A review of Secondary Organic Aerosol (SOA) formation from isoprene

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Abstract. Recent field and laboratory evidence indicates that the oxidation of isoprene, (2-methyl-1,3-butadiene, C5H8) forms secondary organic aerosol (SOA). Global biogenic emissions of isoprene (600 Tg yr−1) are sufficiently large that the formation of SOA in even small yields results in substantial production of atmospheric particulate matter, likely having implications for air quality and climate. Here we present a review of field measurements, experimental work, and modeling studies aimed at understanding the mechanisms, yield, and atmospheric importance of isoprene-derived SOA. SOA yields depend on a number of factors, including organic aerosol loading (MO), NOx level (RO2 chemistry), and, because of the importance of multigenerational chemistry, the degree of oxidation. These dependences are not always included in SOA modules used in atmospheric transport models, and instead most yield parameterizations rely on a single set of chamber experiments (carried out over a limited range of conditions); this may lead to very different estimates of the atmospheric importance of isoprene SOA. New yield parameterizations, based on all available laboratory data (MO=0–50 µg m−3), are presented here, so that SOA formation may be computed as a function of MO, NOx level, and temperature. Current research needs and future research directions are identified.

1 Introduction

Atmospheric fine particles are linked to adverse health effects, visibility reduction and climate change. Particulate organic matter (POM) makes up a large, and often dominant, fraction of fine particulate mass in the atmosphere, typically 20–60% in the continental mid-latitudes (Kanakidou et al., 2005; Yu et al., 2007a; Zhang et al., 2007a; Docherty et al., 2008) and up to 90% in tropical forested areas (Kanakidou et al., 2005). Despite the abundance of atmospheric POM, the ambient composition remains poorly understood due to large measurement uncertainties (Turpin et al., 2000) and chemical complexity (Goldstein and Galbally, 2007). Atmospheric POM has both primary (directly emitted) and secondary (formed in the atmosphere from precursor gases) sources, which can be natural (e.g. vegetation) or anthropogenic (e.g. fossil-based motor vehicle exhaust). Secondary organic aerosol (SOA) contributions to POM vary with season and location but are typically substantial, 20–80% of measured mass (Dechapanya et al., 2004; deGouw et al., 2005; Yu et al., 2007a; Lanz et al., 2007, 2008).

Recently it has been noted that current atmospheric models underpredict organic aerosol mass in both the boundary layer and aloft (Heald et al., 2005; Morris et al., 2005; Volkamer et al., 2006; Morris et al., 2006; Goldstein and Galbally, 2007; Yu et al., 2008). Without proper representation of organic aerosol in atmospheric models, development of effective air quality management plans designed to mitigate adverse POM health, visibility, and climate effects is hindered. The reason for the widespread negative bias in model predictions of POM may result from a number of potential causes,
including: 1) inaccurate representation of POM emissions and treatment, (i.e. not accounting for the full volatility distribution and reaction potential) (Robinson et al., 2007), 2) large uncertainty in emission inventories of precursor volatile organic compound (VOC) emissions (Goldstein and Galbally, 2007), 3) missing SOA precursors, 4) missing physical and chemical processes that contribute to SOA but are not accounted for in atmospheric models, (e.g. cloud processing or other aerosol phase reactions (Volkamer et al., 2009)), 5) errors associated with the extrapolation of laboratory data to the atmosphere, 6) uncertain meteorological inputs that distort concentration calculations (e.g. PBL height (Yu et al., 2007b)), and 7) uncertainties in the measurement of ambient POM. All of these factors may contribute to errors in modeled aerosol loadings, but the specific focus of this review is the importance of SOA formation from isoprene, which has traditionally not been included in models.

Isoprene (2-methyl-1,3-butadiene, C₅H₈) has the largest global atmospheric emissions of all non-methane VOCs, estimated at ~600 Tg yr⁻¹ (Guenther et al., 2006). Because of its two double bonds, isoprene is highly reactive and is readily oxidized in the atmosphere by OH, NO₃, and O₃. Key oxidation products, shown in Fig. 1, include methacrolein, methyl vinyl ketone, glycolaldehyde, hydroxyacetone, methylglyoxal, and formaldehyde. Because these species are volatile, it has been generally accepted that
isoprene does not contribute to atmospheric SOA (Pandis et al., 1991). However, in recent years, the topic of SOA formation from isoprene has been reexamined, and recent field (e.g. Claeys et al., 2004a; Edery et al., 2005; Kleindienst et al., 2007b) and laboratory (e.g. Kroll et al., 2005, 2006; Kleindienst et al., 2006; Ng et al., 2008) studies indicate that isoprene oxidation may indeed contribute to the formation of SOA in the atmosphere. Even if the yield is minor (e.g. 1%), the overall contribution of isoprene to total atmospheric POM could be large (e.g. 6 Tg yr$^{-1}$) owing to the large global source strength. As a result, to obtain a quantitative, predictive understanding of the sources of atmospheric POM, a detailed understanding of the potential of isoprene to form condensable products and contribute to SOA is essential.

This paper presents a comprehensive summary of the recent literature on the topic, including field, laboratory, and modeling studies that tie isoprene and its oxidation products to POM. This review begins by summarizing the field and laboratory results that suggest the importance of isoprene as an SOA precursor, as well as implications of these results for our understanding of the mechanism of SOA formation. Two-product partitioning parameters ($\alpha$ and $K_{OM}$) for prediction of isoprene SOA under high and low-NO$_x$ conditions from pooled laboratory studies are have been developed as part of this review and are presented. Results from modeling studies aimed at estimating the contribution of isoprene to POM on the regional and global scales are then presented. Remaining uncertainties in SOA yields from isoprene oxidation are explored, and finally, the needs for future research in the area are discussed.

2 Evidence for SOA formation from isoprene oxidation

SOA formation from isoprene oxidation has received considerable study over the last several years. There are now three independent (though related) lines of experimental evidence indicating the important role of isoprene in atmospheric SOA formation: (Eq. 1) the measurement of isoprene oxidation products in ambient particulate matter; (Eq. 2) the laboratory measurement of aerosol growth from the multistep oxidation of isoprene; and (Eq. 3) the measurement of low-volatility species from the aqueous reactions of known isoprene oxidation products.

2.1 Field evidence for SOA production from isoprene oxidation

The first field evidence showing that the oxidation of isoprene contributes to ambient organic aerosol was from the work of Claeys et al. (2004a). In that study, aerosol from the Amazonian rain forest was analyzed by extraction and derivatization (BSTFA) of filter samples using GC-MS, showing the presence of two previously unidentified compounds in atmospheric POM: 2-methylthreitol and 2-methylerythritol. These compounds, collectively known as 2-methyltetrols, have the same carbon skeleton as isoprene (Figs. 1 and 2). Subsequent studies have shown that concentrations of these compounds exhibit strong diurnal and seasonal trends similar to those of isoprene emissions, with abundances highest in the periods of highest photochemical activity (daytime (Plewka et al., 2006) and summer months (Xia and Hopke, 2006; Kleindienst et al., 2007a)). These results strongly suggest that methyltetrols are formed from the oxidation of isoprene, and, thus, isoprene is a potentially important SOA precursor. The presence of these compounds in aerosol has since been confirmed in a number of studies.
spanning a range of biogenically-influenced environments (Hallquist et al., 2009, and references therein), including the Amazonian rain forest (Wang et al., 2004, 2005; Schkolnik et al., 2005), a boreal forest in Finland (Kourtchey et al., 2005), forests in central Europe (Ion et al., 2005; Plewka et al., 2006), and regions in the Northeastern (Xia and Hopke, 2006) and Southeastern (Edney et al., 2005; Lewandowski et al., 2007; Clements and Seinfeld, 2007; Kleindienst et al., 2007a; Ding et al., 2008) United States. In addition, other polyhydroxylated compounds with the carbon skeleton of isoprene or methacrolein (a major isoprene oxidation product) have been measured in ambient atmospheric aerosol as well. These include C5 alkene triols and methylglyceric acid (Ion et al., 2005; Wang et al., 2005), as well as accretion products, such as the hemiacetal dimer (Surratt et al., 2006); structures shown in Fig. 2. Organosulfates, including nitrated derivatives (e.g. nitrooxy-organosulfates) have been detected in ambient aerosol collected in the US (Surratt et al., 2007a, b) and Europe (Gómez-González et al., 2008). Diesters, hypothesized to form via esterification of two 2-methylglyceric acid residues and previously characterized by Suratt et al. (2006) and Szmigielski et al. (2007) in high NOx laboratory-generated isoprene SOA, were detected in ambient aerosol by Jaoui et al. (2008). Mass concentrations of tracer species typically total 10–100 ng m−3 in forest environments, but values as high as 365 ng m−3 have been measured for methyltetrols and recent estimates regarding sulfated and nitrated (i.e. nitrooxy organosulfates) derivatives of isoprene suggest that isoprene oxidation may be an important contributor to total organic particulate mass, particularly during the summer (Kleindienst et al., 2007a; Lewandowski et al., 2008; Suratt et al., 2008; Lukács et al., 2009).

In addition to the identification of compounds in ambient aerosol that appear to be unique products of isoprene oxidation, other field results suggest that isoprene oxidation contributes to atmospheric organic aerosol. These include observed correlations between measured concentrations of organic aerosol and isoprene oxidation products at Chebogue Point, Nova Scotia (Holzinger et al., 2007), and the similarity of aerosol mass spectrometer (AMS) data taken in the Gulf of Maine to laboratory mass spectra from isoprene oxidation (Marcolli et al., 2006). Further, Matsunaga and coworkers (Matsunaga et al., 2003, 2004, 2005) have shown that known second- and third-generation isoprene oxidation products (such as glyoxal, methylglyoxal, glycolaldehyde, and hydroxyacetone) are present in the particle phase in concentrations far higher than would be expected based upon their vapor pressures. These higher-than-expected concentrations may arise from aerosol-phase accretion reactions of these isoprene oxidation products, (e.g. oligomers and sulfate derivatives (Surratt et al., 2008; Gómez-González et al., 2008; Galloway et al., 2009)).

### 2.2 Laboratory measurements of aerosol growth from isoprene oxidation

The field evidence of isoprene SOA was intriguing as early laboratory experiments seemed to indicate that SOA formation from isoprene was not atmospherically important. Kamens et al. (1982) demonstrated, but did not quantify, SOA formation during the reaction of isoprene (several hundred ppb) with O3. Pandis et al. (1991) found that isoprene photooxidation (irradiation in the presence of NOx) forms SOA when isoprene concentrations are high (>120 ppb). Miyoshi et al. (1994) also reported aerosol formation from the OH-initiated oxidation of isoprene under NOx-free conditions. In all of these cases, aerosol formation was observed only at isoprene concentrations far higher than those present in the atmosphere (typical levels rarely exceed a few ppb). Therefore, it was concluded from these laboratory experiments that isoprene did not contribute to SOA formation under atmospheric conditions.

The early conclusion that isoprene did not form SOA through gas phase photooxidation was based on the assumption that SOA is formed only when condensable products reach concentrations exceeding their saturation vapor pressures. Pankow, Odum and coworkers showed, however, that SOA is composed of semivolatile organics (Pankow, 1994b; Odum et al., 1996). This finding indicated that SOA can form even when gas-phase concentrations are below their saturation vapor pressures due to absorption into condensed-phase organics. Thus, the early observation of SOA formation from isoprene only at very high isoprene concentrations (Kamens, 1982; Pandis et al., 1991; Miyoshi et al., 1994) was potentially a consequence of missing pre-existing organic aerosol into which semivolatile oxidation products could partition.

Recent laboratory investigations have confirmed that gas phase isoprene oxidation products indeed forms SOA under a broad variety of experimental conditions, spanning wide ranges in particle acidity, NOx concentration, relative humidity, and initiating oxidant (Table 1). Jang, Czoschke, and coworkers showed that SOA yields from the ozonolysis of isoprene are greatly enhanced in the presence of acidic aerosol seed (Jang et al., 2002; Czoschke et al., 2003). These results strongly suggest the importance of particle-phase reactions that lower the volatility of organic species, via accretion (oligomerization) processes. Edney, Kleindienst, and coworkers found similar results for isoprene photooxidation, with SOA yields greatly increased in the presence of SO2 (which forms sulfuric acid aerosol upon oxidation) or H2SO4 seed (Edney et al., 2005; Kleindienst et al., 2007b; Suratt et al., 2007b). Aerosol is also observed when high concentrations of isoprene are exposed to H2SO4 seed in the absence of any oxidants (Limbeck et al., 2003; Liggio et al., 2007). These results likely arise from particle-phase reactions promoting SOA growth, in agreement with the conclusions of Jang et al. (2002).
Subsequent chamber work has shown that isoprene photooxidation can also form SOA in the absence of strong acidity (Kroll et al., 2005, 2006; Dommen et al., 2006), but over delayed timescales (Ng et al., 2006). These results indicate that in addition to particle-phase accretion reactions, a key step in SOA formation is the further gas-phase oxidation of first-generation reaction products. There is strong evidence for continuing chemistry even after aerosol formation, as particles formed under NOx-free conditions were found to decrease in mass and change in composition over the timescales of several hours (Kroll et al., 2006; Surratt et al., 2006). A detailed discussion of chemistry of the SOA formation mechanism is discussed in Sect. 3.

2.3 Studies of formation of low-volatility species from aqueous oxidation

In recent years it has been demonstrated that aqueous-phase processing of organics in clouds and aerosols may contribute an additional source of SOA to the atmosphere. Aqueous aerosol formation pathways are well known for inorganic secondary species, for example, particulate sulfate derived from the oxidation of SO2 and dimethylsulfide (DMS). By analogy, water-soluble organic compounds (WSOCs), even if highly volatile, can partition into cloud droplets and oxidize further, affecting the chemistry of radical, metal, and oxidant species (Aumont et al., 2000), and generating lower volatility products that may remain in the particle phase upon cloud droplet evaporation (Ervens et al., 2004; Lim et al., 2005).

Isoprene oxidation leads to the formation of a number of small, highly water-soluble organics that may then oxidize further in the aqueous phase to form SOA. Isoprene is the largest global source of glyoxal and methylglyoxal (Fu et al., 2008), α-dicarbonyls that are highly water soluble (effective Henry’s law constant >10^5 M atm^-1 and >10^3 M atm^-1 respectively, at 25°C) (Betterton and Hoffmann, 1988; Zhou and Mopper, 1990). Both are often found in cloud and fog water (glyoxal up to 276 µM, methylglyoxal up to 128 µM) (Munger et al., 1984; Gunz and Hoffmann, 1990; Chebbi and Carlier, 1996), as well as in ambient aerosol from a variety of environments (Kawamura and Usukura, 1993; Sempere and Kawamura, 1994; Mochida et al., 2003).

Laboratory experiments have demonstrated formation of low-volatility compounds from aqueous-phase photooxidation of glyoxal and methylglyoxal. For example, oxalic acid forms from glyoxal (Carlton et al., 2007), methylglyoxal (Altieri et al., 2008), and pyruvic acid (a methylglyoxal oxidation product) (Carlton et al., 2006). Such reactions provide a possible explanation for the field observations of particle-phase oxalate in cloud-influenced air parcels (Sorooshian et al., 2007) and the high correlation with aerosol sulfate that has a known predominant in-cloud formation pathway (Yu et al., 2005). Larger, higher molecular weight compounds, some with oligomeric structure, also form from pyruvic acid (Altieri et al., 2006), glyoxal (Carlton et al., 2007), and methylglyoxal (Altieri et al., 2008). Recent work by Volkamer et al. (2009) demonstrates that WSOC photochemistry enhances SOA from glyoxal, which is taken up rapidly by both organic and inorganic aerosol (Schweitzer et al., 1998; Corrigan et al., 2008). This suggests that in addition to cloud processing, oligomerization (Liggio et al., 2005) and oxidation reactions (Volkamer et al., 2009) in the aerosol aqueous phase may also contribute to SOA formation from isoprene-derived products.

3 Mechanism of SOA formation from isoprene oxidation

Results from both field and laboratory studies indicate that the oxidation of isoprene contributes to atmospheric SOA via the formation of low-volatility species. As is the case with all SOA precursors, the detailed chemical mechanism of SOA production from isoprene remains highly uncertain, due to the complexity of the reaction pathways and large number of difficult-to-measure molecular products. However, recent studies of the gas-phase oxidation pathways and the chemical composition of isoprene SOA have yielded substantial insight into many of the general features of the SOA formation mechanism. A highly simplified general mechanism of the OH-initiated oxidation of isoprene is shown in Fig. 1. Not shown are the reaction pathways arising from reactions with other oxidants (O3, NO3, Cl), which in general have received less study. NO3 and Cl pathways are expected to be similar to those formed via OH (Fan and Zhang, 2004); ozonolysis proceeds by a very different channel, but was shown to form SOA in relatively low yields (Kleindienst et al., 2007b).

3.1 Gas-phase oxidation

The first-generation products of the isoprene+OH reaction are volatile and thus are not expected to partition directly into the particle phase (Pandis et al., 1991). These products (Fig. 1) and their yields have received considerable laboratory study (Tuazon and Atkinson, 1990b; Paulson et al., 1992; Miyoshi et al., 1994; Kwok et al., 1995; Sprengnether et al., 2002; Zhao et al., 2004; Fan and Zhang, 2004). The distribution of such products depends on the fate of the hydroxy-peroxy (RO2) radical: products from the RO2+NO reaction include methacrolein, methyl vinyl ketone, and hydroxy nitrites, whereas hydroxymethylene peroxides are formed from RO2+HO2. This branching appears to have important implication for SOA formation, as SOA yields under NOx-free conditions are higher than when NOx is present in high concentrations, suggesting that further reactions of the hydroperoxides lead to lower-volatility products than do reactions of RO2+NO products (Kroll et al., 2006). Self-reactions of RO2 are generally thought to form similar products as RO2+NO reactions (forming diols (Ruppert and
2.4 Second-Generation Products 

Second-generation isoprene oxidation products that have 4–5 carbons and several functional groups may be semivolatile, and therefore can contribute to SOA via absorptive partitioning into the particle phase. They also may undergo additional reactions in either the gas or particle phase, lowering their volatility further. Measurements of the chemical composition of laboratory-generated isoprene SOA provide substantial insight into the nature of these multifunctional species. Several studies have found that a significant fraction of the identifiable SOA constituents are compounds with the same carbon skeleton as isoprene (in the case of C5 compounds) or methacrolein (for C4 compounds) (Edney et al., 2005; Surratt et al., 2006; Szmigielki et al., 2007). These include 2-methyltetrols and methylglyceric acid, as well as structural analogs of each; many such compounds have been measured in ambient aerosol as discussed above (see Fig. 2). Further, a number of multifunctional products have recently been identified in the gas phase (Paulot et al., 2009); some may be semivolatile and hence play a role in SOA formation. Functional groups in these compounds include alcohols, nitrates, acids, and carbonyls. Many of these may then undergo particle-phase accretion reactions: a wide range of higher molecular weight species, including oligomers (esters and hemiacetals) (Surratt et al., 2006; Szmigielki et al., 2007) and organosulfates (Surratt et al., 2007a, b) have been identified (Fig. 2) using liquid chromatography-electrospray ionization-mass spectrometry (LC-ESI-MS). The observed partitioning coefficients of individual reaction products are much higher than their vapor pressures would suggest (Healy et al., 2008). All such results indicate the importance of accretion reactions in isoprene SOA formation.

The abundance of derivatives of methylglyceric acid (with the same carbon skeleton as methacrolein) in SOA formed under high-NOX conditions (Surratt et al., 2006) strongly suggests the importance of methacrolein as a key intermediate in SOA formation from isoprene. This is consistent with observations that methacrolein oxidation forms SOA
that is chemically very similar to aerosol formed from isoprene photooxidation (Kroll et al., 2006; Surratt et al., 2006). By contrast, methyl vinyl ketone oxidation is found to produce no SOA (Kroll et al., 2005). Formation of SOA from the oxidation of most other first-generation isoprene oxidation products shown in Fig. 1 has not been investigated. In particular, further reactions of products formed under low-NO_3 conditions are poorly constrained. SOA formed under these conditions contains high levels of peroxides (Surratt et al., 2006), but individual peroxide species have not yet been identified. There is strong evidence that particulate peroxides formed from isoprene oxidation are photochemically unstable, as SOA mass and peroxide content were observed to decrease with continued irradiation (Kroll et al., 2006; Surratt et al., 2006).

In summary, results from studies of the gas-phase products, aerosol yields, and SOA chemical composition are broadly consistent with aerosol production via methacrolein oxidation under high-NO_3 conditions, and via organic peroxide chemistry under NO_3-free conditions. However, uncertainties in detailed reaction mechanisms lead to a substantial disconnect between known oxidation mechanisms and speciated measurements of isoprene SOA composition. For example, the formation of methylglyceric acid (and other organic acids) cannot be accounted for by established reaction mechanisms, suggesting an important role of as-yet unidentified chemistry (in the gas and/or particle phases) in the formation of SOA from isoprene oxidation. The same is also true for the formation mechanism of 2-methyltetrols. A number of pathways have been put forth, including RO_2 chemistry (Claeys et al., 2004a), aqueous-phase oxidation by H_2O_2 (Claeys et al., 2004b; Boge et al., 2006), reactions of epoxides (Wang et al., 2005; Boge et al., 2006), and hydrolysis of nitrates (Sato, 2008), but at present it is unclear which are most important under ambient conditions.

3.3 Aqueous processing of water-soluble compounds

SOA formation through aqueous-phase photooxidation has received considerably less study when compared to typical smog chamber investigations. Detailed aqueous phase mechanisms for SOA formation from isoprene (or isoprene oxidation products) are not as well-understood, and aqueous phase processing is a critical open area for study. Recent laboratory studies demonstrate that low volatility dicarboxylic acids such as oxalic, succinic, and malic acid (Carlton et al., 2006, 2007; Altieri et al., 2008), as well as higher molecular weight compounds, including some with oligomeric structure (Altieri et al., 2006), form during simulated cloud chemistry. A predominant mechanism for dicarboxylic acid formation is nucleophilic (e.g. OH) attack of the carbonyl carbon in dissolved α-dicarbonyl compounds (e.g. glyoxal) (Carlton et al., 2007). Proposed aqueous phase oligomerization mechanisms suggest that the carboxylic acid monomers (formed via OH radical reactions) undergo esterification reactions with α- and β-hydroxy acids (Altieri et al., 2008). Proposed formation mechanisms for aqueous oligoesters that result in the regular addition of C_2H_4O_2 to the base organic acid monomer are similar to those proposed for the aerosol phase reactions (Gao et al., 2004; Surratt et al., 2006, 2007a). Analogous oxidative processing may occur within aqueous aerosol particles (Volkamer et al., 2009).

4 SOA yields developed from isoprene oxidation chamber studies

Results from several laboratory studies of SOA yields from the photooxidation of isoprene are shown in Fig. 3. Aerosol yields are plotted as a function of organic aerosol loading (Odum et al., 1996), with only yields at atmospherically relevant conditions (M_o=0–50 μg/m^3) shown. All volume-based measurements are converted to mass assuming a density of 1.4 g/cm^3. The shading of symbols in Fig. 3 are by dominant RO_2 reaction channel (which approximately corresponds to NO_3 level): black symbols are experiments in which NO remains at several ppb throughout, so the RO_2+NO reaction dominates; grey symbols are experiments in which NO starts high but falls to sub-ppb levels, so RO_2 radicals may react with NO, HO_2, and RO_2 over the course of the experiment; and open symbols correspond to NO_3-free experiments, in which the RO_2 reacts primarily with HO_2. In all cases, the dependence of SOA yield on organic aerosol loading (M_o) is clear, confirming that isoprene SOA is composed of semivolatile organics that partition between the gas and particle phases onto available condensation sites (Pankow, 1994b; Odum et al., 1996).

Despite the consistency in the observed dependence of SOA yield on M_o, variation among the different studies is quite pronounced, with measured yields spanning over an order of magnitude for a given value of M_o. Model parameterizations based on different studies are thus expected to lead to large differences in simulated SOA formation from isoprene oxidation. It is difficult to compare the degree of variation of measured yields to that from other SOA-forming systems: to our knowledge only one reaction, α-pinene ozonolysis, has been the subject of a larger number of SOA yield measurements (Hoffmann et al., 1997; Pathak et al., 2007; Presto and Donahue, 2006; Shilling et al., 2008). In that case, differences among the studies is substantially smaller than what is seen in Fig. 3 (Pathak et al., 2007), but even so, at organic aerosol loadings typical of the atmosphere (and of isoprene oxidation experiments), uncertainty in yields is still quite high (Shilling et al., 2008). Additionally, reaction conditions generally vary far less in ozonolysis reactions (generally carried out in the dark and in the absence of NO_3) than in photooxidation reactions, so better agreement is probably to be expected in that case.

The high degree of variability in yields measured in the different studies of isoprene photooxidation (Fig. 3; Table 1)
strongly suggests that SOA yields from isoprene are highly sensitive to reaction conditions and/or experimental design and conditions. There are a number of parameters that contribute to the observed variations; these are discussed below.

4.1 Temperature

The different studies varied somewhat in terms of ambient temperature, ranging from 20°C to 30°C (Table 1). Differences in temperature affect SOA yields largely by affecting gas-particle partitioning of semivolatiles; the temperature dependence can be described by \(\Delta H_{\text{vap,eff}}\), the overall effective enthalpy of vaporization of the SOA components. The only measurement of this quantity for isoprene SOA (in the absence of inorganic seed) is by Kleindienst et al. (2007a), finding \(\Delta H_{\text{vap,eff}}\) to be 42 kJ/mol for isoprene ozonolysis SOA, consistent with typically assumed values (Chung and Seinfeld, 2002; Henze and Seinfeld, 2006). Using this value, the gas-particle partitioning coefficient (KOM) will decrease by \(\sim 40\%\) between 20°C and 30°C, corresponding to a difference in yields of less than a factor of two. Thus, temperature differences cannot explain the wide range of SOA yields measured. Additional measurements of \(\Delta H_{\text{vap,eff}}\) would be very useful, particularly as it is believed to depend on reaction conditions such as NO\(_x\) level (Offenberg et al., 2006) and M\(_6\) (Donahue et al., 2006).

4.2 Relative humidity (RH)

RH also varied from study to study (Table 1). Dommen et al. (2006) found that SOA yields did not change when RH was varied over a range of 2% to 85%, suggesting RH has little effect on the gas-phase production or partitioning of semivolatiles. However, RH might affect aerosol formation by controlling the liquid water content of the aerosol, which, in turn, may promote gas-particle partitioning and/or heterogeneous reactions of WSOC (Volkamer et al., 2009). The effect of liquid water content on SOA yields has not been explored for isoprene SOA and is an important area of future research, as recent process-level modeling predicts isoprene SOA yields should be RH dependent (Pankow and Chang, 2008). However, since all experiments so far have been carried out at relatively low RH and/or in the absence of organic seed, this potential effect probably cannot explain the large variability in measured SOA yields (Fig. 3).

4.3 NO\(_x\) level (RO\(_2\) chemistry)

The experiments in which RO\(_2\)+NO dominates (“high NO\(_x\)” conditions) correspond to the lowest measured yields (Pandis et al., 1991; Edney et al., 2005; Kleindienst et al., 2007b), whereas those in which RO\(_2\)+HO\(_2\) (NO\(_x\)-free) is the only pathway by which RO\(_2\) reacts (“NO\(_x\)-free” conditions) are among the highest. Most (though not all) of the experiments involving more complex RO\(_2\) chemistry (in which RO\(_2\) can react with some combination of NO, HO\(_2\), and RO\(_2\)) have SOA yields intermediate to these “high-NO\(_x\)” and “NO\(_x\)-free” limits. This suggests that the RO\(_2\)+HO\(_2\) reaction forms products of lower volatility than the RO\(_2\)+NO reaction (see Fig. 1), consistent with results from studies of the oxidation of monoterpenes (Hatakeyama et al., 1991; Presto et al., 2005) and aromatics (Johnson et al., 2004; Ng et al., 2007).

4.4 OH concentration

Despite the general observations about the NO\(_x\)-dependence of the reaction products, it is clear that NO\(_x\) level (RO\(_2\) chemistry) cannot account for all the differences in yields seen in Fig. 3. Yields measured by Kroll et al. (2006) in the presence of NO\(_x\) (grey diamonds) are actually higher than those under NO\(_x\)-free conditions (open circles) from the same study, and the yields measured by Dommen et al. (2006) (grey squares) are lower than those of Kroll et al. (2005) (grey circles), despite generally being carried out at lower NO\(_x\) levels. A major difference among these studies is the rate of isoprene decay, which varies widely among studies because of the different radical precursors used. The precursors used in these three studies were NO\(_2\) (Dommen et al., 2006), HONO/NO\(_2\) (Kroll et al., 2005), and H\(_2\)O\(_2\)/NO (Kroll et al., 2006); resulting OH concentrations (estimated from reported isoprene decay rates) were \(\sim 1 \times 10^6\) molecules cm\(^{-3}\), \(\sim 4 \times 10^6\) molecules cm\(^{-3}\), and \(1 \times 10^7\) molecules cm\(^{-3}\), respectively. Thus it appears that SOA yields also depend on OH concentration within the experiment. Such an effect could arise from differences in the extent of reaction or in the rate of semivolatile formation; these are described below.
4.4.1 Extent of reaction

Because isoprene SOA formation is a result of multistep reactions (Ng et al., 2006), SOA yields are a strong function of the extent of the reaction in the overall reaction sequence (shown in Fig. 1) and relative concentration of reacting species. Thus, studies that report results at different points in this sequence could arrive at very different SOA yields. For example, as discussed earlier, methacrolein is an important intermediate in SOA formation from isoprene oxidation at high NOx; therefore yields are expected to be highest after all the methacrolein has reacted. However, yields calculated this late in the reaction sequence have not been reported; in most studies, radical reactions slow considerably (and/or wall losses begin to dominate) before this point. Measured final concentrations of methacrolein (+methyl vinyl ketone) vary between different studies (Domen et al., 2006; Ng et al., 2006), likely resulting from different OH levels. Thus, yield values can vary as a function of oxidation time, and so the “final yields” reported may be arbitrarily different based on experimental details. Differences in yields are a result of variations in OH exposure (OH concentration multiplied by reaction time), which serves as an excellent metric for the extent of reaction. However, it is extremely difficult to estimate OH exposures within chambers, since OH concentrations may change dramatically over the course of an experiment and are typically not monitored once the initial precursor has decayed away. Time-dependent measurements of OH concentrations in SOA formation experiments would allow for the estimation of OH exposures, thereby enabling the comparison of different laboratory experiments.

4.4.2 Rate of semivolatile formation

Alternately, OH levels may impact SOA yields by controlling the rate of production of semivolatile organics. Such a “rate effect” is expected, as fast production of semivolatiles will lead to more partitioning into the aerosol phase, where they “lock out” semivolatiles, NOx will be less susceptible to loss processes (Camredon et al., 2006); this effect has been described in detail by Camredon et al. (2006); this effect has been described in detail by Camredon et al. (2006). As the NOx concentration is a major determinant of OH concentration, the overall NOx dependence of SOA formation can be complex (Kroll et al., 2006); this effect has been described in detail by Camredon et al. (2007).

4.5 Other parameters

In summary, the high degree of variability in measured SOA yields from isoprene photooxidation can largely be attributed to: organic aerosol loading M0 (which controls gas-particle partitioning of semivolatiles), NOx level (which controls RO2 chemistry), and OH concentration (which controls extent and rate of reactions). Temperature and relative humidity seem to play a minor role in comparison. Still, the role of other reaction conditions or experimental parameters cannot be ruled out. Composition of seed particles may affect yields: aerosol growth is highly correlated with aerosol acidity, due to the importance of particle-phase reactions (Edney et al., 2005; Kleindienst et al., 2006; Suratt et al., 2007b); however, it should be noted that chamber measurements involving acidic seed (Kleindienst et al., 2006) exhibit a dependence on Mn that is in line with those carried out under neutral conditions (Fig. 3). There is also recent evidence that oxidative processing of WSOC within aqueous aerosol may also promote aerosol growth (Volkamer et al., 2009). Other effects include the intensity and wavelength of irradiation (Presto and Donahue, 2006; Warren et al., 2008) that may photolyze intermediates, the role of high concentrations of radical precursors (H2O2, NO2, etc.), and the loss of semivolatiles and particles to chamber walls. The effects of these parameters on isoprene SOA yields (as a function of Mn) have not yet been systematically studied.

4.6 Fitting of yield data

Modeling atmospheric SOA formation from isoprene oxidation requires parameterization of the above effects on SOA yield. The dependence of yield on Mn is included in most models already, by modeling a distribution of semivolatile organics, each with a stoichiometric formation yield (α) and partitioning coefficient (KOM), and calculating SOA formation according to semivolatile partitioning theory (Pankow, 1994a, b). Here we describe SOA formation in terms of the “two-product model” (Odum et al., 1996); fits to the “volatility basis set” approach (Donahue et al., 2006) are difficult owing to the limited range of Mn studied so far.

The individual laboratory fit parameters for isoprene SOA yields can be pooled and computed as a function of temperature, aerosol loading, and chemistry of the RO2 radicals (related to NOx level). Yields at the limiting NOx cases (high-NOx and NOx-free conditions) can be computed using the two-product model of Odum et al. (1996):

\[ Y_{\text{high NO}_x} = \frac{0.15}{(K_{OM, \text{high NO}_x}(T)M_0)^{-1} + 1} \]

(1)

\[ Y_{\text{NO}_x \text{Free}} = \frac{0.28}{(K_{OM1, \text{NO}_x \text{Free}}(T)M_0)^{-1} + 1} + \frac{0.032}{(K_{OM2, \text{NO}_x \text{Free}}(T)M_0)^{-1} + 1} \]

(2)

Values for KOM(T) can be calculated from KOM values determined in the laboratory using the Clausius-Clapeyron equation:

\[ K_{OM}(T) = K_{\text{ref}} \times \exp \left[ \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right] \]

(3)

in which Kref equals the value of KOM determined from chamber studies (=0.0020 for KOM,high NOx(T), 0.0045...
for $K_{OM1}$, NO$_x$Free($T$), and 0.93 for $K_{OM2}$, NO$_x$Free($T$)), $T_{ref}$ is the temperatures at which the experiments were conducted (=303 $K$ for $K_{OM}$, high NO$_x$($T$), 299 $K$ for $K_{OM1}$, NO$_x$Free($T$) and $K_{OM2}$, NO$_x$Free($T$),) and $\Delta H_{vap}/R$ equals 5050 K, using the best available values of $\Delta H_{vap}$ (Kleinindienst, 2007a).

From the above calculations of yields at limiting NO$_x$ cases, SOA yields can be computed for a range of NO$_x$ levels, following the approach of Presto et al. (2005):

$$Y = \beta \times Y_{high NO_x} + (1 - \beta) \times Y_{NO_x Free}$$

(4)

where $\beta$ is the fraction of peroxy radicals reacting with NO. This value is generally not measured in chambers, since RO$_2$ and HO$_2$ are not measured in most laboratory studies, but can be calculated from modeled peroxy radical concentrations. Thus, from Eqs. (1)–(4), SOA yields from isoprene oxidation can be calculated within atmospheric models, as a function of $T$, $M_O$, and RO$_2$ chemistry (NO$_x$). The parameterizations for both high NO$_x$ and NO$_x$-free conditions are shown in Table 3.

The dependence of yield on OH concentration is more difficult to quantify, as the exact cause is not well-constrained, and OH levels for individual experiments are generally not measured or reported. This suggests the need to conduct photooxidation experiments under atmospherically relevant OH concentrations, though this is difficult to define because of wall loss processes that occur in laboratory chambers but not in nature. OH concentrations in the high- and low-NO$_x$ cases are in the range of 2–4×10$^5$ molecules cm$^{-3}$ (Pandis et al., 1991; Kroll et al., 2006), calculated from reported isoprene decays. This suggests the OH concentrations were representative of the daytime troposphere, but better quantification of this effect is required.

5 Atmospheric modeling of isoprene SOA

In light of the field and laboratory evidence that isoprene oxidation leads to SOA formation, a number of recent modeling studies have proceeded to estimate the importance of isoprene SOA on regional and global scales (see Table 2 for a summary of the published papers) from terrestrial sources and recently from oceanic isoprene emissions as well (Arnold et al., 2009; Gantt et al., 2009). Predicted isoprene SOA concentrations from terrestrial isoprene emissions vary due to differences in modeled emissions, deposition, and climate projections (Tsigaridis et al., 2005), but global modeling efforts imply that isoprene SOA is substantial with annual production rates ranging from 14 Tg yr$^{-1}$ (Henze and Seinfeld, 2006; Hoyle et al., 2007) up to 19 TgC yr$^{-1}$ (Heald et al., 2008). Globally, isoprene-derived SOA is predicted to be 27% (Hoyle et al., 2007) to 48% (Henze and Seinfeld, 2006) of the total SOA, with some estimates as high as 78% (Heald et al., 2008). The importance of isoprene to SOA production has been shown on regional scales as well. For example, in the US, highest isoprene SOA concentrations occur in summer, when biogenic isoprene emissions are greatest (e.g. (Liao et al., 2007; Lane and Pandis, 2007)), and isoprene can contribute as much as 50% of the total modeled SOA (Liao et al., 2007). Heald et al. (2006) predict that for the 2004 summer in the northeastern US, where anthropogenic pollution is more concentrated, isoprene SOA contributes 15–30% of the total simulated SOA in that region. Isoprene SOA affects total POM not just by adding to total SOA, but also by increasing predicted amounts of SOA derived from other precursors, by providing additional organic particulate mass into which semivolatile compounds may partition. Modeled global SOA from sources other than isoprene increases by 17% when isoprene SOA is included (Henze and Seinfeld, 2006). Regionally, the inclusion of modeled isoprene SOA enables the increase of SOA from anthropogenic compounds by 1–10% across the US (Zhang et al., 2007b).

Although isoprene SOA can be a significant component of modeled secondary organic aerosol, there is some question about its overall importance to total aerosol mass (e.g. when primary or inorganic species are considered for relative importance). For example, US summertime organic aerosol mass at the surface is thought to increase any where from 6–50% (Morris et al., 2006; Van Donkelaar et al., 2007) as a result of isoprene SOA. The large range arises, in part, from the differences in the applied isoprene SOA yield parameters. Using a 3-product model for isoprene SOA based on the high NO$_x$ experiments of Pandis et al. (1991), Lane and Pandis (2007) find that summertime isoprene SOA contributes 7% of predicted organic aerosol mass. Using the 2-product parameterization of Henze and Seinfeld (2006) based on the low NO$_x$ experiments of Kroll et al. (2006), Zhang et al. (2007c) show that inclusion of isoprene SOA increases simulated surface concentrations in the US of total organic mass by 65% and total PM$_{2.5}$ mass concentrations by 25%.

5.1 Model predictions of cloud-produced SOA

The extent to which isoprene can form aerosol in the atmosphere via aqueous phase reactions remains unclear; however, the potential is considered substantial. Using a simple calculation assuming a global isoprene emission of 500 Tg yr$^{-1}$, Lim et al. (2005) predict that ~2 Tg yr$^{-1}$ of organic aerosol is formed globally from in-cloud processing of isoprene-specific oxidation products. When aqueous SOA production mechanisms were incorporated in the regional scale Models-3/Community Multiscale Air Quality (CMAQ) model (www.cmascenter.org), domain-wide SOA predictions increase by 9% (Chen et al., 2007) and CMAQ-predicted POM concentrations exhibit better agreement with OC measurements at the surface and WSOC measurements aloft when cloud-produced SOA is included (Carlton et al., 2008). Similarly, Fu et al. (2008) included an irreversible,
reactive uptake coefficient in the global model GEOS-Chem to simulate aqueous phase (e.g. cloud droplets and aqueous aerosol) SOA formation from glyoxal (47% from isoprene oxidation) and methylglyoxal (79% from isoprene oxidation). GEOS-Chem predicts 1.1 TgC yr\(^{-1}\) SOA from aqueous phase processes and model performance improved at the surface and aloft when compared with measurements of OC and WSOC (Fu et al., 2009).

Recently, Ervens et al. (2008) investigated aqueous phase SOA production from isoprene using a detailed chemical mechanism in a cloud parcel model. This work suggests a maximum SOA yield from isoprene of ∼40% compared to ∼3% for gas phase photooxidation pathways. Cloud contact time and initial VOC/NO\(_x\) ratio influence yields most strongly; SOA production yields were less sensitive to pH, liquid water content, and cloud droplet number. The yield parameterizations developed by Ervens et al. (2008) have yet to be applied in 3-dimensional atmospheric models but strongly suggest aqueous pathways are atmospherically relevant and require further development.

The vertical distribution of the isoprene SOA is an important consideration and remains an area for study. Isoprene may contribute more to organic aerosol concentrations aloft than other SOA precursors because 1) the largest sources of isoprene are in regions of large vertical lifting, and 2) cloud-produced SOA can vent to free troposphere due to convective mixing. Lower temperatures in the free troposphere are more conducive to the condensation of semivolatile products (Henze and Seinfeld, 2006; Heald et al., 2008) and loss pathways (e.g. removal mechanisms such as wet deposition) are decreased relative to lower altitudes. The location of isoprene SOA within the atmosphere could have important implications for long-range transport as well as direct and indirect climatic effects.

5.2 Atmospheric modeling of fitted yield data

Predicted isoprene SOA mass concentrations are sensitive to the assigned, laboratory-dependent α and K\(_{OM}\) values. To test this sensitivity, regional-scale model simulations...
were conducted with the CMAQ model, version 4.7 (www.camascenter.org) using the parameterizations developed in this work for high and low-NOx conditions, as described above in Sect. 4.6 (K and α values are listed in Table 3). CMAQ was run for August and September 2003 for the contiguous United States with 36 km horizontal grid spacing, driven by MM5 meteorology (Grell et al., 1994). Anthropogenic emissions were generated from the EPA’s 2002 national emissions inventory (NEI) and biogenic emissions were determined from the Biogenic Emissions Inventory System (BEISv3.13). The results of the CMAQ simulations indicate that fits derived under different laboratory conditions generate large differences in predicted isoprene SOA mass concentrations (Fig. 4). The difference in higher bound (low NOx) and lower bound (high NOx) predictions of isoprene SOA varied up to ~0.5 µg m⁻³ (Fig. 4a) corresponding to a maximum change of 30% of total simulated organic carbon for the entire eastern US (Fig. 4b). Yields derived from pooled experimental data, encompassing a variety of laboratory conditions, should therefore be considered for future isoprene SOA research.

6 Future directions

Based on evidence collected through laboratory, field, and modeling studies, we conclude that isoprene SOA is indeed an important contributor to the atmospheric organic aerosol burden, though substantial uncertainties remain. Estimates for current production rates are ~6–30 Tg yr⁻¹, with aqueous processes potentially providing an additional 2 Tg yr⁻¹ (Lim et al., 2005). For comparison, the global estimate of fossil fuel contribution to the atmospheric POM burden is approximately 2 Tg (Ito and Penner, 2005). Therefore, isoprene-derived SOA mass represents an important component of atmospheric organic aerosol, roughly up to 30% of the global annual POM budget (Heald et al., 2008).

Table 3. Isoprene SOA Parameters associated with High and Low NOx conditions.

<table>
<thead>
<tr>
<th></th>
<th>Upper Bound</th>
<th>Lower Bound</th>
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</thead>
<tbody>
<tr>
<td>α₁</td>
<td>0.28</td>
<td>0.154</td>
</tr>
<tr>
<td>α₂</td>
<td>0.032</td>
<td>0.002</td>
</tr>
<tr>
<td>Kom₁</td>
<td>0.0044</td>
<td>0.002</td>
</tr>
<tr>
<td>Kom₂</td>
<td>0.93</td>
<td></td>
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</tbody>
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Parameters used in CMAQ simulations (Fig. 4). Note: molecular weights and enthalpy of vaporization (ΔH_vap) values are from Henze and Seinfeld (2008) and listed in Table 2.

The large range in estimates of the contribution of isoprene SOA to the total particulate burden derives in part from uncertainties in the parameterization of SOA yields from laboratory studies. We have tried to show that much of the apparent discrepancies in laboratory measurements of isoprene SOA yields (Fig. 3) can be explained in terms of differences in reaction conditions (M_o, NOx, etc.). The suggested yield parameterizations provided here (Table 3), based on all available laboratory data (where M_o=0–50 µg m⁻³), allows for the calculation of SOA yields as a function of both M_o and NOx and provides a means for models to include SOA formation from isoprene in a way that is broadly consistent with chamber results.

It is hoped that this new parameterization will shrink the range in estimates of the importance of isoprene to the total atmospheric particulate burden; however there are still substantial uncertainties that need to be addressed. Examples include the temperature dependence of SOA formation (at present, there is only one measurement of ΔH_vap,eff for isoprene SOA) and the role of particle composition (e.g. acidity) in the formation of low-volatility organics. The importance...
of oxidative processes within clouds and aerosols is also poorly constrained, in part because there are few laboratory measurements and simple parameterizations of SOA yields from such reactions, needed for atmospheric models, are dependent not only on the chemistry but on meteorology as well (Ervens et al., 2008). Finally, standard frameworks for representing SOA formation within atmospheric models assume SOA formation is a single-step process, and do not reflect the multistep nature of isoprene oxidation. This shortcoming may be addressed by modeling SOA formation from individual first-generation products (methacrolein, etc.), rather than collectively as isoprene SOA. However, this will require the laboratory study of SOA formation from a larger number of species, and also an improved understanding of the chemical mechanisms underlying multistep isoprene oxidation (in particular the distribution of 2nd- and later-generation products).

Alternatively, recently-suggested approaches for modeling SOA, such as the “volatility basis set” approach (Donahue et al., 2006) or the “carbon number-polarity grid” (Pankow and Barsanti, 2009) are well-suited for including the effects of multiple generations of oxidation. However, these too require further experimental constraints on the changes of organics upon atmospheric oxidation. We note that most of these uncertainties are not limited only to isoprene SOA, and instead apply to SOA formation in general.

Of course the importance of isoprene as an SOA precursor is determined not only by SOA yields but also by total isoprene emissions, which are also subject to major uncertainties. Current global estimates of biogenic isoprene emissions assign an uncertainty of a factor of two (Guenther et al., 2006). Isoprene emissions are controlled by the type and density of vegetation in a landscape, and also environmental conditions, such as temperature and radiation. A factor of two in emissions estimates arises from uncertainties associated with those underlying surface characteristics, as well as from controlling environmental conditions. Such uncertainties can be exacerbated for isoprene SOA in particular when projecting future conditions: changes to climate and land use may affect the amount of isoprene-derived SOA, which can in turn have climate feedback effects. For example, Sanderson et al. (2003) predict increases in future global isoprene emissions by 27–34% due to changes in temperature and vegetation associated with future climate change. However, Wiedinmyer et al. (2006) suggest that the magnitude of future isoprene emission changes is highly uncertain, and even the sign of change is not well-constrained (i.e. isoprene emissions could decrease due to land use changes). Indeed, work by Heald et al. (2008) suggests that changes to the future global isoprene SOA burden may be anywhere from −15% to +27% due to changes in climate, land cover, and emissions. This broad range considers only the uncertainty in these changes and their effects, and not the uncertainties implicit in isoprene SOA yields.

The continued development of tracers of isoprene SOA (e.g. methyl tetrols, (Kleindienst et al., 2007a)) is a critical area for further research. Identification of unique tracers allow for investigation of specific, individual VOC precursors and their contribution to organic aerosol mass in the atmosphere. Current tracer-based formulations require extrapolation of the laboratory-measured tracer-to-secondary organic carbon (SOC) ratio values (tracer/SOC) to the atmosphere. As a consequence, ambient measurements of VOC-specific SOC mass are considered only estimates, but were found to compare well with an independent chemical mass balance approach (Lewandowski et al., 2008). Continued study of isoprene SOA that combines ambient measurements of tracers, identified in laboratory experiments, coupled with atmospheric modeling will lead to quantitative assessment of isoprene-specific predictive models. The most successful future approaches investigating isoprene SOA will employ a combination of laboratory, emissions, and modeling work.

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