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Anthropogenic influence on biogenic secondary organic aerosol

**C. R. Hoyle^{1,2}, M. Boy³, N. M. Donahue⁴, J. L. Fry⁵, M. Glasius⁶, A. Guenther⁷,
A. G. Hallar⁸, K. Huff Hartz⁹, M. D. Petters¹², T. Petäjä³, T. Rosenoern¹¹, and
A. P. Sullivan¹⁰**

¹Institute for Atmospheric and Climate Science, ETH Zurich, Switzerland

²Department of Geosciences, University of Oslo, Norway

³Department of Physics, University of Helsinki, P.O. Box 64, 00048 Helsinki, Finland

⁴Carnegie Mellon University, Center for Atmospheric Particle Studies, Pittsburgh,
PA 15213, USA

⁵Chemistry Department, Reed College, Portland, OR, 97202, USA

⁶Department of Chemistry, Aarhus University, 8000 Aarhus C, Denmark

⁷National Center for Atmospheric Research, P.O. Box 3000, Boulder, CO, USA

⁸Desert Research Institute, Storm Peak Laboratory, P.O. Box 882530, Steamboat Springs,
Colorado, USA

⁹Department of Chemistry & Biochemistry, 224 Neckers Hall, Southern Illinois University,
Carbondale, IL 62901, USA

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¹⁰ Colorado State University, Department of Atmospheric Science, Fort Collins,
CO 80523, USA

¹¹ Environmental Chemistry, Engineering Sciences Lab 230, Harvard, Cambridge,
MA 02138, USA

¹² North Carolina State University, Marine Earth and Atmospheric Sciences, Raleigh,
NC 27695, USA

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Correspondence to: C. R. Hoyle (christopher.hoyle@env.ethz.ch)

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Abstract

Because of the climate and air quality effects of organic aerosol, it is important to quantify the influence of anthropogenic emissions on the aerosol burden, both globally and regionally, and both in terms of mass and number. Methods exist with which the fractions of organic aerosol resulting directly from anthropogenic and biogenic processes can be estimated. However, until now, the possible anthropogenic enhancement of secondary organic aerosol formation from naturally emitted precursors has not been explicitly accounted for. Here, we describe the mechanisms through which such an effect may occur and suggest methods suitable to detect it in measurements. An examination of published data reveals qualitative support for the existence of the enhancement effect.

1 Introduction

Organic material can comprise a significant fraction of particulate aerosol mass at urban and remote locations (e.g. Chow et al., 1994; Malm et al., 1994; Andrews et al., 2000; Zhang et al., 2006; Jimenez et al., 2009). The last decade saw significant improvements in the characterisation of organic aerosols and the understanding of their sources and impacts on the environment. This research has provided insight into the contribution of organics to fine particulate matter, and thus potentially negative health effects (Ostro and Chestnut, 1998). Organic aerosols play an important role in the climate system. They affect the Earth's radiation balance directly by scattering sunlight, but also indirectly through their role as cloud condensation nuclei (CCN) (Twomey, 1974; Twomey et al., 1984; Albrecht, 1989; Charlson et al., 1992; Chuang et al., 1997; Adams et al., 2001; Hansen and Sato, 2001; Schulz et al., 2006). Further, the presence of organic species in atmospheric aerosol can affect the hygroscopicity and the ability of internally mixed aerosol particles to serve as CCN (Corrigan and Novakov, 1999; Prenni et al., 2001; Giebl et al., 2002; Raymond and Pandis, 2002; Kumar et al.,

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2003; Prenni et al., 2003; Merikanto et al., 2009).

The role of organic aerosols in visibility-reducing haze on the regional scale (e.g. Tanner, 2000) has also been examined. Because of the effects of organic aerosols on air quality and climate, it is desirable to separate the anthropogenic contribution from the natural background, to guide future regulatory measures that may be implemented in order to lower emissions contributing to the organic aerosol burden. Usually, regulation targets the control of various kinds of emissions such as SOA precursors, nitrogen oxides (NO_x), particulate matter mass, or sulphate mass. Before implementing emission controls, chemistry models at a range of scales are used to assess the effect of changes in emissions on the organic aerosol burden. In large scale chemical transport models, organic aerosols have commonly been classified in two groups; essentially non-volatile species emitted as aerosols (primary organic aerosol, or POA), and the volatile compounds which oxidize and then partition to the condensed phase in the atmosphere (secondary organic aerosol, or SOA) (e.g. Chung and Seinfeld, 2002; Tsigaridis and Kanakidou, 2003; Hoyle et al., 2007). Recently, POA has been shown to be, if anything, more volatile than SOA (Robinson et al., 2007; Huffman et al., 2009), but the designation of POA as un-reacted and generally reduced primary emissions is still valid (Donahue et al., 2009). Starting from an experimental point of view, Fuzzi et al. (2006) introduced a source-based classification of anthropogenic POA (APOA) and anthropogenic SOA (ASOA) and proposed a set of measurable distinguishing characteristics of the carbonaceous particles in these groups. Sources of anthropogenic OA include not only aerosol mass from fossil fuel combustion, but also from meat cooking, biomass burning, the use of biofuels, and other human activities that lead to the emission of both fossil and modern (i.e. not fossil) volatile organic carbon. Consequently, one must separate modern OA into biogenic and anthropogenic fractions. However, even determining a fraction of modern VOC that is actually emitted through anthropogenic activities does not capture the whole human influence on the organic aerosol budget, as it ignores any possible enhancement, through anthropogenically emitted compounds, of SOA formation from true biogenic precursors.

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In this paper we summarize the various feedbacks between anthropogenic activities and BSOA formation, and we describe methods for separating SOA due to the different sources. In Sect. 2 we discuss the mechanisms through which anthropogenic emissions may influence the formation of SOA from naturally emitted precursors. Section 3 presents the various methods which are used to attribute observed organic aerosol to a source, while in Sect. 4 we discuss the available observations that are suitable for detecting the enhancement effect. Section 5 presents a summary and conclusions.

2 Mechanisms for an anthropogenic effect on BSOA

2.1 Partitioning

Possibly the most obvious effect of anthropogenic emissions on BSOA is through a modification of the gas to condensed-phase partitioning. Most condensed-phase products formed in the first-generation oxidation step of biogenic volatile organic compounds (BVOC) are sufficiently volatile to evaporate fully within 16 s at 75 °C (An et al., 2007), suggesting that these compounds have saturation vapour pressures (p_{sat}) similar to pinic acid (Bilde and Pandis, 2001; An et al., 2007). Lower vapour pressure compounds, however, may also form when the reaction proceeds at low precursor mass concentrations (Shilling et al., 2008). In the equilibrium gas/particle partitioning framework (Pankow, 1994; Odum et al., 1996; Donahue et al., 2006b), these relatively high values of p_{sat} imply that the fraction of BVOC reaction products that partitions into the condensed phase is low in environments with low organic aerosol loadings ($0.1\text{--}1\ \mu\text{g m}^{-3}$). Within this framework it is implicitly assumed that the aerosol forms a well-mixed liquid phase containing myriad mutually miscible organic compounds, and that dissolution of organic vapours in a pre-existing organic liquid will increase the equilibrium uptake of the reacted BVOC products (Seinfeld and Pankow, 2003; Kroll and Seinfeld, 2008). The overall uptake depends on the miscibility and activity coefficients of the semi-volatile compounds. Thus, if BSOA is miscible in pre-existing organic

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aerosol from anthropogenic activity, it should in principle enhance the incorporation of BVOC oxidation products into the condensed phase.

Defining the properties of “anthropogenically derived organic aerosol” is difficult as it can be soot, primary organic aerosol from combustion (e.g. meat cooking or diesel exhaust), or SOA from the oxidation of anthropogenic VOCs. Generally seen, soot is primarily composed of carbon in its elemental form (Seinfeld and Pandis, 1998), POA is composed of linear, cyclic and branched hydrocarbons with few oxygenated carbons and large carbon numbers ($\text{C}_{18}\text{--}\text{C}_{40}$) (Sakurai et al., 2003), and SOA is composed of highly functionalized molecules with relatively short carbon chains (typical molecular weights $<500\ \text{Da}$, assuming a typical C:O ratio ~ 0.4 , molecules have carbon numbers $<\text{C}_{15}$) (Baltensperger et al., 2005). Clearly, the partitioning of BVOCs in these different types of anthropogenic organic aerosol will depend on the composition. Song et al. (2007) and Asa-Awuku et al. (2009) found that model POA hydrocarbons do not form a miscible phase with monoterpene SOA, suggesting no anthropogenic enhancement effect. However, Asa-Awuku et al. (2009) did find the opposite for diesel exhaust particles. Further, to our knowledge, there are no studies testing the effect of incorporation of BVOC products in SOA from anthropogenic precursors or chemically aged POA. Since these compounds are more oxidized, and hence more similar to BVOC oxidation products, enhancement effects due to partitioning are plausible and should be investigated further.

Water may also contribute to the organic phase and generally increases partitioning into the condensed phase (Seinfeld et al., 2001). The presence of water also causes repartitioning due to preferential uptake of more polar compounds while simultaneously driving less polar compounds into the gas phase (Seinfeld and Pankow, 2003). Chamber studies suggest that the water uptake behaviour of SOA generated from biogenic and anthropogenic precursors is generally similar (Baltensperger et al., 2005; Varutbangkul et al., 2006; Prenni et al., 2007) and thus differences in organic aerosol water uptake are unlikely to result in major differences in partitioning between urban and rural areas. These studies, however, cannot distinguish between a single aqueous-organic

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phase and a mixture containing an aqueous-organic and liquid pure organic phase. Therefore, the hygroscopicity measurements do not necessarily suggest that anthropogenic and biogenic organic aqueous solutions result in the same degree of repartitioning of polar and non-polar compounds. Furthermore, the role of inorganic water uptake, which exceeds that of most organic compounds (Petters and Kreidenweis, 2007), is unclear. Initial experiments by Prisle et al. (2010) suggest that partitioning enhancement due to inorganically bound water is modest for fresh α -pinene-derived SOA at atmospherically relevant mass concentrations, but more data are needed to establish the generality of this finding. In particular, the enhancement depends on the solubility of the organic compounds in water. There is a clear need for more data including systems that produce more oxidized compounds (e.g. SOA from isoprene), more water soluble compounds (e.g. aged SOA), and more high vapour pressure but water soluble compounds (e.g. glyoxal).

The preceding discussion highlights the importance of both aerosol mixing state and single particle phase state of the organic compounds. The presence of a well-mixed organic phase with little or no water present is likely in controlled chamber experiments, and is generally observed far from point sources (Murphy et al., 2006). The aerosol in urban areas and near sources, however, is more complex and typically externally mixed (Moffet et al., 2008), further complicating the interaction of reacted BVOC products and pre-existing aerosol.

Finally, reversible and irreversible condensed-phase accretion reactions (Barsanti and Pankow, 2004), may significantly increase condensed-phase products due to esterification, oligomerization, hemiacetal formation, aldol addition, or Criegee intermediate adduct reactions (Kroll and Seinfeld, 2008), though at least in chamber experiments condensation of biogenic SOA remains reversible upon dilution after many hours (Grieshop et al., 2007). Thus, the composition of the condensed phase, in particular particle acidity, is likely important, and certainly differs when comparing urban to rural settings. For all of the reasons stated above, the pre-existing (organic) aerosol properties may affect the partitioning of BSOA in unanticipated ways, perhaps explaining

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the correlation of modern carbon found in the condensed phase with concentrations of anthropogenic OA precursors.

2.2 The role of NO_x

Anthropogenic emissions of NO compete with HO_2 for peroxy radicals formed in the initial stages of VOC oxidation, leading to changes in functional groups and affecting subsequent fragmentation, oligomerization, and isomerization reactions. Since both carbon chain length and identity of the functional groups affect vapour pressures and solubility in the organic phase, aerosol yields depend on NO_x concentrations.

While the formation of SOA from biogenic VOCs in the presence of NO_x has been the subject of many chamber studies, the effect of NO_x on aerosol yields is complex. The yields depend on many factors including the VOC precursor, the concentration of NO_x , reaction time, and the primary oxidant. A widely used ratio in parameterising yield results, and in yield predictions in models, is the VOC/ NO_x ratio (ppbC/ppb).

2.2.1 Nitrate-initiated SOA yields

SOA mass yields have been reported for the reaction of the nitrate radical (NO_3), a night-time product of $\text{NO}_2 + \text{O}_3$, with isoprene and several monoterpenes (Table 1). Partitioning theory suggests that SOA mass yields should vary with the total SOA mass concentration (Odum et al., 1996; Donahue et al., 2006a), so one must always be careful when comparing experimental datasets. However, direct comparisons for equivalent initial concentrations are certainly valid, and these measurements show a variability well beyond that predicted by partitioning theory alone. This suggests spurious dependences on other experimental conditions and indicates the need for further corroborating studies.

Despite the uncertainties, these large SOA yields from nitrate oxidation present a mechanism for a positive correlation between NO_x concentrations and SOA formation: regions of high NO_x and O_3 have an additional pathway for SOA formation available

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Ng et al., 2007) and the relative roles of different oxidation pathways. It is typically assumed that more SOA is formed from monoterpenes under low-NO_x conditions, such as prevail in the Amazon. However, this is not true for all compounds and conditions (see Sect. 2.2), therefore a change in the amount of NO_x due to anthropogenic emissions would lead to a change in the amount of SOA. The magnitude and the sign of this change depend on the predominant VOC species. The available mass of existing OA also plays a role, as described above.

It is, however, the number of SOA particles that exceed a certain size threshold determined by their chemical composition (or hygroscopicity), that determines the number of cloud droplets that are formed (Roberts et al., 2002). The latter is the necessary quantity to assess indirect effects of aerosols on clouds and precipitation (Lohmann and Feichter 2005). One of the potentially largest anthropogenic influences on the SOA in pristine environments would be an increase in the number of aerosol particles through a modification of new particle formation.

2.4 New particle formation and growth

A modelling study by Merikanto et al. (2009) showed that on a global average, about half of all Cloud Condensation Nuclei (CCN) originated from SOA. Yu and Luo (2009) claimed that secondary particles even dominate the number abundance in most parts of the troposphere (>80%). However, other studies suggest that the effect of new-particle formation on CCN numbers, even with artificially enhanced SOA formation, remains modest (Pierce et al., 2008). Both the initial formation of the new particles and their subsequent growth to CCN size play a crucial role in the global climate.

New particle formation events have been observed to occur in both the cleanest environments (e.g. Antarctica, Koponen et al., 2003) and the most polluted regions, (e.g. India and China Monkkonen et al., 2005; Wehner et al., 2005) of our planet, as reviewed in Kulmala et al. (2004) and Kulmala and Kerminen (2008). At coastal locations, biogenic iodine has been identified as a key component (Hoffmann et al., 2001; O'Dowd et al., 2002) influencing particle formation. In continental locations, sulphuric

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acid has been proposed as a plausible candidate for the initial particle formation (Weber et al., 1996; Kulmala et al., 2004; Kuang et al., 2008; Nieminen et al., 2009). On the other hand, chamber experiments (e.g. VanReken et al., 2006; Burkholder et al., 2007) and theoretical studies (Bonn et al., 2008, 2009; Boy et al., 2008) raise the possibility that organic vapours may be the key molecules for the nucleation mechanism.

Boy et al. (2003, 2008) showed that for the boreal forest in Central Finland and for an elevated forest in the Front Range of the Colorado Rocky Mountains, USA, sulphuric acid can only explain a small fraction (10–30%) of the observed particle growth. In boreal forest Kulmala et al. (2001) attributed the rest of the growth to condensable organics, which is in line with the aerosol mass spectrometer results by Allan et al. (2006) and indirect results by Tunved et al. (2006). There is, however, large variability in the relative roles of the organics and anthropogenic sulphuric acid. In more anthropogenically influenced areas, such as Pittsburgh, USA, the contribution of sulphuric acid was found to be up to 100% (Stolzenburg et al., 2005), depending on local conditions and air mass origin. The details of the participating compounds and their relative roles are still uncertain, but the oxidized organics are definitely involved in the growth of the freshly formed aerosol particles to climatically active sizes (Kulmala et al., 2001; Stolzenburg et al., 2005; Wehner et al., 2005; Smith et al., 2008). Thus, oxidized organics strongly contribute to the global indirect effect via cloud droplet activation.

The precursors for sulphuric acid are both anthropogenic (i.e. SO₂) and biogenic (i.e. DMS). Also the VOCs have sources in both categories, which oxidize in the atmosphere to form condensable organic vapours. Assuming that sulphuric acid (Sipila et al., 2010) and consequently sulphur dioxide is the limiting factor in new particle formation, the predicted global average decrease of SO₂ emissions by more than half assumed for the global model simulation in the next IPCC report would cause a dramatic decrease in SOA number concentrations, with an associated reduction in the negative radiative forcing via the indirect aerosol effect. By contrast, if regional SO₂ emissions would increase – particularly in countries with fast growing populations and less financial and technological emission reduction possibilities – relatively unpolluted regions such as

cannot be accurately quantified and will not be addressed here. We can in turn split the BVOC fraction into two sub fractions: natural BSOA and anthropogenically enhanced BSOA (eBSOA). eBSOA represents the SOA fraction from naturally emitted BVOC which may result from an interaction with anthropogenic emissions, as discussed above and in more detail below.

5 A major objective of this paper is to propose a methodology for separating OA into the fractions identified above. Furthermore, the essential challenge can be summarised as follows. OA levels are almost without fail higher in urban areas than in remote areas. This includes extremely high levels in megacities such as Mexico City (Salcedo et al., 10 2006; DeCarlo et al., 2008; Aiken et al., 2009; Hodzic et al., 2009) and Beijing (Sun et al., 2010). However, even in these settings OOA is the major OA fraction (Zhang et al., 2007; Jimenez et al., 2009). While source attribution and modelling studies point to a very large anthropogenic SOA source from mobile sources (i.e. transportation using fossil fuels), (e.g. Schauer et al., 2002; Docherty et al., 2008; Yin et al., 2010), ¹⁴C 15 measurements suggest a substantial modern fraction. Understanding this is a great challenge.

We propose the following general methodology: beginning with an SOA sample containing a certain fraction from each of the above categories, a separation of the sources may be made as follows:

20 The apportionment of the fossil fuel combustion fraction of organic aerosol can be made via ¹⁴C analysis, as ¹⁴C is depleted in compounds of fossil origin due to radioactive decay.

25 The remaining fraction then contains OA from BVOCs and combustion of modern biogenic matter. Combustion processes result in the formation of elemental carbon (black carbon, or soot) aerosols ("EC", "BC" or soot), and a correlation between a time series of these and that of OA can be used to determine the fraction of OA which results from combustion (e.g. Gustafsson et al., 2009; Szidat et al., 2009). This requires knowledge of the average emission ratios for OC and EC from the various burning processes that need to be taken into account (e.g. domestic wood fires, Szidat et al.,

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2006). To extract the contemporary fraction of the combustion related OA, only the modern fraction of the EC aerosol must be considered.

5 The fraction of the sample which is not from combustion processes contains mostly OA formed from natural emissions of BVOC, however it may still be comprised of a natural fraction and an anthropogenically enhanced fraction. Qualitatively, these fractions may be separated by the comparison of measurements from an urban and nearby rural site (e.g. Szidat et al., 2009).

10 A quantitative separation may be achieved via measurements within the urban area, as well as up- and downstream of it. A tracer of anthropogenic emissions (CO levels which are elevated over the background values, for example) may be used to estimate the dilution of the urban plume (e.g. de Gouw et al., 2005; Weber et al., 2007). De Gouw et al. (2005) suggests that the removal of anthropogenic VOCs and production of ASOA in an air mass, as it travels from an urban source region, can be estimated by using three parameters, namely a relatively inert pollution tracer (e.g. acetylene or 15 CO), hydrocarbon ratios, and the chemical kinetics of the reactions occurring in the air mass. If the production of ASOA, as the plume ages downstream of the urban area, is known, as well as BVOC and BSOA concentrations upstream of the urban area, an anthropogenic enhancement of BSOA can be calculated. The kinetics of BSOA formation from BVOC in chemically unperturbed conditions must also be known, and 20 there are considerable uncertainties associated with the modelling of SOA production.

A further way to separate the two fractions is to use a model where a simulation with and without anthropogenic emissions can be performed. Of course, such a simulation must accurately represent the chemistry and thermodynamics of both biogenic and anthropogenic OA, as well as their interactions.

25 The sample fraction related to emissions via the combustion of modern biogenic material, for example from natural and non-natural forest fires, agricultural waste burning, cooking and heating can also be further broken down into a natural and an anthropogenic fraction. Almost all combustion of modern biogenic material in urban areas is anthropogenic, therefore an urban plume tracer correlation analysis can be carried out,

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and all modern combustion related OA coming from the urban area can be categorised as anthropogenic, if no natural biomass burning events took place upwind of the urban area.

On the other hand, emissions of molecular markers as a function of OC emissions, (for example levoglucosan/OC or n-alkane/OC ratios) have been measured for different biomass types and for different burning situations such as residential, wild fire or agricultural burning (e.g. Fine et al., 2001, 2002; Hays et al., 2005; Iinuma et al., 2007; Mazzoleni et al., 2007). Shrivastava et al. (2007) suggest that large even-numbered alkanolic acids (hexacosanoic, octacosanoic, triacontanoic and dotriacontanoic acids) can be used to identify open burning as well as non-combustion emissions of low volatility organic compounds, where the use of levoglucosan as a tracer can separate the combustion and non-combustion fractions. There are some significant uncertainties in these methods, as the ratio of the molecular marker to OC is rather variable, even for the same combustion material and situation, and the ambient concentrations of the markers is highly variable due to the multitude of different sources with different emission profiles (e.g. Fine et al., 2001; Robinson et al., 2006; Mazzoleni et al., 2007).

Nevertheless, the use of such molecular markers makes it possible to estimate the fraction of the combustion-related modern OA that comes from different burning situations, allowing an approximate separation of clearly anthropogenic sources such as domestic wood burning for heating or cooking and agricultural waste burning. Obviously, in the case of forest fires, it is not generally possible to differentiate between natural and anthropogenic events based on molecular markers. Trajectory modelling from known fires, combined with an emissions estimate may be the only useful method in this case. The seasonality of burning events can also be used in longer time series to apportion observed OA to its source – emissions from fires for domestic heating peak in winter, and agricultural waste burning and other open fires also have a seasonal dependence.

The only suitable method that would account for the anthropogenic enhancement of OA from natural fires would be a modelling study, where anthropogenic emissions were

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turned on and off.

In the possibilities for source apportionment described above, emissions of modern, non-volatile organic compounds through non-combustion related anthropogenic activities have not been accounted for. This includes emissions such as the natural rubber content of tire dust, and paved road dust (Fine et al., 2001). However, these are comparatively small sources, and in relation to the other substantial uncertainties in the source separation they are unlikely to lead to significant errors.

Given the possibilities for source apportionment, we next consider whether there is any evidence from observational work for a substantial enhancement of natural SOA via interaction with anthropogenic emissions.

4 Observational and modelling data

4.1 Observations from rural and urban areas

An overview of several investigations of atmospheric compounds and components is presented in Fig. 2. Measurements of total VOCs in urban areas show low contemporary carbon percentages (0–40%), probably reflecting the contribution of long-lived VOCs from the combustion of fossil fuels. In these studies, a larger contribution of contemporary carbon to atmospheric oxidation products, such as carbonyl compounds, formic and acetic acids, was found during summer than during winter. Both carbonyl compounds and formic and acetic acids have relatively high percentages of contemporary carbon (carbonyls 39–84%, formic and acetic acids 55–100%) even in urban environments. As the main urban source of modern VOC stems from the use of biofuels such as wood, for heating, this greater abundance of contemporary carbon in the oxidation products in summer points to a very large influence of BVOC emissions from natural sources. Indeed, the separation of the OC values into wood-burning OC and biological OC in the work of Szidat et al. (2009), show that the higher levels of modern OC observed in Goteborg in summer than winter are natural in origin.

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A number of studies have investigated the relative contribution of fossil and contemporary carbon in particulate matter (PM) and a few are included in Fig. 2. The range of contemporary carbon contribution is broader for the fine PM than for individual compounds or compound groups in Fig. 2, reflecting the diversity in chemical composition and sources of carbon in PM. Observed fractions of contemporary carbon in fine PM range from 0.46 to 0.95 in summer (Szidat et al., 2004; Lewis and Stiles 2006; Bench et al., 2007; Gelencsér et al., 2007; Takahashi et al., 2007; Szidat et al., 2009).

Generally, measurements made in urban areas have lower percentages of contemporary carbon in fine PM compared to those made in rural and remote sites due to local emissions from fossil-fuel combustion (e.g. Schichtel et al., 2008; Glasius et al., 2010). However, in some areas meat cooking (Schauer and Cass 2000) and residential wood combustion (e.g. Gelencsér et al., 2007) may contribute to contemporary carbon during certain periods. As expected, modern sources of carbon dominate PM_{2.5} in rural areas with fractions of 0.75 to 0.95 for the US (Bench et al., 2007) and 0.63 to 0.76 for Europe (Gelencsér et al., 2007). However, high contributions of contemporary carbon to fine PM (0.46 to 0.90) are also observed in urban areas during summer. In several cities in Europe, Japan and the western U.S. about half of the carbon in fine PM is contemporary, while higher values are found in south-eastern US cities (Lewis et al., 2004; Szidat et al., 2004; Lewis and Stiles 2006; Bench et al., 2007; Takahashi et al., 2007; Szidat et al., 2009). Schichtel et al. (2008) examined measurements at paired rural and urban sites, and found urban contributions (above regional background levels) to contemporary carbon in PM_{2.5} of 0.23 µg C/m³ (or 11%) in north-west USA and 0.42 µg C/m³ (or 17%) in south-west USA during summer, when residential wood combustion is expected to be of minor significance.

However, this contribution was calculated by simply comparing the values at the two sites, and no allowance was made for wind direction. During periods when the wind was blowing from the urban to the rural site, the measured OA at the rural site would be greater than the background OA, and urban contribution calculated would be too low. On the other hand, slightly higher temperatures (and corresponding volatilisation of

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particulate matter) in urban areas could lead to a very slight lowering of the calculated urban contribution. It is difficult to determine whether any of this urban contribution is the result of an urban enhancement of natural organic aerosol or not, since a quantitative source apportionment was not performed in this study.

In the work of Szidat et al. (2009), sources of contemporary and fossil carbon were investigated by combining individual ¹⁴C measurements of organic carbon, water-insoluble organic carbon, and elemental carbon with a bottom-up approach using levoglucosan as an organic tracer for biomass combustion. Comparing measurements from an urban area and a rural site, located 35 km away, they showed an enhancement (by a factor of 2–3) of non-combustion related modern OC in aerosols from the urban site. These measurements suggest an enhancement of biological SOA due to interaction with anthropogenic emissions. Unfortunately measurements were not made at the rural site in summer.

An urban tracer and SOA formation modelling analysis was carried out on the data collected during the New England Air Quality Study (NEAQS) 2002, leading to the conclusion that the dominant fraction of the organic carbon aerosol could be attributed to anthropogenic secondary aerosol formation (de Gouw et al., 2005). This conclusion was based on the findings that firstly, air masses which showed high toluene/benzene ratios (indicating that little processing had taken place) had no subsequent peak in the organic carbon aerosol concentration. Secondly, when sampling took place off of the coast of Maine, where monoterpene emissions are high, no increase in the OA was observed and OA concentrations correlated with those of isopropyl nitrate, an anthropogenic VOC. This latter observation is consistent with an anthropogenic control of SOA even in a region with very high biogenic emissions.

A similar analysis was applied to data collected by aeroplane and ship during NEAQS-ITCT (New England Air Quality Study – Intercontinental Transport and Chemical Transformation) 2004 (de Gouw et al., 2008). The aircraft tracked a plume originating in New York City, which contained biogenic and anthropogenic VOCs, for two days. The concentrations of CO and WSOC were well correlated throughout the obser-

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vational period, indicating the urban air masses contained more WSOC than ambient air. $\Delta\text{WSOC}/\Delta\text{CO}$ ratios increased by a factor of two by the second day and were considerably higher than those for primary emissions of organic carbon, suggesting the contribution of primary organic matter was low. However, even when using published particulate yields for low NO_x conditions (Ng et al., 2007), the measured concentrations of the anthropogenic VOCs could only explain around 37% of the observed growth of the organic carbon aerosol, and the biogenic VOCs could explain less than 10%. The authors speculate that the yields derived from chamber measurements may be lower than those in the real atmosphere, that the observed SOA could have been formed by VOCs which were not measured, or that SOA formation from biogenic precursors is more efficient in urban plumes.

In another study Weber et al. (2007) used measurements of WSOC as an estimate of SOA mass. They found high correlations between WSOC and anthropogenic emissions, such as isopropyl nitrate and carbon monoxide, in urban plumes originating in both Atlanta and New York City, during NEAQS-ITCT 2004. This suggested a strong linkage between WSOC (or SOA) and anthropogenic emissions. Interestingly, the ratios of anthropogenic VOCs to WSOC were similar in Atlanta and New York City, even though biogenic VOC concentrations were 10 to 100 times higher in Atlanta. This indicates that the mechanisms for SOA formation in Atlanta and New York City were similar, regardless of the much higher concentrations of biogenic VOCs in Atlanta, and that the process was strongly linked to anthropogenic emissions. However, ^{14}C analysis performed on WSOC extracted from filter samples collected during the same summer of 2004 in Atlanta showed that 70 to 80% of WSOC was biogenic in origin. This is consistent with biogenic VOCs being involved in most of the SOA formation.

The results from these studies suggest that it is possible that the incorporation of biogenic species into organic aerosol is more efficient in polluted air; however, they do not provide any quantitative evidence for this being the case.

In the studies above, CO was used as a tracer of anthropogenic emissions, however it has recently been shown that the majority of CO, at least during the summer

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months, comes from oxidation of methane and BVOC, and from biomass burning, but not from fossil-fuel combustion (Miller et al., 2008). Although the CO concentrations used to trace the urban plumes, in the work discussed here, were calculated as an enhancement over the background levels, the uncertainty in the use of CO as a tracer increases as the difference between the CO values within and outside of the plume decreases. Further, production of CO within the plume, unless accounted for, will lead to an underestimation in the calculated plume dilution.

^{14}C analysis would suggest that most of the SOA is modern, however these measurements seem to disagree with other experimental evidence. A possible explanation may be that most ^{14}C measurements have been performed on bulk filters rather than on different fractions of the organic aerosol. Interestingly, the work of Weber et al. (2007) is one of the few studies to perform ^{14}C analysis on only the WSOC (not the total organic carbon) and yet they observed similar results to studies (e.g., Lemire et al., 2002; Lewis et al., 2004; Lewis and Stiles, 2006) using ^{14}C measurements from bulk filter samples. The possibility cannot be ruled out that biogenic VOCs which are not accounted for in the plume modelling studies provide at least some of the missing biogenic OA mass. Another factor which would lead to higher modern SOA fractions, while maintaining a correlation with anthropogenic tracers, is an anthropogenic enhancement of SOA formation from naturally emitted BVOC.

4.2 Large scale modelling of the anthropogenic contribution

All global modelling studies examining the change in SOA burden since pre-industrial times show an increase in BSOA due to anthropogenic emissions (Table 3).

Anthropogenic VOC were not included as SOA precursors in Chung and Seinfeld (2002), however, the percentage of the present day SOA burden resulting directly from anthropogenic VOC was approximately 6% and 8% in Tsigaridis et al. (2006) and Hoyle et al. (2009) respectively. Thus, in each of these studies, the majority of the SOA increase since pre-industrial times is due to an enhancement of SOA formation from biogenic precursors due to changes in SOA partitioning, oxidation patterns and de-

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position rates. The contributions of biogenic and anthropogenic sources in Liao and Seinfeld (2005) were not listed separately.

The global distribution of the change in SOA from Hoyle et al. (2009) is shown in Fig. 3. The total increase in SOA since the pre-industrial period was modelled by performing two experiments in which the only difference was in the anthropogenic emissions. The total change in SOA column burden is shown in panel A. The largest tropospheric column increases are found near industrialized areas or in areas with large amounts of biomass burning. SOA burdens decrease at high southern latitudes and over eastern Russia, due to changes in SOA partitioning, oxidation and deposition patterns and due to lower biomass-burning emissions in the present day inventory than in the pre-industrial inventory, respectively. Panel B shows the contribution to the total SOA increase from aromatic species predominantly emitted during fossil-fuel combustion, but also emitted during biomass burning. Maximum SOA burdens from these mostly anthropogenic SOA precursors are lower than $600 \mu\text{g}/\text{m}^2$, even over industrialised areas. The vast majority of the modelled increase in SOA formation is due to anthropogenic enhancement of SOA formation from biogenic precursors, in this case mainly by the provision of additional low volatility POA, which shifts the partitioning of secondary organic species in the model towards the condensed phase. The annual global emissions of POA in Hoyle et al. (2009) increased from $10.3 \text{ Tg}(\text{C})/\text{yr}$ for the pre-industrial period to $30.4 \text{ Tg}(\text{C})/\text{yr}$ for the present day model run. Predictions of future changes in SOA burdens are generally consistent with this effect, for example Heald et al. (2008) predict a 10% increase in SOA from monoterpene sources with a 60% increase in anthropogenic POA emissions between the years 2000 and 2100, while Liao et al. (2006) predict a 31% increase in SOA from 2000 to 2100 as POA emissions more than double during this period.

In such models, the partitioning of SOA is based on the Pankow/Odum (Pankow, 1994; Odum et al., 1996) framework, and thus corresponds with chamber measurements of SOA partitioning. Models generally contain a single organic condensed phase, combining both SOA and hydrophilic POA. The applicability of this single phase

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for partitioning calculations is discussed in Sect. 2.1. Tsigaridis et al. (2006) found that accounting for the VOC/ NO_x ratio on the production of SOA resulted in a 20% decrease in BSOA globally and a 20% increase in ASOA.

The effect of anthropogenic emissions on the formation of BSOA was investigated by Carlton et al. (2010), using the CMAQ regional model. They found that the SOA burden on the east coast of the USA was reduced, at the surface, by about 50% if all controllable non-natural emissions were shut off. The greatest reductions in BSOA were achieved by removing anthropogenic POA (-30%), NO_x (-20%) and reactive non methane carbon species (-10%). However, the modelling study was only carried out for the time period of 15 August–4 September, 2003, and therefore represents a time period where high concentrations of natural VOC are expected.

As the dominant sink of SOA precursor VOC is oxidation followed by deposition (Chung and Seinfeld, 2002), the distribution of oxidants plays a role in determining the SOA burden. If the concentration of atmospheric oxidants increases, the VOCs are oxidised closer to the surface and their source regions, resulting in faster removal, and a shorter SOA lifetime. When the total global burden of SOA increases, such processes can lead to a greater increase in SOA in the boundary layer than in the upper troposphere (Tsigaridis et al., 2006), or even to lower SOA burdens in the upper troposphere, and in remote regions (Chung and Seinfeld, 2002; Hoyle et al., 2009). The opposite effect is seen when emissions of VOC are so large that the oxidant concentrations are depleted. In these areas, the concentration of SOA is lower and the precursor VOC are transported further from their source (Heald et al., 2008). Global models therefore predict a change in the distribution and lifetime of SOA. An increase in the global burden of SOA of 36% by 2100 was predicted by Heald et al. (2008), using the A1B emissions from the IPCC Special Report on Emissions Scenario (SRES), primarily due to increases in biogenic and anthropogenic emissions. However, an experiment examining only the effects of land use change found a 14% decrease in global SOA, mainly due to cropland expansion. Other studies have predicted a 54% increase in SOA by 2100, using the A2 scenario (Liao et al., 2006) – (a 31% increase was found

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when only the anthropogenic emissions were changed to projected 2100 values), and a doubling of SOA (Tsigaridis and Kanakidou, 2007), due to changes in emissions, using the IS92a scenario.

5 Summary and conclusion

5 The biosphere is undoubtedly the major source of VOC in the atmosphere, however the research discussed here shows that the anthropogenic modification of this source is significant. Anthropogenic VOC and particulate emissions contribute directly to the total OA burden, both in, and downwind of urban areas. On the other hand, the enhancement, through anthropogenic emissions, of SOA formation from true biogenic precursors is currently a poorly characterised effect. We define this enhanced SOA fraction, eBSOA, as that fraction of SOA which is produced from modern (non-fossil), naturally emitted biogenic organic compounds, which would not be in the condensed phase in the absence of anthropogenic effects. Emissions from biofuel combustion, cooking, and human-initiated biomass burning do not contribute directly to eBSOA.

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15 The importance of eBSOA lies in the fact that it must be considered an anthropogenic contribution to the aerosol burden, while it does not directly consist of species emitted via human activity.

We describe several mechanisms by which anthropogenic modification of the atmosphere may affect the formation of SOA from biogenic compounds, however, to date, these effects have been poorly quantified. In the equilibrium gas/particle partitioning framework, an increase in aerosol leads to a shift in partitioning from the gas to the condensed phase, therefore increased anthropogenic emissions of organic particulate matter or semi-volatile VOC may lead to a shift of biogenic carbon from the gas to the condensed phase. The magnitude of this effect depends on the miscibility of the condensed and gas phase species, a quantity that is extremely variable between different compounds, and not well described for atmospherically relevant mixtures. A further complication is the formation of different liquid phases within the same aerosol

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droplet. Condensed phase reactions have been shown to reduce the volatility of organic species once they partition to the aerosol, and the efficiency of these reactions depends on the aerosol composition.

5 Anthropogenic emissions of NO_x can greatly affect yields of SOA, but again the total effect depends on the organic species involved. A comparison of the yields from different experiments is difficult due to the dependence of yield on the concentration of the organic species.

10 The formation of new particles in the atmosphere can occur both due to organic species or sulphuric acid. Gas phase organics certainly partition to the newly formed particles, being responsible for much of their growth (Kulmala et al., 2001; Bonn et al., 2008; Boy et al., 2008). Thus new particle formation may be an important SOA formation mechanism. Because of the role of sulphuric acid in new particle formation, changes in emissions of sulphur compounds may lead to changes in SOA concentrations.

15 A general approach for isolating the eBSOA contribution to the observed OA burden was outlined, taking advantage of various measurement techniques to apportion the carbon to sources, based on properties such as age and correlation with other tracers.

The evidence for substantial contributions of eBSOA to the OA burden in existing measurements was discussed.

20 Most large scale modelling studies show a clear contribution of eBSOA to the increase in SOA since pre-industrial times, for example only 8% and 13% of the SOA increase consisted of SOA formed from anthropogenic VOC in the studies of Tsigaridis et al. (2006) and Hoyle et al. (2007) respectively, the vast majority of the remainder being eBSOA. An eBSOA contribution of around 50% is estimated by Carlton et al. (2010) for the east coast of the USA in summer.

25 However, despite the multitude of mechanisms possible for eBSOA formation, the evidence from current observations is less clear. Modern carbon certainly accounts for large fractions of the urban OA burden, even in summer (Lewis et al., 2004; Bench et al., 2007), when anthropogenic emissions of modern carbon, for example through

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wood burning, should be relatively low. However, there may be other substantial urban sources of modern OA. More direct evidence is found in the comparison of measurements at closely located urban and rural sites, where for example the measurements of Szidat et al. (2009) would suggest the contribution of eBSOA to the observed OC mass concentration could be around 50–60%. Detailed modelling of OA in urban plumes (e.g. de Gouw et al., 2008) cannot account for the observed OA mass, and although there are several possible reasons for this, such as unknown biogenic OC species, eBSOA may help to explain some of the discrepancy.

More work is needed, both with respect to the theoretical understanding of mechanisms leading to eBSOA, and its detection in the atmosphere in order to better quantify the contribution of eBSOA to the OA burden.

The partitioning of biogenic semi-volatile organic species to atmospherically relevant aerosols needs to be better characterised. Such aerosols include, for example, SOA from mixtures of anthropogenic and/or biogenic precursors, POA from different sources, chemically aged POA, and soot. The effect of anthropogenic emissions on condensed phase reactions, and thus on the partitioning of biogenic species, also needs to be better quantified, including the effect of aerosol acidity.

The net effect of NO_x on yields of SOA from mixtures of biogenic precursors needs to be systematically assessed, not only for different VOC/ NO_x ratios, but for different VOC concentrations, so that the yields are known for the range of conditions encountered in the atmosphere.

The mechanisms behind new particle formation in the atmosphere need to be better understood, in particular the relative roles of different species such as sulphuric acid or organic species, in polluted and non-polluted environments, and the dependence of particle formation rates on the concentrations of these compounds. The effect of changes in new particle formation on the burden and lifetime of SOA needs to be assessed.

More effort needs to be made to quantify, or at least constrain, the proportion of eBSOA in the observed atmospheric OA burden. As there is no specific marker for

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eBSOA, this task can only be achieved by the apportionment of the observed OA mass to its various sources. To this end, measurements upstream, within and downstream of urban areas are required, where the enhancement of the urban OA over the regional background can be determined, and where the contribution of anthropogenic VOC emissions can be removed based on the age of carbon and the correlation with markers of particular emissions such as wood burning.

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Table 1. SOA yields for NO₃-initiated experiments.

VOC	Yield	Notes
18–120 ppb isoprene	4–24% ¹	Higher yields observed when oxidant was introduced slowly
11 ppb isoprene	2% ²	Second generation products contribute to the yield more than first generation products
50–500 ppb α -pinene	4–16% ³	Higher yields at lower RH and the use of organic seed aerosol
18–580 ppb α -pinene	0–16% ²	–
7–358 ppb β -pinene	10–52% ²	Found largest yields at intermediate concentrations
15 ppb β -pinene	50% ⁵	No yield dependence on relative humidity (0–60%)
18 ppb limonene	17% ⁴	–
500 ppb limonene	21–40% ³	Higher yields found with organic vs. (NH ₄) ₂ SO ₄ seed
7–395 ppb Δ^3 -carene	15–62% ⁴	–

¹ Ng et al., 2008, ² Rollins et al., 2009, ³ Spittler et al., 2006, ⁴ Hallquist et al., 1999, ⁵ Fry et al., 2009.

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Table 2. SOA yields from VOCs in the presence of NO_x.

VOC	Mass Yield	Oxidant	VOC/NO _x ratio (ppbC/ppb NO _x)
Oxygenated compounds			
72 ppb linalool ¹	6%	Photo-oxidation	4
80–230 ppb linalool ²	3–5%	Photo-oxidation	8–11
124 ppb linalool ³	13%	Photo-oxidation	10
78 ppb linalool ²	8%	Ozone	No NO _x
116 ppb terpinen-4-ol ¹	6%	Photo-oxidation	4
70–230 ppb terpinen-4-ol ²	3–6%	Photo-oxidation	8–11
90 ppb terpinen-4-ol ²	34%	Ozone	No NO _x
105 ppb verbenone ³	19%	Photo-oxidation	11
79 ppb methyl chavicol ³	40%	Photo-oxidation	8
Sesquiterpenes			
5–9 ppb α -humulene ¹	32–73%	Photo-oxidation	1–3
46 ppb α -humulene ³	65%	Photo-oxidation	9
6–13 ppb β -caryophyllene ¹	37–79%	Photo-oxidation	3–8
100 ppb β -caryophyllene ²	100–125%	Photo-oxidation	9
37 ppb β -caryophyllene ³	68%	Photo-oxidation	19
118 ppb γ -caryophyllene ³	29%	Photo-oxidation	11
34 ppb longifolene ⁴	65%	Photo-oxidation	19
34 ppb aromadrene ⁴	37%	Photo-oxidation	21

¹ Griffin et al., 1999; ² Hoffmann et al., 1997; ³ Lee et al., 2006; ⁴ Ng et al., 2007b.

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Table 3. The pre-industrial and present day burdens of SOA calculated in several modelling studies. The abbreviations in the last column are as follows: Ox – change in atmospheric oxidants, APOA – changes in anthropogenic POA, BPOA – changes in biogenic POA, NO_x – NO_x effect on SOA yields, BVOC-changed BVOC emissions since pre-industrial period. For a full description of the models, see the individual papers.

Study	Preindustrial burden of SOA (Tg)	Present day burden of SOA (Tg)	Change Tg (% accounted for)	Effects
Chung and Seinfeld (2002)	0.06	0.19	0.13 (216%)	Ox,APOA,BPOA
Tsigaridis et al. (2006)	0.64	0.8	0.16 (25%)	Ox,APOA,BVOC, NO _x ,BPOA
Hoyle et al. (2009)	0.44	0.70	0.26 (59%)	Ox,APOA,BPOA
Liao and Seinfeld (2005) (baseline scenario)	0.23	0.33	0.10 (43%)	Ox,APOA,BPOA

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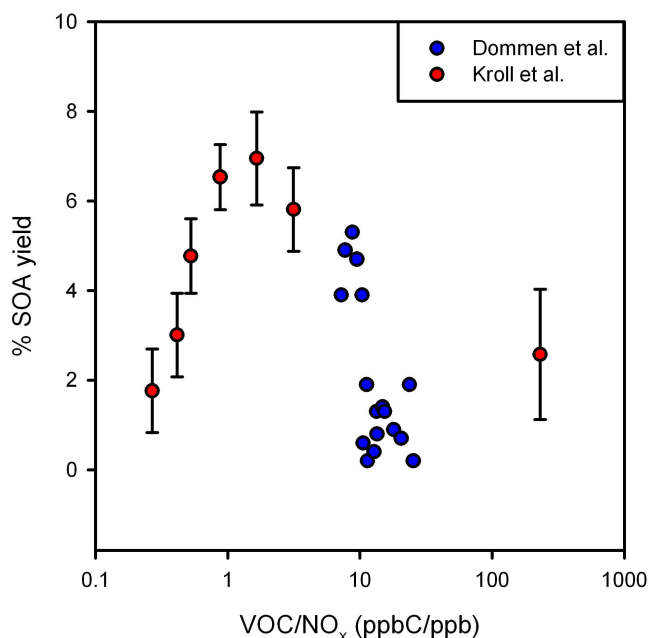


Fig. 1. Percentage yield of SOA vs VOC/NO_x ratio, for experiments performed by Dommen et al. (2006) and Kroll et al. (2006). The highest yields are observed at VOC/NO_x ratios between 1 and 10. All data are normalized to density = 1.4 g/cm³. Because the NO_x concentration for the data point at the highest VOC/NO_x ratio is <1ppb, this data point represents the lower bound for the VOC/NO_x ratios.

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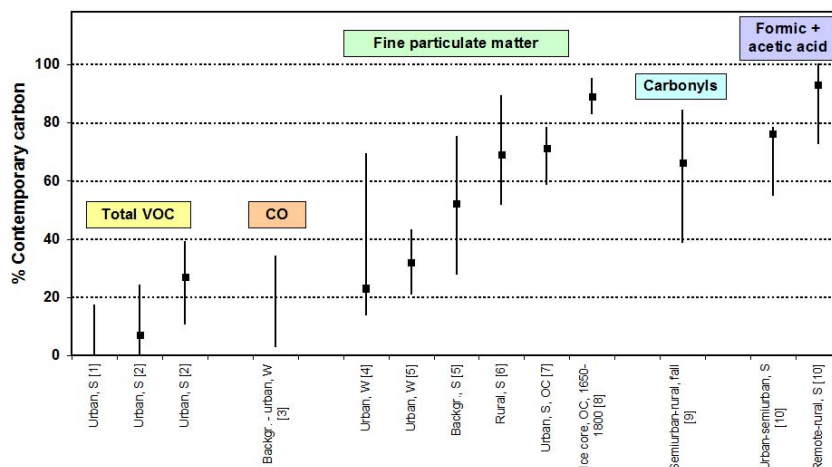


Fig. 2. Relative amount of contemporary carbon in measurements made in different situations and seasons. Ranges are shown together with the median value. Summer is indicated by “S” and winter by “W”. The plot is an update of the one shown in Larsen et al. (2001). “Total VOC” are volatile organic compounds excluding methane. [1] (Klouda et al., 1996) [2] (Klouda et al., 2002) [3] (Klouda and Connolly, 1995) [4] (Klinedinst and Currie, 1999a) [5] (Glasius et al., 2009) [6] (Lewis and Stiles, 2006) [7] (Szidat et al., 2009) [8] (Jenk et al., 2006) [9] (Larsen et al., 2001) [10] (Glasius et al., 2001).

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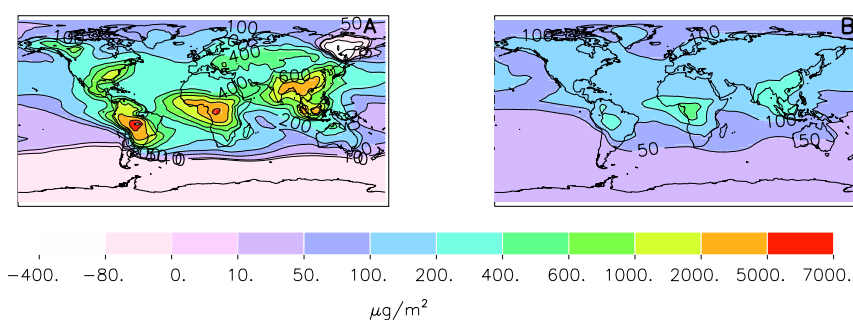


Fig. 3. (A) shows the modelled total column increase in SOA since the pre-industrial period, while (B) shows the mass formed directly from anthropogenic SOA precursors.

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