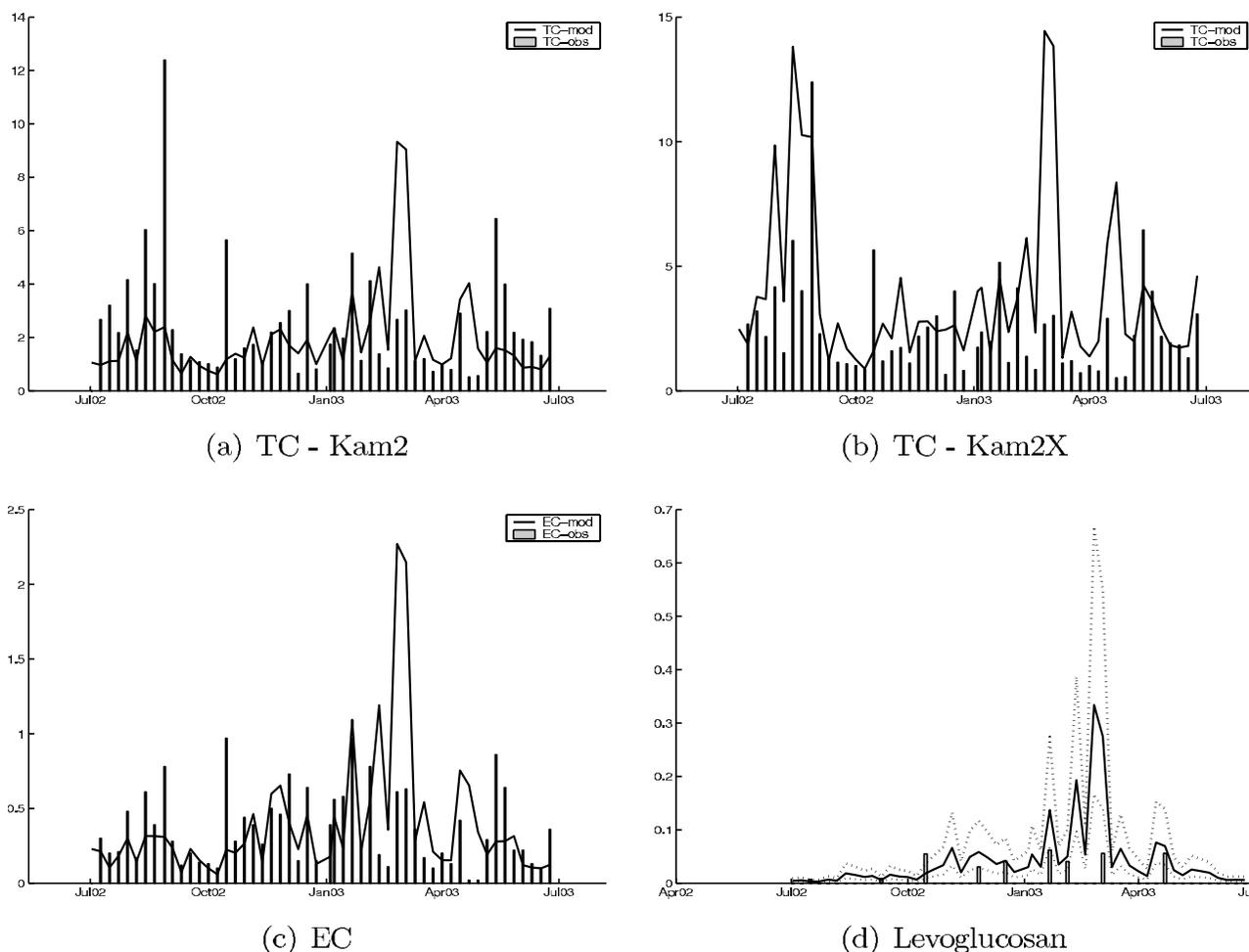


Figure 8. Modeled and observed results for Virolahti, Finland. Units and setup are as for Figure 5.

at SIL (not shown), the modeled levoglucosan is 50% greater than the observed values, as is the modeled TC.

[63] For the Nordic EMEP sites Virolahti and Birkenes (Figures 8 and 9), model performance for TC with either Kam-2 or Kam-2X is much better than for the more southerly CARBOSOL sites, and now with a tendency to overpredict rather than underpredict TC. The use of Kam-2X rather than Kam-2 leads to a better reproduction of the summer peaks, e.g., in August 2002. Although Kam-2X seems to improve the performance of the model during summertime, it also seems to cause some degradation of performance in winter. An interesting example occurs at Virolahti during spring 2003. The model overpredicts EC and TC significantly in this period, suggesting a problem with dispersion or advection. The use of Kam-2X instead of Kam-2 leads to an even higher prediction, as a result of the greater partitioning of any SVOC into the aerosol organic phase (see Figures 4a and 4b).

[64] As an interesting aside, we can note that a number of episodes at Nordic sites during August and September 2002 have been associated with biomass burning in eastern Europe [Niemi *et al.*, 2005]. Although the evidence for such a biomass burning contribution was very sound (supported by elemental analysis and other observations), the EMEP + Kam-2X model as used here is also able to

reproduce the peaks in August 2002 without any inclusion of forest fires or specific agricultural fires. This suggests that dispersion conditions and probably SOA formation, as well as biomass burning played a strong role in the production of elevated TC levels on those days.

[65] Although the number of levoglucosan samples is limited for the EMEP sites, the results are very similar for all Nordic sites; the model overpredicts by factors of 2–4. Thus, in contrast to the results found above for the more southerly CARBOSOL sites, there is no evidence of missing wood-burning sources in the Nordic areas, and some indication that such sources may be overpredicted in the model. (We cannot rule out however that the ratio levoglucosan/OM is much lower in Nordic areas than our model assumes. This would also explain the overprediction of levoglucosan.)

[66] The site Mace Head on the coast of Ireland (Figure 10) provides a nice example where the model's simulation of EC is very good with only two occasions where episodes were missed. In wintertime a correlation of $r = 0.91$ was achieved for EC. The results for levoglucosan are mixed, but levels are very low in both the model and measurement ($\leq 0.01 \mu\text{g m}^{-3}$), suggesting almost no impact of wood burning on measured TC levels. The model also does a fair job of simulating observed TC levels ($r = 0.77$).

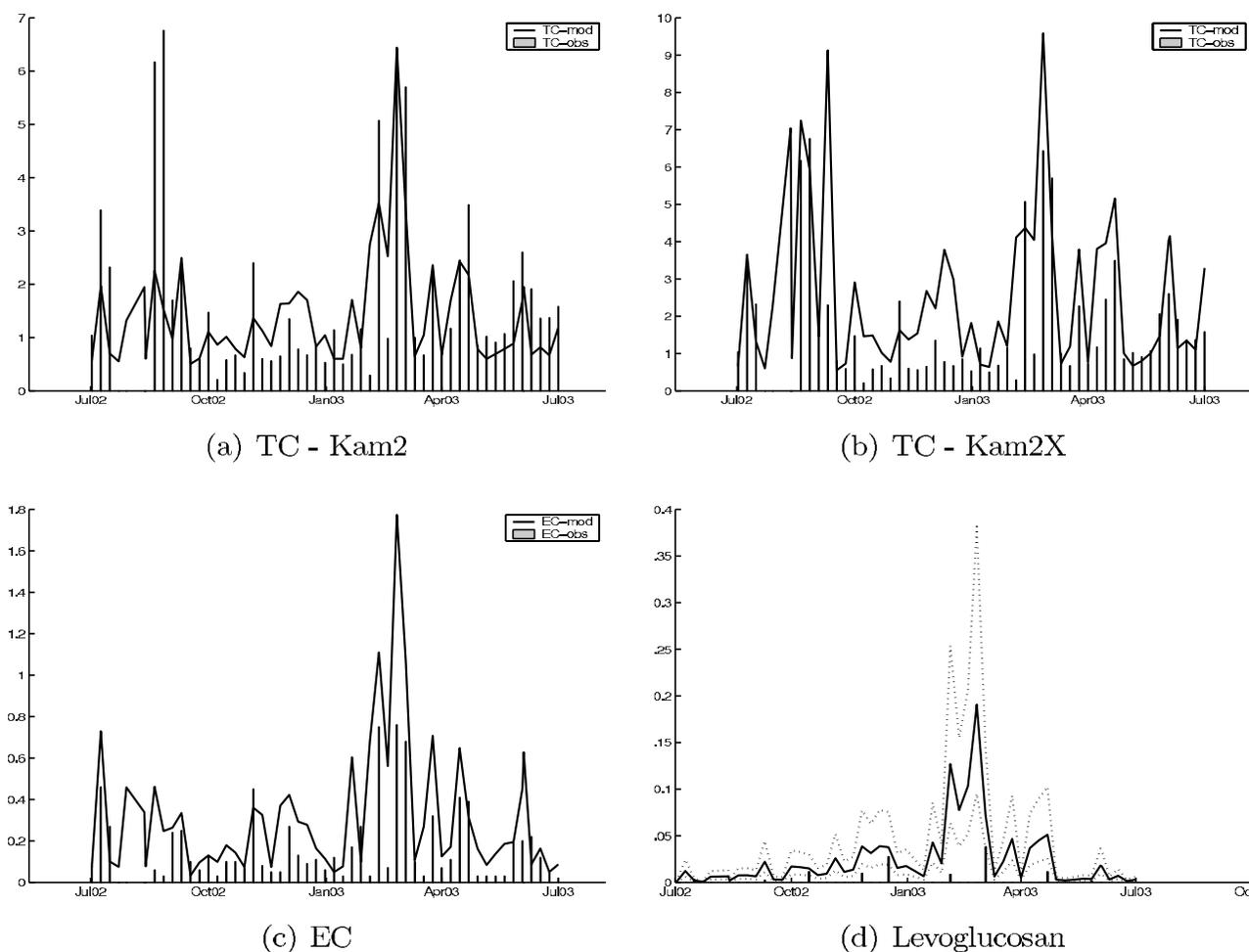


Figure 9. Modeled and observed results for Birkenes, Norway. Units and setup are as for Figure 5.

[67] Results for the German site Langenbrügge (not shown) are also somewhat similar to those found at Mace Head, although there are significant underpredictions of TC during December 2002 to January 2003 that are not seen in the EC results. Levoglucosan could not be detected in the (albeit few) samples from Langenbrügge, so wood burning is not likely to explain this discrepancy.

[68] The more southerly EMEP sites (Illmitz in Austria, Ispra in Italy) show rather similar patterns to the CARBOSOL sites. EC is often simulated reasonably well, but TC significantly underpredicted. Although few in number, the observed levoglucosan levels at these sites lie within the range of model assumptions. The biggest discrepancies for TC occur during the winter months rather than during summertime. Indeed, it is interesting to note that almost all these southerly sites show winter maxima in TC concentrations. Some of the larger discrepancies in TC occur at the same time as the larger discrepancies for EC, e.g., in February–March 2003 for Ispra. However, we are unable to say if this represents a problem with dispersion or POA/EC emissions.

7.1. Comparison With Derived Components

[69] One of the main features of the CARBOSOL project was the sampling of tracer species. Levoglucosan can be used as a tracer of organic carbon from biomass burning

(OCbb) and EC as a tracer (albeit crude) of primary OC emissions from fossil fuel (OCff). Measurements of cellulose can be used to determine the contribution of primary biogenic sources (OCbio). Pooled filter samples from summer and winter periods were also analyzed for ^{14}C , in order to determine the percentage of modern carbon versus C from fossil fuel sources. In the source-apportionment analysis of CARBOSOL, *Gelencsér et al.* [2007, hereinafter referred to as GSA] combined all of these sources of information in an effort to calculate the relative contributions of the primary sources of C (OCbb, OCbio, OCff, ECbb, ECff) and of the secondary sources, denoted SOAnf (SOA from non-fossil-fuel sources, which included condensation of SVOC from biomass burning as well as BSOA as used here) and SOAff (SOA from fossil fuel sources, equivalent to ASOA as used here, as well as condensation of SVOC from fossil fuel sources).

[70] Each step of this analysis, e.g., to estimate OCbb from levoglucosan, is of course very uncertain, so GSA defined both a central best estimate value for each factor with a plausible range of uncertainty. A form of Monte Carlo analysis was used to explore all possible combinations of these uncertain factors. In most cases, the results turned out to be rather robust, e.g., that SOAnf dominated

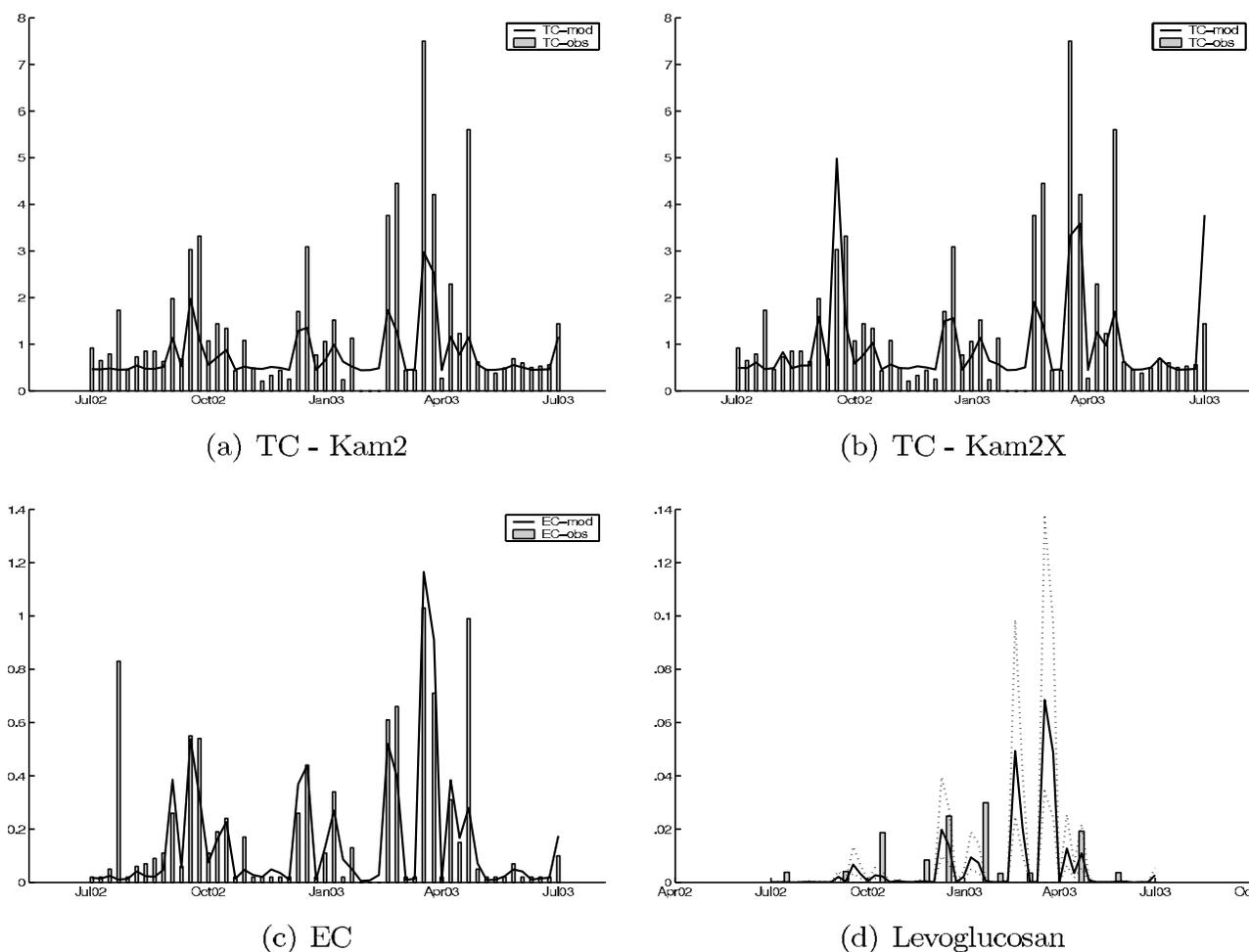


Figure 10. Modeled and observed results for Mace Head, Ireland. Units and setup are as for Figure 5.

TC levels at most sites in summertime, and that OCbb was often a major contributor in wintertime.

[71] Here we compare the results of the EMEP model with the GSA analysis. One problem in doing a true comparison is that the BGND-OC from the EMEP model is of unknown origin or composition, so we cannot analyze this fraction. Still, we can identify GSA's OCff with our FFUEL, OCbb with our WOOD, SOAnf with our BSOA, and SOAff with ASOA.

[72] We have pooled the results of the model to match the time periods used by GSA. Table 7 compares the components from the EMEP Kam-2 and Kam-2X model outputs with the corresponding component from GSA, for the three sites AVE, KPZ and PDD. For PDD only the summertime results are shown, as in winter the BGND-OC accounted for more than 80% of TC. As well as the central estimates of each contribution from GSA, Table 7 also includes the range of estimates (5–95th percentiles, which we will denote as the low and high estimates) as derived from the statistical analysis. For example, the central estimate for the contribution of OCbb to TC at Aveiro in summertime is $0.28 \mu\text{g C m}^{-3}$, but the statistical analysis suggests that the lowest estimate would be $0.23 \mu\text{g C m}^{-3}$, and the highest $0.44 \mu\text{g C m}^{-3}$.

[73] Considering first the wintertime values, Table 7 confirms the earlier observation that the EMEP model significantly underpredicts TC at AVE and KPZ. The OCbb derived from GSA is much greater than the model's WOOD (even if we use the low estimates for OCbb), again consistent with the findings from the time series comparisons. The model's EC is lower by a factor of about two than the central EC estimate at both sites, but is just within the lower limit of the uncertainty range for both sites. For KPZ the central observation-derived OCff matches well the model's FFUEL outputs. At AVE the model underpredicts the central OCff estimate by $\sim 50\%$, but is well within the uncertainty range for this component. For the ASOA components, the model gives very much smaller estimates than even the lowest bound of the observation-derived values in wintertime at both sites. Both Kam-2 and Kam-2X schemes underpredict the wintertime BSOA, but the Kam-2X scheme for AVE is just outside the lowest uncertainty bound, and for KPZ Kam-2X lies within the uncertainty range.

[74] In summertime, TC is again underpredicted at all sites, by factors of 1.6 (AVE), 1.9 (KPZ) or 2.7 (PDD), for the Kam-2X model. Concentrations of OCbb are underpredicted to some extent at AVE, and by a factor of at least 6 at KPZ. For PDD the model's predictions of WOOD lie just outside the lowest limit of the observation-derived OCbb

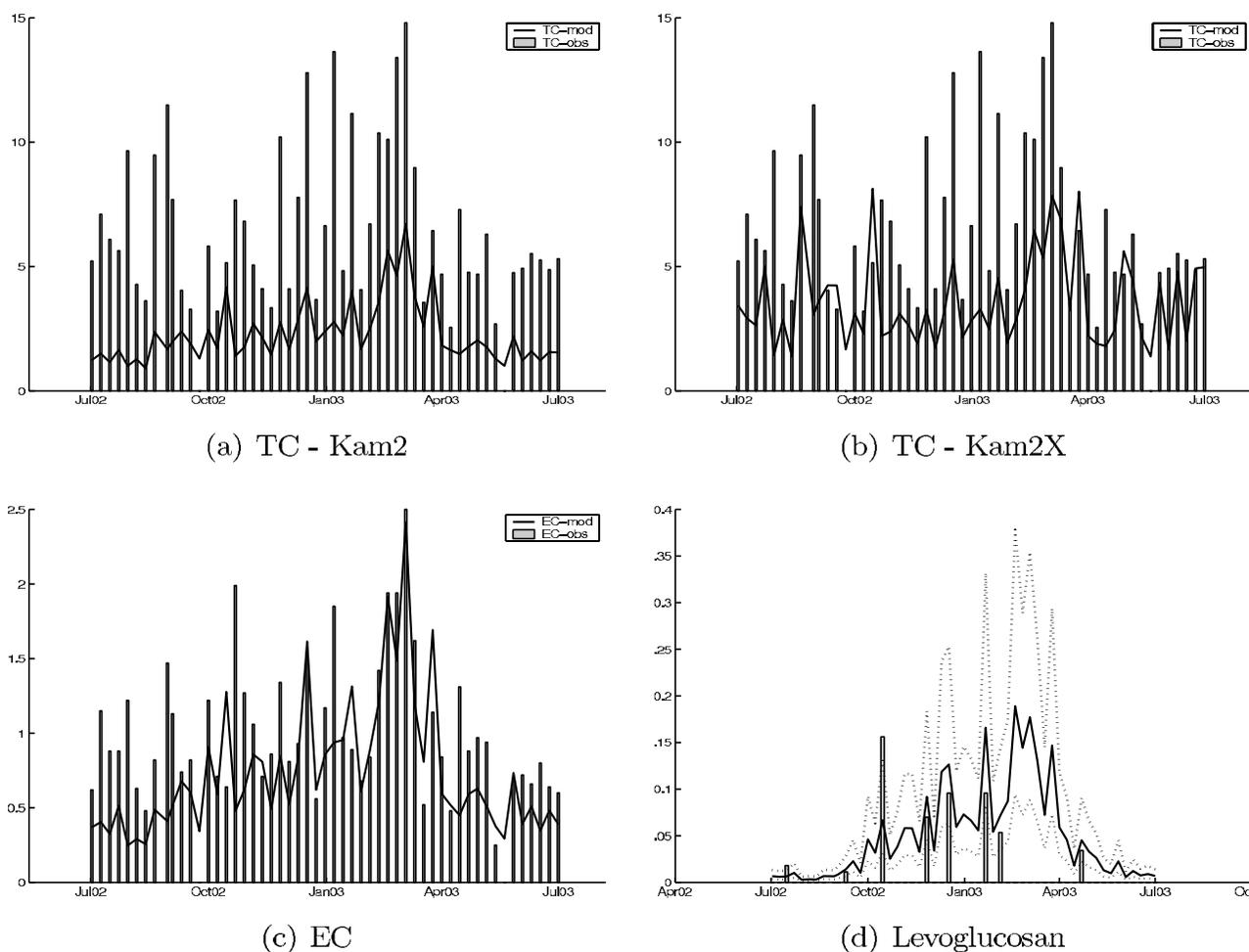


Figure 11. Modeled and observed results for Illmitz, Austria. Units and setup are as for Figure 5.

values. Levels of EC are predicted very well at all sites. For OCff, the model values lie well within the observed range at KPZ and AVE sites, and just outside for PDD. The biggest discrepancies are again seen for SOA components. The Kam-2 scheme severely underpredicts the observed SOAnf and SOAff values, lying well outside the uncertainty ranges. Kam-2X predicts more SOAff and SOAnf than Kam-2, but still gives values below the uncertainty range at all sites, typically underestimating by factors of 2–3. (For PDD it may be that the compounds included in the EMEP model’s BGND-OC species, which likely consist of a high fraction of SOA, could well account for some of the “missing” SOA when compared to the observation-derived data.)

7.2. Sensitivity to Wood-Burning Emissions

[75] The analysis of levoglucosan and the source-apportionment comparisons strongly suggest that OC from wood-burning emissions are underestimated at three of the CARBOSOL sites and some of the more southerly EMEP sites. Such underestimation may be the result of large-scale problems in the emissions inventory, or simply reflect the proximity of the site to nearby wood-burning activities, but whatever the cause the underestimate of WOOD-OC directly affects the model versus observed comparison of TC.

[76] In order to illustrate the possible significance of the wood-burning underestimates for total TC results, we have

used the wintertime levoglucosan results from Table 4 to rescale the modeled WOOD-OC values. For example, Table 4 shows that the model underestimates levoglucosan at Aveiro by a factor 4.3 (1.0/0.23). We have therefore multiplied the wood-burning contribution to OC by a factor 4.3 also for this site. For simplicity, we have ignored the much smaller changes brought about in the EC contribution to TC. We have also ignored the fact that increased OC brought about by this scaling of the WOOD contribution should promote further condensation of SVOC from non-wood sources, however this effect should be small. Figure 13 illustrates the resulting TC comparisons for Aveiro and K-Puszt, using the Kam-2X scheme. Compared to the original comparisons (Figures 5 and 6), the scaled TC results lie much closer to the observed TC levels. Indeed, for Aveiro the ratio of modeled to observed (M/O) wintertime values increases from 0.23 in the base case (Table 6) to 0.9, and the wintertime correlation coefficient increases from 0.63 to 0.72. For K-Puszt the correlation gets slightly worse (r decreases from 0.70 to 0.68), but the ratio of modeled to observed (M/O) wintertime values increases significantly, from 0.36 to 0.78.

[77] Changes for other sites are generally much smaller, reflecting the smaller contribution and influence of WOOD-OC at these sites. Still, the levoglucosan-based scaling of

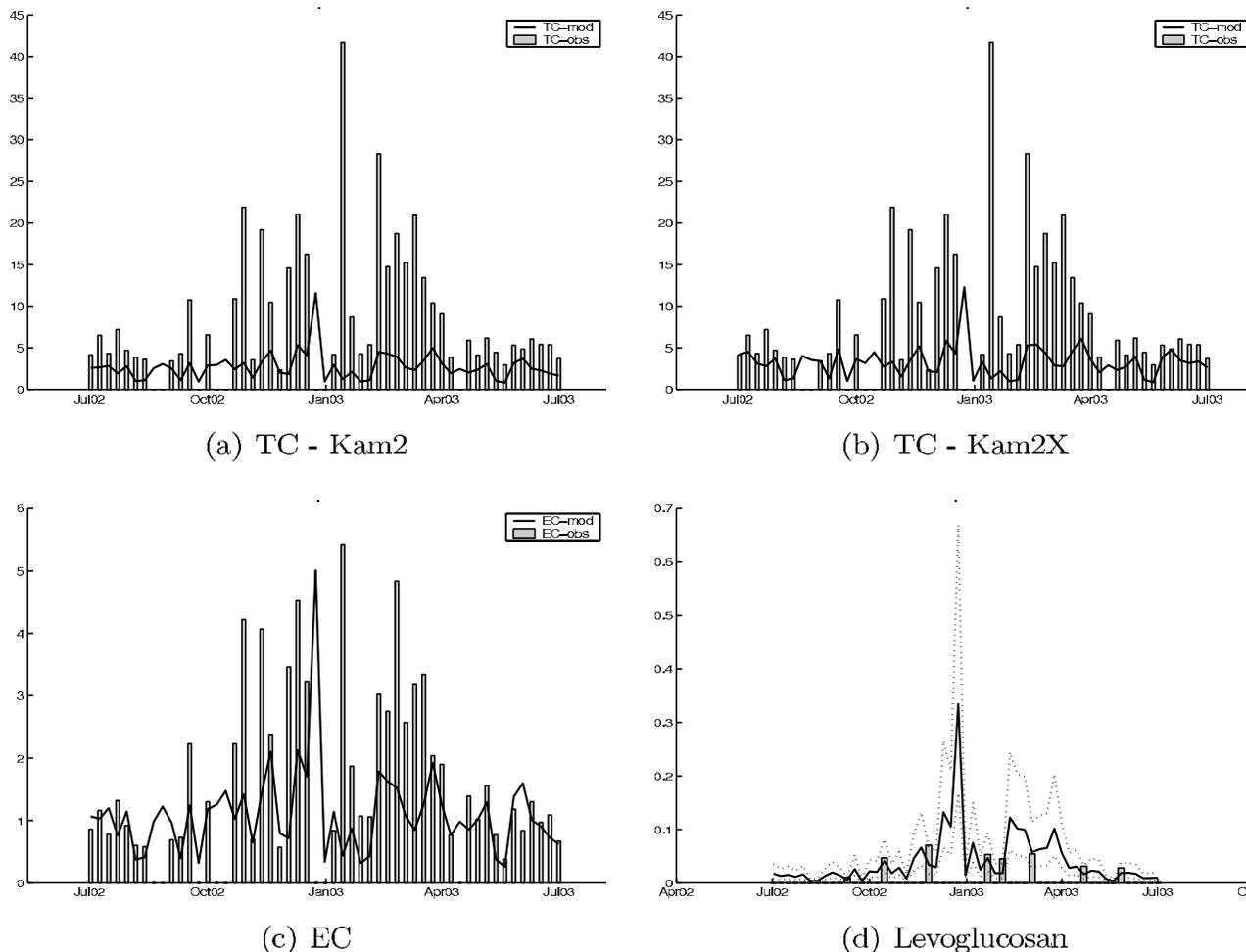


Figure 12. Modeled and observed results for Ispra, Italy. Units and setup are as for Figure 5.

WOOD-OC generally gives slightly better agreement and correlation with observed TC values.

8. Discussion

[78] A large number of factors make it difficult to conduct a true verification of modeled versus observed concentrations for EC and OC. One major problem has always been that measurements of OC and TC actually contain thousands of different and largely unidentified molecules, usually with no information on the proportion of primary, secondary, anthropogenic, or biogenic sources. Without such a distinction model verification will always be severely limited.

[79] The comparison discussed above of model results compared to the results from *Gelencsér et al.* [2007], denoted GSA represents the first time, to our knowledge, that model results for PCM can be compared against the components of TC and OC rather than just their totals. One important conclusion from this comparison (albeit limited to a few locations in south-central Europe) is that the model and inventory seem to do a decent job of reproducing primary fossil fuel EC and OC sources, which gives confidence in the emission inventory being used for these sources. The most notable feature of this comparison was the strong underprediction of (1) the biomass-burning components and (2) the SOA components, especially for

SOA. The possible reasons for problems in modeling SOA, biomass burning and other emissions are discussed below.

8.1. Status of SOA Mechanisms

[80] We noted in the introduction that recent reviews have highlighted the complexity of carbonaceous aerosol both in terms of known composition and formation mechanisms. Indeed, *Donahue et al.* [2005] commented that the understanding behind SOA formation from α -pinene, the most well studied and best understood monoterpene, was in “its infancy.” Even with the standard gas/particle (Odum/Pankow based) approaches as used here, the results of SOA models are subject to great uncertainties. This has been shown previously by *Pun et al.* [2003] in the U.S., and *Tsigaridis and Kanakidou* [2003] for global modeling. Here we have illustrated that two sets of assumptions for setting partitioning coefficients (our Kam-2, Kam-2X models), both derived from smog chamber experiments, can lead to markedly different predictions of TC. Compared to the GSA results our scheme with the greater partitioning (Kam-2X) seems to give better results, but when compared to observed time series of TC (Tables 5 and 6) then this scheme sometimes performs less well than Kam-2, and in any case both schemes substantially underpredict SOA formation compared to GSA. Given that both

Table 4. Comparison of Modeled Versus Observed Levoglucosan for CARBOSOL and EMEP Campaigns^a

Site	Annual				Summer				Winter			
	N	O	M/O	<i>r</i>	N	O	M/O	<i>r</i>	N	O	M/O	<i>r</i>
Aveiro	24	0.52	0.09	0.83	12	0.076	0.38	0.58	12	0.96	0.07	0.78
PuyDome	20	0.02	0.24	0.46	9	0.011	0.43	0.41	11	0.02	0.16	0.77
K-Puszt	21	0.31	0.13	0.91	11	0.066	0.16	0.86	10	0.58	0.13	0.65
Schauinsland	24	0.02	1.2	0.70	12	0.017	0.65	0.72	12	0.03	1.50	0.49
Virolahti	9	0.04	1.85	0.34	3	0.02	1.09	1.00	6	0.05	2.03	0.24
Aspvreten	10	0.01	4.32	0.13	4	0.00	87.2	0.95	6	0.02	3.00	0.28
Birkenes	10	0.01	3.63	0.11	4	0.00	4.28	0.79	6	0.02	3.50	0.00
Mace Head	10	0.01	0.24	0.34	4	0.01	0.38	1.00	6	0.01	0.19	0.24
Kollumer.	10	0.01	3.64	0.03	4	0.00	4.55	0.80	6	0.01	3.51	0.10
Kosetice	7	0.03	1.82	0.54	2	0.02	1.07	1.00	5	0.04	1.94	0.53
Stara-L.	10	0.05	0.94	0.17	4	0.04	0.30	0.06	6	0.05	1.26	0.20
Illmitz	9	0.06	1.14	0.43	4	0.02	1.39	0.34	5	0.09	1.11	0.01
Ispra	8	0.04	0.70	0.55	3	0.02	0.59	0.90	5	0.05	0.73	0.02
Braganca	9	0.04	0.36	0.25	3	0.02	0.40	0.63	6	0.04	0.34	0.19

^aUnit is $\mu\text{g m}^{-3}$. N, number of samples; O, observed concentration; M/O, ratio of modeled/observed; *r*, correlation coefficient. Summer here refers to April–September, and winter refers to October–March.

schemes likely miss many important aspects of SOA formation it should not be surprising that correlations with observations vary from site to site.

8.2. Other Sources of SOA

[81] A simplification made in this work has been to make use of a scheme for just one monoterpene species, α -pinene. This species was chosen because of the advantages of the Kam-2 type schemes as discussed in section 4.2, but many terpenes are believed to be more effective SOA producers. Indeed, results for northern Europe presented by *Andersson-Sköld and Simpson* [2001], making use of ten different terpene compounds (with speciation based upon *Lindfors et al.* [2000]), suggested about 50% more SOA formation with a mixture of species than with everything represented by just α -pinene. Although a significant uncertainty, it should be noted that the uncertainties associated with BVOC emissions and especially the SOA formation mechanisms are likely even greater than this. Further, modeling studies concerning multiple BSOA precursors can only be done with simple two-product schemes (e.g., *Andersson-Sköld and Simpson* [2001] used *Griffin et al.* [1999a, 1999b]), with accompanying limitations.

[82] Another biogenic VOC, isoprene, is potentially also a significant contributor to SOA formation [e.g., *Limbeck et al.*, 2003; *Claeys et al.*, 2004; *Kroll et al.*, 2006]. On a global scale the modeling study of *Henze and Seinfeld* [2006] found an increase of a factor of two in the global SOA budget, with largest changes in the free troposphere. The role of this compound deserve further investigation, as isoprene emissions are estimated to be comparable to those of terpenes in Europe [*Simpson et al.*, 1999].

[83] Finally, some of the model's apparent underprediction of SOAnf discussed in section 7.1 could be because of the definition of SOA used by *Gelencsér et al.* [2007]. SOAnf and SOAff are essentially defined as being OC which cannot be accounted for in terms of the primary emissions. Thus SOAff and SOAnf can include compounds which are emitted as gases, but later condense. This class of primary SVOC is not captured in PM emission inventories, and possibly not in current VOC inventories (which are often restricted to lighter compounds, with less than 20–30 C atoms). Indeed, *Makar et al.* [2003] showed that condensation of even a small percentage of anthropogenic VOC can have significant effects on OC formation.

Table 5. Comparison of Modeled Versus Observed Total Carbon (TC) for CARBOSOL and EMEP Campaigns, With Kam-2 BSOA Scheme^a

Site	Annual				Summer				Winter			
	N	O	M/O	<i>r</i>	N	O	M/O	<i>r</i>	N	O	M/O	<i>r</i>
Aveiro	103	6.33	0.25	0.65	51	3.71	0.39	0.68	52	8.90	0.20	0.68
PuyDome	86	1.70	0.42	0.74	38	2.62	0.32	0.59	48	0.97	0.64	0.73
Schauinsland	106	2.65	0.66	−0.01	56	3.64	0.42	0.29	50	1.53	1.30	0.52
K-Puszt	77	7.31	0.30	0.69	39	5.85	0.27	0.56	38	8.81	0.32	0.73
Virolahti	51	2.44	0.80	0.03	25	2.83	0.54	0.10	26	2.07	1.14	0.09
Aspvreten	48	2.41	0.81	0.01	24	2.79	0.48	0.03	24	2.03	1.26	0.08
Birkenes	49	1.74	0.82	0.44	23	2.07	0.57	0.39	26	1.44	1.14	0.68
Mace Head	50	1.39	0.56	0.77	27	1.20	0.56	0.55	23	1.63	0.56	0.88
Kollumer.	50	3.22	0.64	0.34	25	2.73	0.54	0.29	25	3.71	0.71	0.35
Waldhof	50	4.93	0.40	0.40	25	4.01	0.34	0.65	25	5.86	0.45	0.37
Kosetice	36	5.64	0.42	0.41	13	5.00	0.30	0.00	23	6.00	0.48	0.54
Stara-L.	51	5.10	0.36	0.05	25	5.58	0.26	0.12	26	4.65	0.48	0.20
Illmitz	51	6.58	0.35	0.39	25	5.65	0.28	0.00	26	7.48	0.41	0.47
Ispra	45	9.62	0.27	0.13	23	5.22	0.43	0.26	22	14.22	0.21	0.04
Braganca	50	4.89	0.18	0.26	26	3.34	0.26	0.38	24	6.58	0.14	0.35

^aUnit is $\mu\text{g C m}^{-3}$. Notation is as for Table 4.

Table 6. Comparison of Modeled Versus Observed Total Carbon (TC) for CARBOSOL and EMEP Campaigns, With Kam-2X BSOA Scheme^a

Site	Annual				Summer				Winter			
	N	O	M/O	<i>r</i>	N	O	M/O	<i>r</i>	N	O	M/O	<i>r</i>
Aveiro	103	6.33	0.32	0.46	51	3.71	0.55	0.64	52	8.90	0.23	0.63
PuyDome	86	1.70	0.60	0.75	38	2.62	0.53	0.60	48	0.97	0.73	0.69
Schauinsland	106	2.65	1.10	0.50	56	3.64	0.92	0.43	50	1.53	1.70	0.63
K-Puszt	77	7.31	0.38	0.62	39	5.85	0.42	0.37	38	8.81	0.36	0.70
Virolahti	51	2.44	1.61	0.23	25	2.83	1.53	0.39	26	2.07	1.72	0.06
Aspvreten	48	2.41	1.43	0.07	24	2.79	1.12	0.20	24	2.03	1.84	0.05
Birkenes	49	1.74	1.45	0.51	23	2.07	1.26	0.52	26	1.44	1.68	0.54
Mace Head	50	1.39	0.72	0.47	27	1.20	0.81	0.30	23	1.63	0.63	0.80
Kollumer.	50	3.22	0.85	0.26	25	2.73	0.87	0.18	25	3.71	0.83	0.35
Waldhof	50	4.93	0.60	0.48	25	4.01	0.67	0.73	25	5.86	0.56	0.37
Kosetice	36	5.64	0.63	0.30	13	5.00	0.61	0.00	23	6.00	0.64	0.53
Stara-L.	51	5.10	0.63	0.13	25	5.58	0.65	0.10	26	4.65	0.62	0.16
Illmitz	51	6.58	0.56	0.17	25	5.65	0.61	0.02	26	7.48	0.52	0.26
Ispra	45	9.62	0.33	0.07	23	5.22	0.57	0.30	22	14.22	0.24	0.03
Braganca	50	4.89	0.26	0.05	26	3.34	0.39	0.29	24	6.58	0.18	0.05

^aUnit is $\mu\text{g C m}^{-3}$. Notation is as for Table 4.

8.3. POA Emissions

[84] There are a large number of uncertainties surrounding emission factors and estimates for POA, arising from both the lack of emission measurements under ambient conditions (as opposed to laboratory tests or single-stack measurements, e.g., of domestic appliances), and the technological difficulties of PM measurements.

[85] The large contribution of domestic sources, and especially wood burning, to both EC and OC emissions

and to the CARBOSOL sites as discussed above is particularly troublesome. These sources are much more variable in time and space than industrial emissions, Although many of the problems of assessing wood-burning emissions have been discussed above, three other factors need to be recognized for modeling purposes. Firstly, the OC/EC ratio from wood burning is very uncertain. Table 3 suggests a European mean ratio OC:EC ratio of about 2.1:1, resulting from a mixture of fireplaces with OC:EC = 5:1, stoves with

Table 7. Comparison of Modeled Versus Observation-Derived Components of TC^a

	TC (TC)	OCbb (WOOD)	EC (EC)	OCff (FFUEL)	SOAnf (BSOA)	SOAff (ASOA)	OCbio ^b	BGND ^b
<i>Summer</i>								
AVE								
Obs-Der	4.0	0.28	0.54	0.31	2.4	0.39	0.062	N/A
Range		0.23–0.44	0.40–0.75	0.19–0.55	2.1–2.6	0.07–0.77	0.03–0.12	
Kam2	1.6	0.18	0.56	0.25	0.14	0.022	N/A	0.44
Kam2X	2.5	0.18	0.56	0.25	1.0	0.028	N/A	0.44
KPZ								
Obs-Der	5.2	0.33	0.49	0.27	3.2	0.35	0.24	N/A
Range		0.27–0.52	0.28–0.82	0.15–0.49	2.8–3.6	0.05–0.77	0.13–0.46	
Kam2	1.6	0.05	0.43	0.42	0.23	0.029	N/A	0.44
Kam2X	2.7	0.05	0.43	0.42	1.4	0.038	N/A	0.44
PDD								
Obs-Der	4.9	0.051	0.28	0.17	3.6	0.61	0.20	N/A
Range		0.043–0.082	0.021–0.38	0.11–0.33	3.2–3.8	0.31–0.93	0.11–0.38	
Kam2	0.95	0.036	0.21	0.09	0.16	0.022	N/A	0.43
Kam2X	1.8	0.036	0.21	0.09	1.0	0.028	N/A	0.43
<i>Winter</i>								
AVE								
Obs-Der	14.1	8.2	1.7	0.50	1.9	1.3	0.17	N/A
Range		7.4–9.8	0.7–3.1	0.09–1.1	0.3–3.2	0.2–2.8	0.09–0.33	
Kam2	2.6	0.97	0.9	0.26	0.06	0.01	N/A	0.44
Kam2X	2.9	0.97	0.9	0.26	0.27	0.01	N/A	0.44
KPZ								
Obs-Der	10.7	4.1	1.7	0.69	2.2	1.5	0.15	N/A
Range		3.6–5.9	0.6–3.1	0.2–1.32	0.4–3.4	0.3–3.0	0.08–0.27	
Kam2	3.0	0.72	0.9	0.75	0.21	0.02	N/A	0.44
Kam2X	3.4	0.72	0.9	0.75	0.60	0.02	N/A	0.44

^aUnits are $\mu\text{g C m}^{-3}$ for all components. Obs-Der refers to derived values of observed components as estimated by *Gelencsér et al.* [2007], denoted GSA. Range gives 5–95% percentiles of estimates from the same paper. Suffixes are as follows: bb, biomass burning; ff, fossil fuel; nf, non-fossil-fuel; bio, primary biogenic. The nearest EMEP model equivalents to the GSA categories are given in parentheses.

^bSome equivalent modeled or observed values are not available (indicated by N/A).

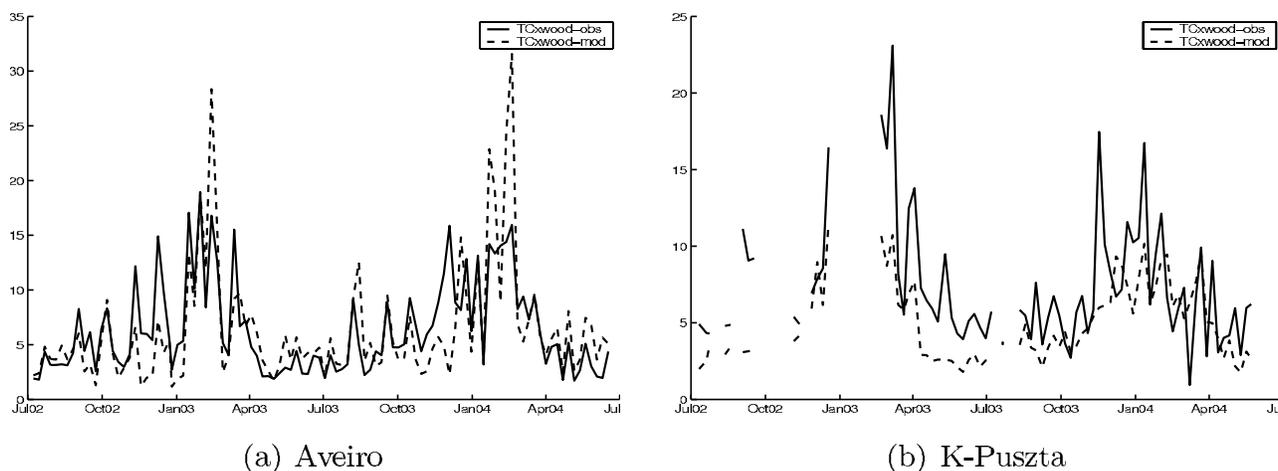


Figure 13. Modeled and observed results ($\mu\text{g C m}^{-3}$) for Aveiro (Portugal) and K-Pusztza (Hungary) after levoglucosan-based scaling of modeled OC. Scheme is Kam-2X.

3:1 and boilers with 1:1 or less [Kupiainen and Klimont, 2007]. Gelencsér *et al.* [2007] suggested a range from 1:1 to 15:1, with a central value of 6:1. If the ratio 6:1 is more appropriate than 2.1:1, all wood-derived OC levels in the model results would be increased by $\sim 27\%$ (EC levels would be only 44% of those we use).

[86] Secondly, the temporal variation of such emissions are modeled only crudely. Usage of wood in residential heating is expected to be strongly dependent on temperature, so that day to day variation in emissions is greater than for most other sources. The EMEP model specifies only the monthly variation of emissions for the residential sector as a whole for each country (including both wood and fossil fuel sources). When the model is compared to a large number of samples, or over long periods, the inability to capture day to day variations should cancel out to a large extent and a valid comparison can be performed. However, when the number of samples is few, this problem can introduce substantial uncertainty. Further, the model does not take into account heating season differences within the same country (e.g., north-south in Italy).

[87] Finally, domestic emission factors and activity statistics are highly uncertain. Emission factors are very technology-dependent, with older appliances typically emitting orders of magnitude more than modern devices. The number of emissions measurements is far too few in any region to deliver reliable emission rates. Further, many households make use of fuel wood which is not recorded in official statistics. This will occur especially in rural forested areas, or where summer/winter cabins are popular for weekend recreation, e.g., Scandinavia, or in northern Italy.

[88] Uncertainties in other anthropogenic emissions sectors are also significant. As discussed by Bond *et al.* [2004], superemitters can easily emit 10 times more PM than well-maintained vehicles, and so a fleet with just 5% superemitters can emit 45% more than a fleet without superemitters. Bond *et al.* quoted very wide ranges for the fraction of superemitters though, from 1 to 10% for countries such the U.S. and western Europe, and 5–20% for eastern Europe and the former U.S.S.R.

[89] Finally, forest and agricultural fires certainly do contribute to ambient TC levels, but forest fire emissions are not yet implemented in the EMEP OC/SOA model, and agricultural fires have only crude seasonal variations. However, Tsyro *et al.* [2007] did implement monthly fire emissions (from the GFED2 database [van der Werf *et al.*, 2006]) into the EMEP EC model, and we can derive rough OC contributions from these results. Tsyro *et al.* [2007] found EC contributions of around 50 ng m^{-3} (with a wide range however, up to 200 ng m^{-3} in 2002) in the areas influenced by fires (notably northern and eastern Europe, and Portugal). Changes in modeled levoglucosan levels would be of the same order of magnitude using the emission factors suggested by Andreae and Merlet [2001], and this would help to explain some of the underprediction in summertime levoglucosan observed at sites such as Aveiro. Assuming an OC/EC ratio of around ten [Andreae and Merlet, 2001] would suggest a much more significant OC contribution from forest fires of around $0.5 \mu\text{g m}^{-3}$. Such levels in Portugal, or NE Europe, are significant compared to the Kam-2 results presented in Figure 3, but less so for the Kam-2X results of Figure 2. Still, it seems clear that inclusion of forest fire OC emissions would help to account for some of the missing TC mass observed during summertime at sites like Aveiro (Figure 5), and should be addressed in future studies.

8.4. BVOC Emissions

[90] Both the modeling studies (especially using Kam-2X) and the source-apportionment of Gelencsér *et al.* [2007] suggest that biogenic SOA formation is a major source of OC over Europe. Unfortunately, the emission inventories for these compounds are still subject to very large uncertainties [Simpson *et al.*, 1995, 1999; Stewart *et al.*, 2003]. Difficulties in establishing emission factors include the natural variability of vegetation, seasonal variations in emission patterns (affecting composition of emissions), and difficulties with both chamber and micrometeorological techniques [e.g., Janson and de Serves, 2001]. For example, recent measurements for Norway spruce by Janson and de Serves [2001] and Hakola *et al.* [2003] would suggest standard (30°C , full sunlight)

emission factors of $\sim 1 \mu\text{g g}^{-1}\text{h}^{-1}$, whereas *Stewart et al.* [2003] suggested $4.0 \mu\text{g g}^{-1}\text{h}^{-1}$. Further, although there is evidence for a seasonal dependence of the standard emission rates [*Hakola et al.*, 2006; *Staudt et al.*, 2000; *Tarvainen et al.*, 2005] the observed seasonal variations are complex and difficult to parameterize [*Komenda and Koppmann*, 2002].

[91] It should be noted that emission estimates of monoterpenes are particularly uncertain for the Mediterranean region, since emission factors vary greatly among the species characteristic of this region, and many species have not been adequately assessed. Indeed, measured emission factors often vary significantly even for one species, possibly because of seasonal and climatic effects on emission rates [e.g., *Owen et al.*, 1997; *Seufert et al.*, 1997; *Staudt et al.*, 2000]. As a final example, beech (*Fagus sylvatica*) is widespread across Europe, and has not previously considered to be a great source of monoterpenes [*Guenther et al.*, 1994; *Simpson et al.*, 1999]. However, recent measurements [*Spirig et al.*, 2005] have suggested emission factors an order of magnitude greater than assumed here. In summary, it seems quite likely that emission estimates of monoterpenes in Europe still suffer uncertainties of several hundred percent, and this uncertainty will propagate directly to estimates of BSOA formation.

9. Conclusions

[92] We have presented the results of an extended version of the EMEP model, designed for studies of carbonaceous aerosol and especially SOA formation over Europe. This model has been compared to the results of measurements made at sites from the CARBOSOL network, and from the EMEP EC/OC campaign. Comparisons have included SO_4^{2-} , EC, TC, and levoglucosan, the latter being a useful tracer for biomass-burning emissions. For the first time, we have been able to compare the model's estimates of the different fractions of TC (denoted FFUEL, WOOD, ASOA, BSOA) with values derived from observations by *Gelencsér et al.* [2007], denoted GSA.

[93] The EMEP model was run with two versions of the SOA chemical mechanism, denoted Kam-2 and Kam-2X, with the latter giving a higher partitioning from gas to aerosol phase. This work suggests the following:

[94] 1. The EMEP model does a good job of reproducing concentrations of pollutants with well-known emissions and chemistry, for example of sulphate as presented here.

[95] 2. In northern Europe the model predicts TC levels which are in line with measured values, especially with the Kam-2X scheme. These predictions are dominated by modeled BSOA.

[96] 3. In southern Europe, including the CARBOSOL sites, both versions of the model significantly underpredict TC levels, especially in wintertime. Comparison with the results of *Gelencsér et al.* [2007], and with levoglucosan, suggests that the model underpredicts both the biomass burning and SOA components of the measured TC at these sites.

[97] 4. At all sites, the contribution of BSOA far exceeds that of ASOA. The relative contribution of BSOA compared to POA and background components varies significantly across Europe though, and at different times of the year.

[98] 5. Model results regarding SOA are extremely sensitive to assumptions about unknown variables.

[99] 6. The major uncertainties associated with modeling of PCM lie with the inventories and modeling of biomass-burning emissions, and with SOA modeling.

[100] A major problem in the modeling of PCM is that too many steps in the calculation process are very uncertain, and there are too few constraints. With so many free variables, it is quite likely that judicious (or unscrupulous!) tuning of the various parameters can result in a model version which would fit the measurements quite well, but the danger of getting the right answer for the wrong reasons is great. It seems clear that much more work is needed to constrain the various steps of the PCM modeling process in atmospheric conditions, including the following:

[101] 1. The emissions of BVOC need to be evaluated. Modeled concentrations of various monoterpenes can in principle be validated against measured concentrations, but very few data are available. Further, the short lifetime of many terpene species (and especially of sesquiterpenes) makes such comparisons tricky. Still, given the importance of BVOC to SOA formation, and the fact that emissions validation is possible with today's measurement methods, this step alone would act to significantly improve one of the most important inputs for PCM modeling.

[102] 2. The emissions of PM from anthropogenic sources need to be evaluated. Mobile source as well as residential combustion emissions are still highly uncertain, but very amenable to near-source validation experiments.

[103] 3. The emissions of heavy VOC from anthropogenic sources need to be evaluated. A fraction of the nonprimary TC classified as SOAnf or SOAff by GSA may consist of high-molecular-weight compounds which are still volatile at the point and temperature of emission, but which quickly condense to the particle phase. These VOC may fall outside the scope of both VOC and PM inventories, but contribute to measured TC.

[104] 4. Further use of tracers, such as ^{14}C , cellulose, levoglucosan, elemental analysis, etc., combined with source-apportionment and/or mass balance approaches is urgently needed to understand the components of PCM in the atmosphere. These aerosol phase measurements should be backed up by simultaneous measurements of the likely gas phase precursors to PCM, including BVOC, anthropogenically emitted VOCs, their degradation products, and compounds such as HCHO and glyoxal with multiple sources.

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