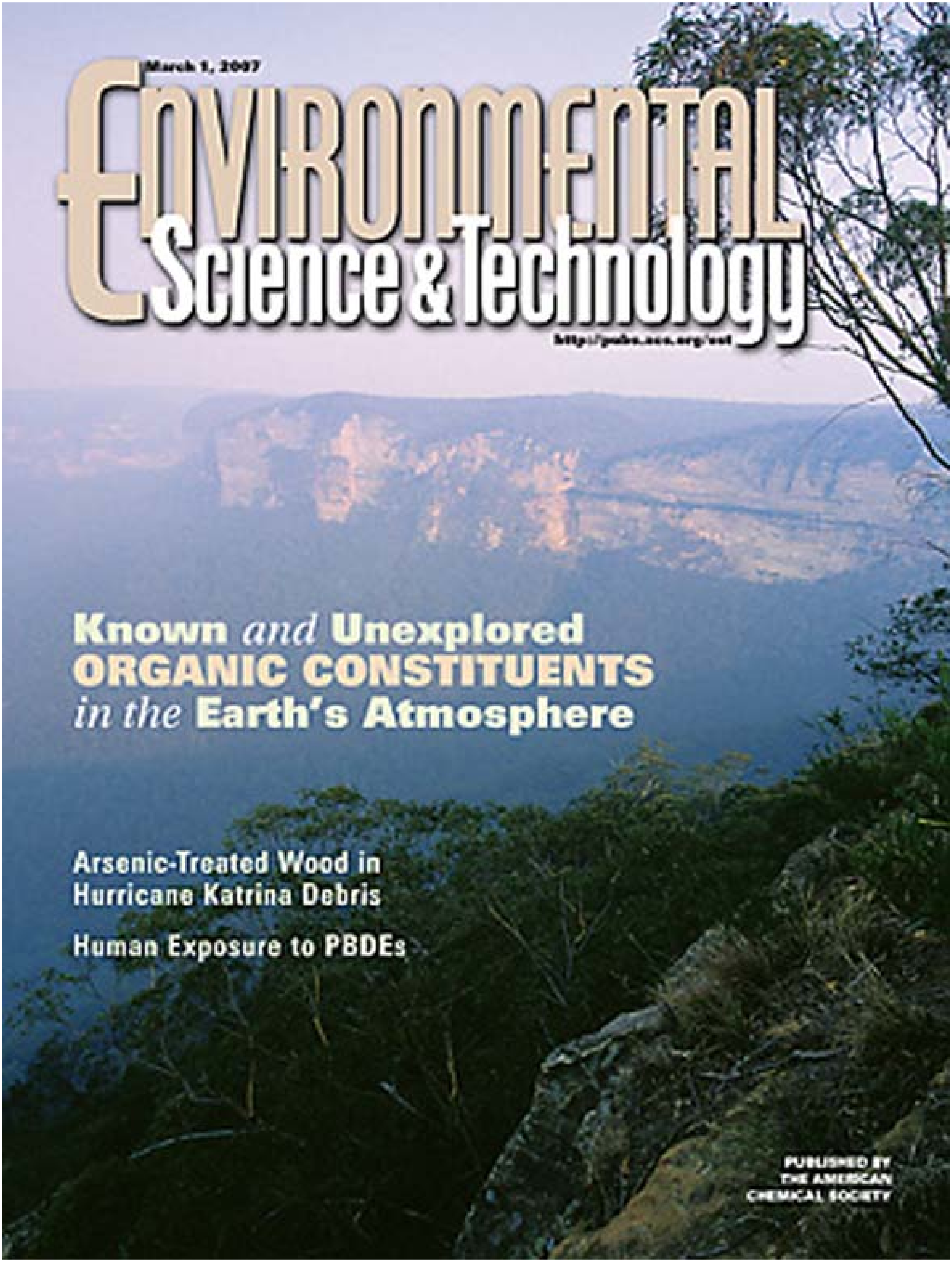

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Known *and* Unexplored ORGANIC CONSTITUENTS *in the* Earth's Atmosphere

Arsenic-Treated Wood in Hurricane Katrina Debris

Human Exposure to PBDEs

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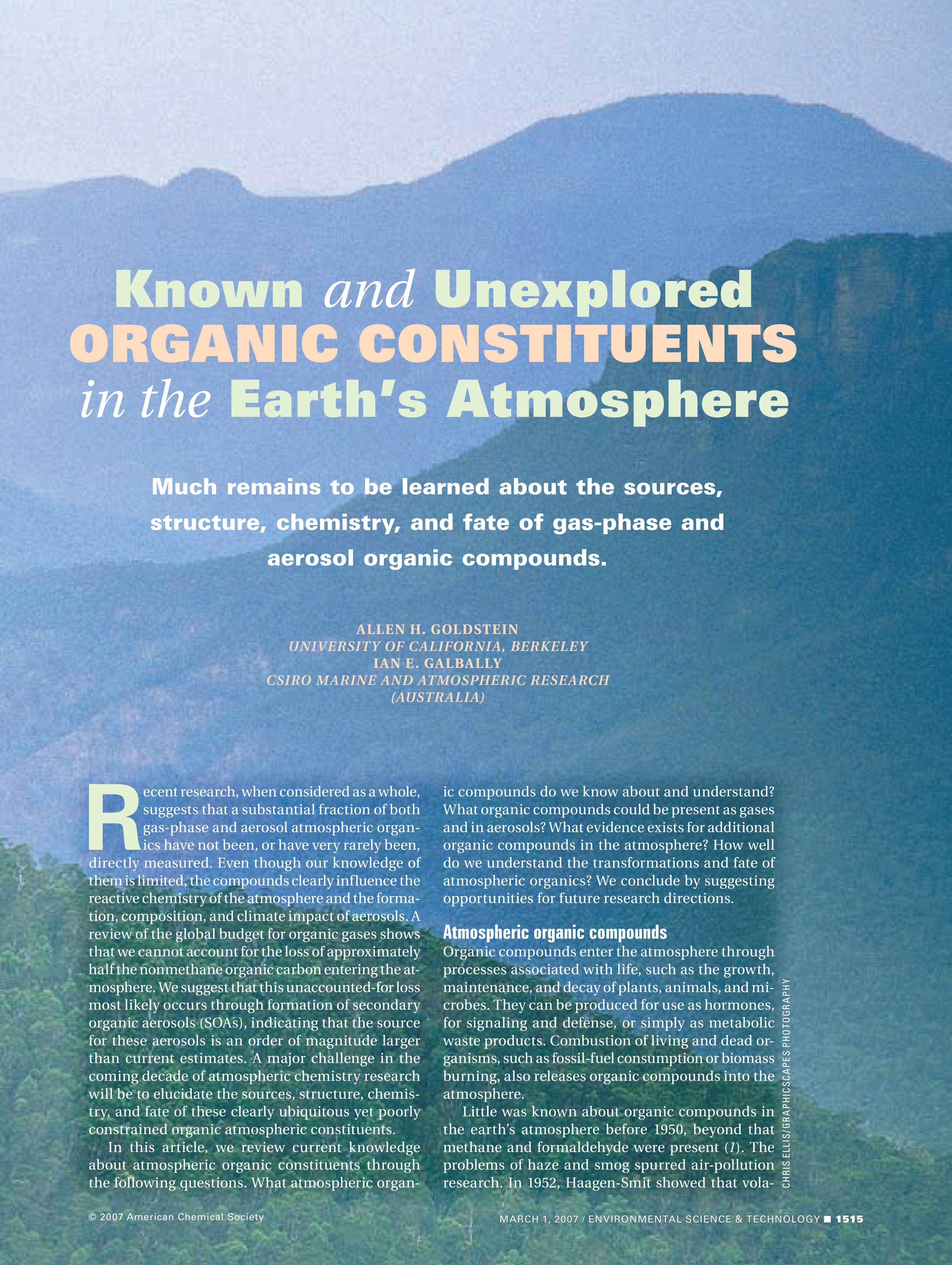

Known *and* Unexplored ORGANIC CONSTITUENTS *in the* Earth's Atmosphere

Much remains to be learned about the sources, structure, chemistry, and fate of gas-phase and aerosol organic compounds.

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Recent research, when considered as a whole, suggests that a substantial fraction of both gas-phase and aerosol atmospheric organics have not been, or have very rarely been, directly measured. Even though our knowledge of them is limited, the compounds clearly influence the reactive chemistry of the atmosphere and the formation, composition, and climate impact of aerosols. A review of the global budget for organic gases shows that we cannot account for the loss of approximately half the nonmethane organic carbon entering the atmosphere. We suggest that this unaccounted-for loss most likely occurs through formation of secondary organic aerosols (SOAs), indicating that the source for these aerosols is an order of magnitude larger than current estimates. A major challenge in the coming decade of atmospheric chemistry research will be to elucidate the sources, structure, chemistry, and fate of these clearly ubiquitous yet poorly constrained organic atmospheric constituents.

In this article, we review current knowledge about atmospheric organic constituents through the following questions. What atmospheric organic compounds do we know about and understand? What organic compounds could be present as gases and in aerosols? What evidence exists for additional organic compounds in the atmosphere? How well do we understand the transformations and fate of atmospheric organics? We conclude by suggesting opportunities for future research directions.

Atmospheric organic compounds

Organic compounds enter the atmosphere through processes associated with life, such as the growth, maintenance, and decay of plants, animals, and microbes. They can be produced for use as hormones, for signaling and defense, or simply as metabolic waste products. Combustion of living and dead organisms, such as fossil-fuel consumption or biomass burning, also releases organic compounds into the atmosphere.

Little was known about organic compounds in the earth's atmosphere before 1950, beyond that methane and formaldehyde were present (*1*). The problems of haze and smog spurred air-pollution research. In 1952, Haagen-Smit showed that vola-

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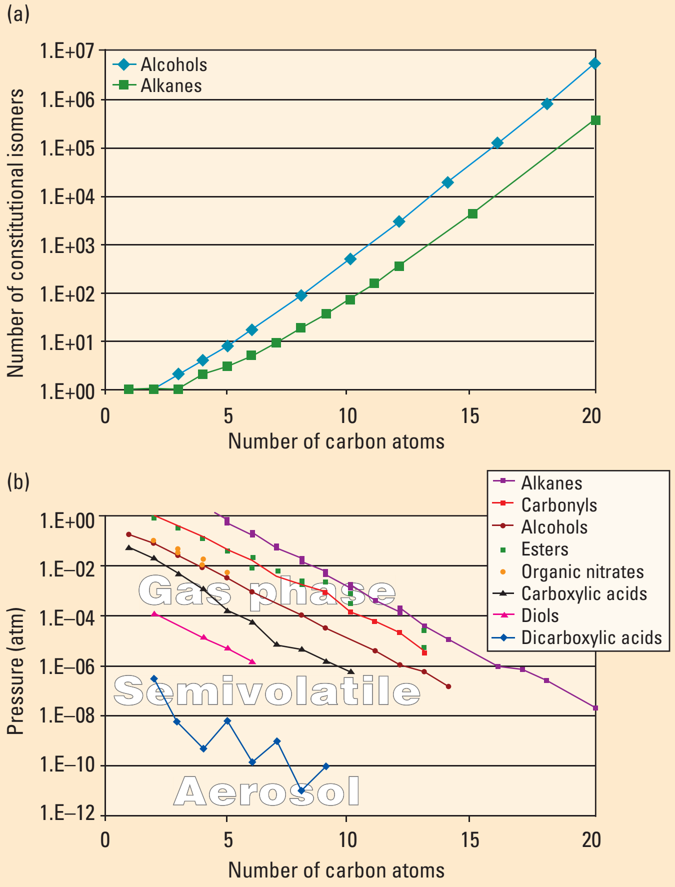
tile organic compounds (VOCs) and nitrogen oxides (NO$_x$) combine photochemically to produce ozone (*2*), and Mader et al. provided the first detailed chemical characterization of organic aerosols (*3*). Chromatographic measurements of hydrocarbon composition in automobile emissions and in the urban atmosphere were reported shortly thereafter (*4*). By 1961, Leighton, in his classic book *Photochemistry of Air Pollution*, had used fundamental chemical understanding to identify the roles of alkanes, alkenes, alkynes, arenes (aromatics), aldehydes, ketones, and organonitrate compounds in urban smog (*5*).

FIGURE 1

Multiple carbon atoms

(a) Number of unique isomers possible as a function of the number of carbon atoms in the molecule for alkanes and alcohols. (b) Vapor pressure of organic compounds at 298 K as a function of the number of carbon atoms and functional groups in the molecule (data from Refs. 46–50).



Knowledge of organic composition in the background atmosphere lagged behind urban pollution studies. In 1960, Went theorized that biogenically emitted VOCs created the blue haze observed in the atmosphere above many forested regions, such as the Blue Mountains in Australia shown on p 1514 (*6*). Subsequent research has shown that, on a global scale, emissions of VOCs from vegetation are an order of magnitude greater than those from petrochemical production and use (*7*). Even in some urban environments, biogenic VOC emissions were shown to be as important for regional photochemical ozone production as anthropogenic VOC emissions (*8*). Furthermore, studies of plant signaling, defense, and food and flavor chemistry have led to the detection of thousands of individual VOCs (*9*), yet only a small fraction of these have been studied by the atmospheric science community.

VOCs are now known to be essential components of tropospheric chemistry; their oxidation leads to ozone and aerosol production. However, knowledge of organic aerosols' composition, sources, chemistry, and role in the atmosphere and the earth's climate system is still extremely limited, and the importance of biogenic and anthropogenic precursors for SOA production is a major current research topic (*10*, *11*).

By 1978, 606 organic compounds had been identified in the atmosphere, and by 1986 the number had climbed to 2857 (*12*, *13*). Unfortunately, no more recent comprehensive summary has been compiled. We guess that 10^4–10^5 different atmospheric organic species have been measured. That may be only a small fraction of the number actually present.

Organic compounds as gases and in aerosols

We queried the Beilstein preparative organic chemistry database for C1 organic compounds with boiling points <300 °C and a total of <11 atoms, criteria appropriate for compounds that might occur in the atmosphere. Excluding isotopes and complexes, 791 known compounds met these criteria. We also calculated the number of C1 compounds that could include the following atoms or groups connected by single bonds (H, F, Cl, Br, I, NO$_2$, NO$_3$, OH, OOH, NH$_2$, SH), double bonds (O, S, Se), and triple bonds (N, P, As). The result was 1232 possible compounds, which, if they exist, could occur in the atmosphere. Either result is surprisingly large for compounds with only one carbon atom.

For molecules with multiple carbon atoms, we illustrate the logarithmic growth in the possible number of alkane isomers and their monosubstituted alcohols as a function of carbon number (Figure 1a). By C10, 100 possible alkane isomers could exist. If all the substitutions listed above are considered, well over 1 million possible C10 organic compounds, many of which are likely to occur in the atmosphere, could exist. Developing measurement methodologies to deal with this range of organic compounds is a key challenge in atmospheric chemistry. Understanding the transformations and processes that lead to the partitioning of these compounds between the gaseous and aerosol phases is another key challenge.

Some atmospheric organic compounds occur entirely in the gas phase, whereas others occur as liquids or solids in aerosols. Partitioning between the gas and aerosol phases in the atmosphere depends on the liquid- or solid-phase vapor pressure of the compound, whether it occurs as a pure substance or as a mixture in the aerosol phase, and its water solubility when the aerosol phase is primarily aqueous. Most emissions of organic compounds to the atmosphere are gaseous. Although primary organic compounds typically have high vapor pressures

(Figure 1b), the vapor pressure decreases with increasing polarity, as oxidation proceeds first to carbonyls and esters. With further oxidation to alcohols and carboxylic acids, the vapor pressure decreases because of hydrogen bonding. Vapor pressures get even lower for multifunctional compounds, such as diols, and extremely low for dicarboxylic acids. The partitioning favors the aerosol phase for alkanes with >20 carbon atoms and for dicarboxylic acids with ≥3 carbon atoms. Generally, compounds in the atmosphere will be gas phase if their vapor pressure at ambient temperature is $>10^{-5}$ atm, semivolatile if vapor pressures are between 10^{-5} and 10^{-11} atm, and aerosols at vapor pressures below this. As temperature decreases (or altitude increases), vapor pressure decreases and more compounds become aerosols.

Evidence for additional organic compounds

In this section, we highlight a few of the many recent discoveries that provide direct and indirect evidence of unexplored organics from observations of gas, combined gas and aerosol, and aerosol phases.

Gas-phase direct evidence. Multidimensional or comprehensive gas chromatography (GC × GC) has greatly enhanced separating powers and provided novel direct evidence of additional organic compounds in the atmosphere. In the first paper to use GC × GC for gas-phase measurements of urban air samples, >500 individual VOC species were isolated and classified, including a much broader array of multisubstituted compounds than had previously been identified (*14*). In situ measurements of C7–C14 compounds in urban air in Crete (Greece) revealed ~650 identifiable compounds and at least as many unidentifiable peaks (*15*). Analysis of ambient air in an urban environment (Leeds, U.K.) detected the presence of 147 monoaromatic species with up to 8 carbon atoms added to the aromatic ring. State-of-the-art, single-column measurements typically reveal only 8–15 of these compounds (*16*). These previously unmeasured monoaromatic compounds may be of particular significance in urban areas because of their high and variable SOA and ozone production potential.

Measurement by chemical ionization mass spectrometry (CIMS) techniques, such as proton transfer reaction mass spectrometry (PTR-MS) (*17*), provides an opportunity to observe compounds that do not survive preconcentration and chromatography. PTR-MS was used to observe the sum of all individual monoterpenes in a forest environment; 30% more terpenes were revealed than could be measured by preconcentration followed by GC separation (*18*). PTR-MS has also been used to scan the atmosphere for known and potentially unknown compounds in a variety of environments, including forested areas in Surinam (*19*) and California (*20*). The results included quantifiable measurements of a range of previously undetected biogenic terpenoid oxidation products. An ideal set of instrumentation for comprehensive measurement of atmospheric organic composition would combine the scanning ability of techniques such as PTR-MS for broad coverage with separation techniques to enable specific identification.

Multifunctional oxygenated species are generally difficult to analyze directly by chromatography. Derivatization has allowed atmospheric observations of abundant gas-phase VOCs (e.g., 2-hydroxy-2-methylpropanal, glycolaldehyde, hydroxyacetone, methylglyoxal, and glyoxal), which were rarely or never measured before (*21*). Some of these observations overlap with the CIMS observations described above (e.g., hydroxyacetone by PTR-MS, *19*) but with more definitive separation and identification following derivatization.

Measurements of total gas-phase VOC versus speciated VOC measurements in ambient air showed that the fraction of total VOCs (nonmethane organic carbon) quantified as speciated VOCs was, at least in part, a function of photochemical age. Of the total VOCs, 80–85% were accounted for as speciated compounds in fresh urban pollution in Burbank, Calif., whereas only 55–80% were accounted for at Azusa, Calif., and the University of California, Los Angeles, during summer, when more extensive oxidation of primary compounds had already occurred (*22*). Key reasons for this are that fresh pollution is often made up of gasoline-derived emissions, which have already been differentiated from their heavier or harder-to-measure components in refineries. In addition, the oxidation products present in photochemically aged air have not been as thoroughly studied and are not as easy to measure with current sample-collection techniques.

Combined gas and aerosol direct evidence. The carbon balance in smog-chamber oxidation studies can provide insight into the potential completeness of current measurements of atmospherically relevant organic composition. For well-studied molecules such as isoprene and *m*-xylene, the carbon balance is reasonably complete when total VOC measurements are used, but only about half of the isoprene oxidation products and essentially none of the *m*-xylene oxidation products are detected by traditional, air-sampling GC methods (*23*). Experiments quantifying the oxidation products of a wide variety of terpenoid compounds show that often much less than 100% of the oxidized carbon is accounted for in the gas and aerosol phases combined (*24–26*), as illustrated in Figure 2. The growth of SOAs in smog chambers is indicative of low-volatility oxidation products leaving the gas phase. The lack of chemical carbon mass balance in smog-chamber studies (VOC oxidized is more than the total carbon measured in gas plus aerosol phases) indicates that, for some of the reactions studied, oxidized organic material must remain undetected in the gas phase. Similar gas-phase organic material is likely to be undetected in the ambient atmosphere. For example, on the basis of chamber studies, hydroxycarbonyls have been estimated to account for between one-third and two-thirds of the products formed from oxidation of C5–C10 alkanes (*27*, *28*) and 22% of isoprene oxidation products (*29*), but this range of hydroxycarbonyls has not been measured in the atmosphere.

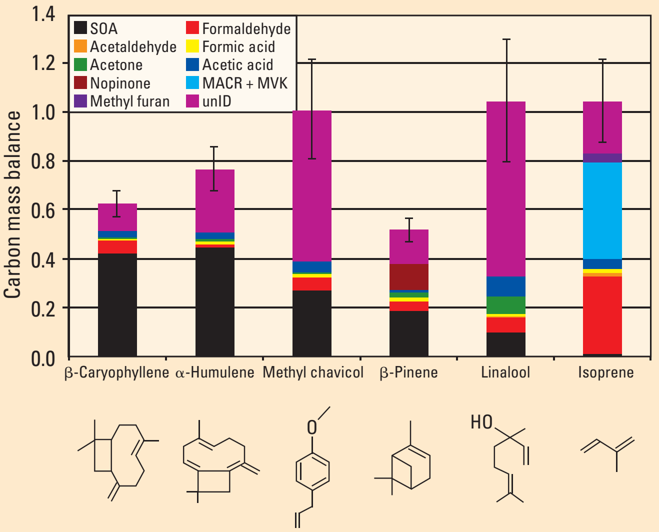
Aerosol direct evidence. Thermal desorption of filter samples followed by GC × GC has been used to

analyze the organic composition of $PM_{2.5}$ aerosols collected in London. A separation of >10,000 individual organic species ranging in functionality from alkanes to polyoxygenated species was achieved (*30*). Although only a small fraction of observed compounds in the aerosol samples were positively identified, the observations revealed dramatic limitations of more commonly used single-dimension chromatography for measuring organic chemicals in atmospheric aerosols. Multifunctional oxygenated species are abundant in aerosols and generally require derivatization for direct analysis by chromatography. Derivatization was recently used to observe that tetrols, which originate from oxidation of biogenically emitted isoprene, provide a substantial source of SOAs (*31*).

FIGURE 2

Carbon mass balance for photochemical oxidation of six different terpenoid compounds

All SOA and gas-phase products detected are included. Compounds measured as *m/z* ratios by PTR-MS that were not specifically identified are referred to as unID (adapted with permission from Ref. 26).



Chemical transformations within aerosols can produce a range of new compounds and contribute to the movement of organic compounds from the gas to aerosol phase. For example, aldehydes can hydrate to diols and be oxidized to organic acids. The presence of organic oligomers, in which smaller organics have combined to form larger chains, has been suggested to account for much of the unidentified organic aerosol mass (*32*).

Indirect evidence of unknown organics. Indirect evidence for additional organics in the atmosphere can be obtained through observation of their chemical influence. Production or loss of oxidants (e.g., O_3, OH) or production of stable products (organic nitrates, oxygenated organic gases, SOAs, etc.) can indicate organic precursors that have yet to be measured.

Ozone chemical loss observed in a forest canopy was argued to indicate oxidation of very reactive terpenes before they escape the forest (*33*, *34*). However, these very reactive terpenes have yet to be measured in the forest canopy. Corroborating evidence was obtained by measuring vertical gradients of terpene oxidation products with maximum concentrations just above the trees (*20*) and showing that they match products observed in the laboratory from terpene plus ozone reactions (*24*).

Measurements of total OH reactivity, which is primarily due to VOCs and CO, have been compared with the expected reactivity of all measured compounds in a variety of environments and then used to infer the presence of unmeasured reactive compounds (*35*). A large temperature-dependent difference was found between measured and expected total OH reactivity in a forest environment; this provided indirect evidence that unmeasured terpenes were likely responsible. In an urban environment, agreement between measured and expected OH reactivity was much better, which is in general agreement with the total-VOC versus speciated-VOC studies discussed previously (*22*).

Several studies have shown evidence of SOAs for which the VOC precursors have not been identified. In one example over the Pacific Ocean, the observed vertical concentration profiles for sulfate and elemental carbon aerosols showed lower concentrations in the free troposphere than in the boundary layer because of wet scavenging, yet a very different vertical profile was observed for organic aerosols with high concentrations in the free troposphere. A global chemical-transport model was able to reproduce observed vertical profiles of sulfate and elemental carbon aerosols, but organic aerosols in the free troposphere were 10–100× more abundant than the model estimate. A large and sustained source of SOAs from oxidation of VOCs, which are long-lived enough to be transported into the free troposphere and not included in current models, could explain this discrepancy (*36*). In another example in Mexico City, observed SOA growth in the real urban atmosphere was a factor of 8 higher than predicted by state-of-the-art SOA models based on oxidation of the simultaneously observed gas-phase VOCs (*37*). This observation suggests either higher than expected SOA yields or unmeasured precursors that together could be even more important for SOA formation than the measured compounds.

A key to understanding atmospheric organic aerosols is that the major transformation processes leading to SOA production are typically not the initial oxidation steps of the parent compound but rather the second- and later-generation oxidation steps, as was recently shown for the dominant biogenic compound isoprene and for many terpenes (*38*). SOA formation may therefore occur relatively far from the primary emission source, even for compounds such as isoprene, whose atmospheric lifetime is ~1 h.

Transformation and fate of atmospheric organics

VOCs must eventually be removed from the atmosphere by either deposition, oxidation to CO and CO_2, or conversion to SOAs. The SOAs must then be removed by either deposition or oxidation to CO or CO_2 or recycled back to VOCs. To complete this review, we apply a conservation-of-mass approach to the atmospheric budget of VOCs and SOAs (Figure 3) and explore what such a budget reveals.

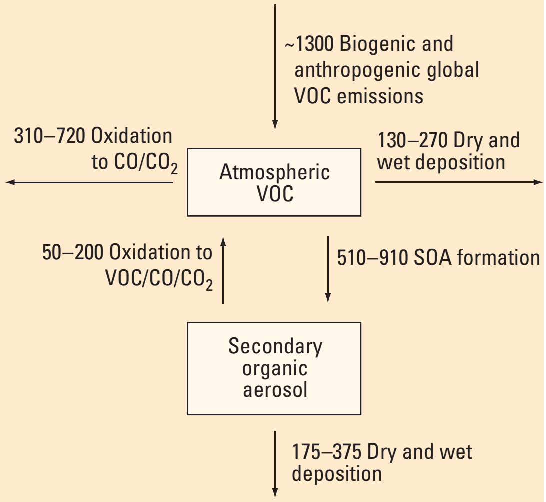
Atmospheric VOC sources include nonmethane biogenic emissions from terrestrial ecosystems and the ocean of 1150 Tg C/yr (*7*) (Tg = 10^{12} g), anthropogenic emissions of 142 Tg C/yr (*39*), and a small additional source from biomass burning and plant decay. This gives a total, albeit highly uncertain, global VOC emissions estimate of 1300 Tg C/yr, of which one-third is isoprene (500 Tg C/yr).

VOC oxidation follows two pathways, one leading to production of CO_2 mainly via CO and another leading to production of lower-vapor-pressure or more highly soluble products that ultimately wet or dry deposit or transform into SOAs.

FIGURE 3

Mass-balance-based estimate of the global budget for atmospheric VOCs

The total source of VOCs emitted into the atmosphere (arrows indicate fluxes) must be removed through one of three possible pathways: oxidation to CO and CO_2, dry or wet deposition, or SOA formation. The SOAs must be removed through oxidation, or wet or dry deposition. Best estimates for these rates are included. Units = Tg C/yr.

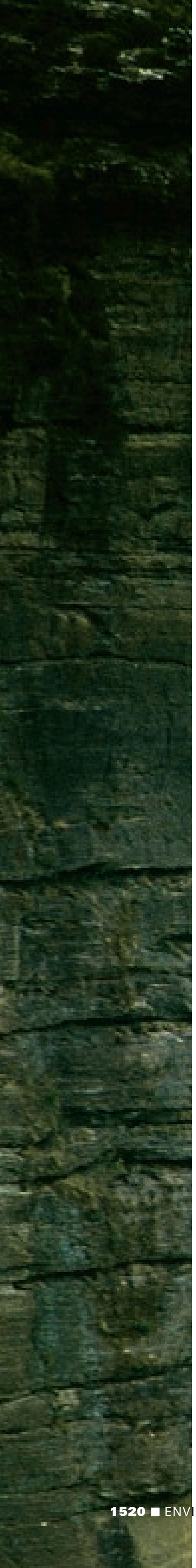


The amount of nonmethane VOC oxidation proceeding through CO to CO_2 has been assessed to provide constraints on the CO budget, with an estimate of 280 Tg C/yr as CO (*40*) accounting for ~22% of the VOC emissions. For isoprene alone, CO production accounts for a similar percentage (23%) of the amount emitted. Transformation of carbonyls via peroxy radicals leads to additional oxidation to CO_2 that does not pass through CO first. Though the magnitude is not known for many VOCs, we estimate on the basis of what is known for isoprene oxidation that direct formation of CO_2 is ~25% of the CO pathway. This is consistent with estimates from a comprehensive model of the evolution of organic carbon during gas-phase oxidation (*41*). That model predicts that for the simple alkane heptane, 20–30% should be oxidized into CO or CO_2 after 5 days, even though >90% of the heptane is transformed through oxidation during this time frame. The remaining heptane and some of the heptane oxidation products should also be eventually converted to CO or CO_2. Given these constraints, we estimate that 260–520 Tg C/yr (20–40%) of atmospheric VOCs are likely converted to CO or CO_2 during initial gas-phase VOC oxidation.

To our knowledge, neither wet nor dry deposition of gas-phase VOC to terrestrial and ocean surfaces has been quantified. The global wet deposition of dissolved organic carbon (DOC) from the atmosphere has been estimated as 430 ± 150 Tg C/yr (*42*). This total DOC must be the sum of aerosol organic carbon (primary and SOA) and gas-phase VOC contributions. The composition of DOC reported (and we infer the likely phase) is 42% organic acids, including amino acids (should be mostly from aerosol phase), 8% small aldehydes (should be almost all from gas-phase VOCs), and 50% uncharacterized (similar to atmospheric aerosols in which humic-like substances that cannot be separated into individual compounds make up most of the organic carbon; thus this is likely almost all from aerosols). Because aldehydes, acids, and some of the uncharacterized organic carbon may all be VOCs, we assume the 8% aldehydes and an additional 15% of the DOC that is wet deposited comes from gas-phase VOCs. Thus, we estimate 23% of the 430 ± 150 Tg C/yr, or 100 ± 35 Tg C/yr, in rain is likely wet deposition of gas-phase VOCs. Because little information is available on the dry deposition of VOCs, we take a first guess that dry deposition and wet deposition will be of similar magnitude and estimate total gas-phase VOC deposition is 130–270 Tg C/yr.

We now have the basis to attempt a mass-balance estimate to address the fate of atmospheric VOCs at the global scale. Of the 1300 Tg C/yr of VOCs emitted, oxidation to CO and CO_2 accounts for removal of ~260–520 Tg C/yr, and deposition accounts for removal of ~130–270 Tg C/yr. Mass balance of the VOC budget requires that SOA production of ~510–910 Tg C/yr (about half of the VOC emissions to the atmosphere) must account for removal of the remaining VOCs. Otherwise, either the deposition of gas-phase VOCs or their oxidation to CO and CO_2 has been underestimated, or the total source of atmospheric VOCs has been overestimated.

The atmospheric wet deposition of DOC (430 ± 150 Tg C/yr, *42*) discussed above also provides information about the sink rate of atmospheric SOAs. If 100 ± 35 Tg C/yr is from gas-phase VOC (as estimated above), then 330 ± 115 Tg C/yr must be wet deposition of aerosol organic carbon. This aerosol organic carbon is from a combination of primary and secondary sources. Most analyses of primary versus secondary organic carbon in the atmosphere suggest that SOAs dominate the total source, particularly outside urban regions. Assuming that SOAs are two-thirds of the total aerosol organic carbon



source, we infer the global SOA wet deposition is 140–300 Tg C/yr. Wet deposition of carbonaceous aerosols is generally modeled to account for 70–85% of the total wet plus dry deposition (*10*). We therefore estimate that dry deposition of SOAs is 25% of the wet deposition and suggest that total SOA deposition should be 175–375 Tg C/yr.

Oxidation of SOAs to volatile compounds provides another sink for aerosol organic carbon from the atmosphere, with a volatilization lifetime that is similar to the wet-deposition lifetime (*43*). The only published global estimate of this process suggests that 50–200 Tg C/yr gas-phase oxygenated VOCs (OVOCs) are produced from OH oxidation of aerosol organic carbon (*44*), and the authors state that this is an upper limit due to the data and assumptions used. We include this estimate as a first guess in our budget of aerosol organic carbon and assume the OVOC oxidation products eventually form CO or CO_2. Because this is an additional source of CO/CO_2, above that produced from initial VOC oxidation, the total increases to 310–720 Tg C/yr. When oxidation of SOAs is combined with wet and dry deposition, the total SOA sink becomes 225–575 Tg C/yr.

An alternative rough estimate of the global organic aerosol source can be derived from the global estimates of sulfate aerosol sources and the observed organic-to-sulfate ratio in tropospheric aerosols. The mass ratio of organic to sulfate in aerosols ranges from ~1 in urban regions up to 3–4 in the free troposphere (*36*). Global estimates of total sulfate aerosol are ~340 Tg/yr (190 anthropogenic, 150 biogenic, *45*). If we assume the ratio should be 1–4, the ratio of mass carbon/mass organic is 0.6, and the organic carbon is two-thirds SOA, we estimate the organic aerosol source must be 140–540 Tg C/yr.

Another independent estimate of the global SOA source can be derived from its atmospheric burden and lifetime. Unfortunately, the distribution of SOAs in the atmosphere is quite variable and, so far, poorly constrained. However, if we assume the mean global SOA vertical distribution includes 3 µg C/m^3 up to 2 km, 2 µg C/m^3 to 6 km, and 1 µg C/m^3 to 12 km, we estimate a global atmospheric burden of 6.7 Tg C. If we assume SOA lifetimes of 4–11 days (as suggested by current global models, *10*), a steady-state source of 223–615 Tg C/yr would be required to maintain this burden.

Our approaches for inferring SOA production result in four independent estimates: 510–910 Tg C/yr based on the global mass balance of VOC removal, 225–575 Tg C/yr based on SOA deposition plus oxidation, 140–540 Tg C/yr based on comparison with the sulfate budget, and 223–615 Tg C/yr required to maintain the assumed global mean vertical SOA distribution. The current estimates in the published literature based on bottom-up examination of SOA production rates for individual compounds range from 12 to 70 Tg aerosol/yr (*10*). The bottom-up estimates of SOA production are based on the same emissions of VOCs used in our mass-balance global-VOC budget presented here. The bottom-up approach relies on the initial SOA yields from smog-chamber studies to estimate global SOA yields. These yields may substantially underestimate total SOA production during the full course of the VOC oxidation process because smog-chamber studies are of a shorter duration than the time required to follow all products to their final state. Our alternative estimates of SOA production, if utilized, would have significant impact within models of global climate.

Opportunities for progress

The knowledge that additional organic compounds, which are not routinely measured, exist in the earth's atmosphere provides multiple opportunities for progress in atmospheric chemistry. These include the development of conceptual approaches that use the budget of organic material in the atmosphere as a diagnostic tool to test current understanding, to predict compounds that should be in the atmosphere and to systematically search for them, and to consider the role of multifunctional gas-phase and aerosol organics in human health. In addition, opportunities exist for development of measurement techniques to scan the atmosphere for specific classes of currently unmeasured compounds, to observe sums of compounds by functional classes for direct comparison with measurements of known individual species, to more broadly use comprehensive separation technology, and to further quantify the deposition of organic material from the atmosphere. Models could be developed to constrain the fate of products from atmospheric VOC reactions, assess the importance of additional organic compounds for atmospheric photochemistry and aerosol formation, and include the full range of VOCs and their aerosol products in global-climate simulations.

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