Organic Trace Gases in the Atmosphere: An Overview

Jonathan Williams[A]

[A] Air Chemistry Department, Max Planck Institute for Chemistry, Mainz 55128, Germany.
Email: williams@mpch-mainz.mpg.de

> ***Environmental Context.***   *The major carbon-containing atmospheric gases (carbon dioxide, carbon monoxide, and methane) are found in the atmosphere at the parts-per-million levels, where they affect physical phenomena such as the greenhouse effect. There are however many more carbon-containing gases at much lower levels with many and varied roles; in the main these gases are more chemically active and affect principally chemical phenomena such as the ozone budget.*

Abstract.   An overview of atmospheric organic trace gases is presented. This work is suited to those new to the field and to those seeking to place related activities in a broader context.

Introduction

The aim of this overview is to highlight the importance of trace organic gases in the atmosphere. Tens of thousands of organic compounds have been detected in the air we breathe, and the focus here is on carbon-containing gases (hereafter termed organic gases) present at mixing ratios below a few tens of parts per billion (10^{-9} or nmol mol^{-1}). This excludes the three most abundant organic gases—carbon dioxide, carbon monoxide, and methane—which have been discussed in great depth elsewhere. Despite being found at extremely low concentrations, organic trace gases can have profound effects in the atmosphere; their sources, sinks, and residence times are the subject of much current research. This article is divided into short summary sections entitled *Emissions*, *Detection and Measurement*, *Removal from the Atmosphere*, *Spatial Distribution*, *Atmospheric Chemistry Relevance*, *Climate and Radiative Effects*, *Organic Gases and Aerosols*, *Current Open Questions*, and *Future Prospects*. The intention here is to provide an up-to-date, referenced overview of the field emphasizing the recent progress made in an exciting and rapidly developing area of research. Recent and review-type references have been preferentially cited along with key older articles so that the interested reader may quickly access more detailed information.

Emissions

Almost everything we do in daily life results in the release of organic species to the atmosphere. Driving a car,[1] painting the house,[2] cooking,[3] making a fire,[4] cutting the grass,[5,6] and even breathing[7]—all of these processes result in the emission of organic compounds such as carbonyls,

alcohols, alkanes, alkenes, esters, aromatics, ethers, and amides. In addition to emissions from human activities, the Earth's vegetation naturally releases huge amounts of organic gases into the air. As plants assimilate carbon dioxide into biomass through photosynthesis, a fraction of the carbon leaks out to the atmosphere, predominantly in highly reduced forms such as isoprene and terpenes.[8–10] Exactly which compounds are emitted from a particular plant, and how much of each, depends on the age and health of the vegetation, as well as ambient temperature, moisture, and light levels.[11,12] Both plants and invertebrates have been shown to use emission of specific organic species into the air for signalling.[13,14] Examples of elaborate chemical mimicry have been found in insects[15] and amongst plants to deter attack by herbivores.[16,17] While the natural world uses the air as a communication medium, man often uses it as a repository for waste products, and deleterious effects have already been noted.[18]

The anthropogenic contribution to organic emissions in the atmosphere is dominated by the exploitation of fossil fuels (oil and gas). Petrochemical products typically contain a limited number of compound classes (e.g. acyclic alkanes, cyclic alkanes, monoaromatics, diaromatics) each consisting of a very large number (tens of thousands) of individual homologues and isomers.[19] A smaller emission contribution comes from the solvents industry and global inventories of these anthropogenic emissions have been compiled.[20] A further strong source of global emissions is from burning of biomass. These emissions are the most difficult to assess, as they are highly dependent on fuel type, humidity, and burn rate amongst other factors.[21] Spatial and temporal variability further complicates global budget assessments, and

satellite measurements are now being used to monitor the size and location of burning regions (e.g. ref. [22]). Most burning occurs during human-initiated land clearance but a large component also comes from the domestic use of biomass fuels.[23]

On a global scale, the total amount of reactive biogenic emissions is not well established, although recent estimates indicate circa 1300 Tg(C) yr^{-1} are emitted.[9] The strongest biogenic emission is thought to be isoprene (C_5H_8), and biogenic sources in total are considered to be approximately ten times larger than the sum of anthropogenic emissions including fossil fuel emissions and biomass burning.[9,20] Relatively small amounts of organics (in the form of alkanes and alkenes) are thought to be emitted from the ocean (e.g. ref. [24]), although several important species have a predominately marine source (dimethyl sulphide, DMS,[25] and methyl iodide[26]). Seen globally, geographical location and season determine the relative importance of anthropogenic and biogenic emissions: biogenics are emitted mostly in the tropics, whereas most anthropogenic emissions occur in the northern hemisphere between 40° and 50°N. All these diverse organic emissions are broken down in the atmosphere into a wider array of partially oxidized species,[27–29] and many thousands of gases have been detected in the atmosphere, from the tropics to Antarctica.[30,31]

Detection and Measurement

The human nose is particularly sensitive to several chemical groups.[32,33] Familiar examples include: forests, which emit terpenes;[34,35] oil refineries, which emit aromatic compounds and alkenes;[36] fish markets, which emit amines;[37] and freshly cut onions, which emit sulfur compounds.[38] While human subjects are widely used in odour-identification studies,[39,40] the nose's response is inherently subjective[41] and difficult to quantify. Therefore to investigate the atmosphere quantitatively, researchers have employed a variety of sensitive and specific sensors, including mass spectrometers, flame-ionization detectors, electron-capture detectors, optical absorption, chemiluminesence, and atomic emission detectors.[42–45] Both animal- and plant-type biological detectors have also been deployed for detection of certain molecules. In some studies the amputated sensory antennae of small insects have been connected into measurement devices[46] and elsewhere the leaves of plants have been analyzed for long-term exposure statistics.[47] Detectors must also be capable of measuring the huge range of concentrations in the atmosphere. High mixing ratios of several tens of ppbv (nmol mol^{-1}) can be found for alkanes and aromatics in polluted urban areas,[48] while halons can be reliably measured at only 0.045 pptv (pmol mol^{-1}).[49] The recently reported compound SF_5CF_3 was first detected at 0.005 pptv.[50] This means that if 200 tonnes of such material would be emitted anywhere in the world it would be detectable by this instrument. Global networks of detectors are in place to monitor changes in greenhouse gases.[51]

Much of our atmospheric knowledge to date has been driven by what can be reliably measured and how rapidly.[52] Although the first atmospheric research on organic trace gases (specifically peroxy acetyl nitrate) was made using infrared spectroscopy in the late 1950s,[53,54] in the following 30 to 40 years research on atmospheric organic gases has been dominated by gas chromatography coupled to some form of detector. Samples are either introduced directly into the instrument in the field or collected in pressurized canisters, absorbent-packed cartridges, or filters for later analysis in the laboratory. The alkanes (major components of fossil fuels) were one of the first and most widely investigated subset of the reactive organic species to be researched.[55] This is because these fully saturated compounds do not interact strongly with most inlet materials or collection vessel surfaces, and the long-established technique of gas chromatographic separation with flame ionization detection has allowed widely available quantitative analysis.[42] Many oxidized gases are more difficult to quantify as they may stick to surfaces, thermally decompose, or may even be produced in measurement systems.[56–61] These techniques are sensitive and specific but, due to the pre-detector sample separation, limited in sampling frequency.

Recently several important new advances have been made in the analytical techniques. These have permitted more organic species to be investigated more sensitively (e.g. multi-dimensional gas chromatography[62]) or at higher frequency with chemical ionization mass spectrometry (CIMS) through use of proton transfer reactions,[63–65] or by other chemical ionization techniques.[66,67] Further measurement systems have developed high precision to enable $\delta^{13}C$ isotopic ratios to be determined in organics at mixing ratios below ppbv levels,[68] while various high-frequency methods have been developed to measure emission fluxes directly.[69,70] With the arrival of this new generation of measurement systems, more species and timescales are accessible and a new golden age of discovery for field measurement has begun. Researchers are now exploiting these latest techniques on aeroplanes, ships, balloons, and ground sites to establish the global budgets of a wide range of organic species.

Removal from the Atmosphere

If a gas-phase organic species in the air does not photolyze, is not physically removed by dry deposition to surfaces such

Jonathan Williams is an atmospheric chemist. He received his B.Sc. in Chemistry and French and his Ph.D. in Environmental Science from the University of East Anglia, England. Between 1995 and 1997 he worked at the NOAA Aeronomy laboratory in Boulder, USA. He has participated in many international field campaigns, on aircraft and ships, and at ground stations. His present research involves investigating the chemistry of reactive organic species in the atmosphere, and he leads a group with this aim at the Max Planck Institute for Chemistry in Mainz, Germany. In his spare time he enjoys sailing, swimming, and the occasional beer.

as vegetation[71,72] or aerosols,[73] or removed by wet deposition in rain,[74,75] then it will be chemically oxidized in the gas phase by the hydroxyl radical HO (or to a lesser extent O_3, NO_3, and halogen radicals).[27,76,77] The gas-phase oxidation of organic compounds in air is mostly initiated by HO, with carbon dioxide and water being the final products. In this way atmospheric oxidation is analogous to combustion. Using an everyday example as an analogy, when a cigarette lighter is lit, the hydrocarbon butane burns directly in the flame to form H_2O and CO_2. When the flame is not ignited, then the escaping butane gas is oxidized in the air to the same products, only much more slowly and via many other intermediates. The intermediate oxidation products may have lower vapour pressures, higher polarities, or absorb light better than the precursors, making the intermediate products potentially more susceptible to physical removal or photolysis. An alkane must be larger than C_{20} to be effectively adsorbed onto solid particles,[78] but much smaller multifunctional organic compounds, such as oxalic acid, more readily adsorb and are commonly found on aerosols.[79] Further oxidative transformation of these species on the aerosol is also possible.[80,81]

The overall rate of removal of an organic species from the atmosphere can be derived by summing the reaction rates with radical species, rates of photolysis, and the wet and dry deposition rates. From this we may determine the atmospheric lifetime of a species (see *Spatial Distribution*). In contrast to Earth, on Saturn's moon Titan there is apparently no effective removal atmospheric mechanism for hydrocarbons and as a result they can accumulate in large oceans.[82] The rate of reaction of HO with many individual organic compounds under terrestrial conditions is well established from laboratory experiments as a function of temperature and pressure.[83,84] Likewise, global photolysis rates can be calculated for many compounds from laboratory absorption cross-section and quantum yield measurements.[83] These rates can be profoundly influenced by clouds, and this in turn can affect trace gas concentrations.[85] The wet and dry deposition rates for organic compounds are highly variable and are generally empirically determined in the field.

Generally, organic compounds measured at high and invariable concentrations in the atmosphere are less efficiently removed.[86] Relationships between the variability of organic gas measurements and their rate of removal by HO have been derived[87,88] and exploited to derive HO trends. If a long-lived and hence well-distributed organic compound is known to react predominantly with HO, and its emission and HO reaction rate are known, then the global HO concentration can theoretically be estimated. Initial attempts based on methyl chloroform indicated large changes in HO concentrations over the past two decades[89] although more recent evidence suggests that uncertainty in the temporal and spatial emission pattern of methyl chloroform complicates such trend analysis.[90]

Direct biological uptake can also be an effective atmospheric removal process for some organic species.[91,92] The rate of uptake is dependent on the ambient concentration, being strongest when ambient concentrations are high. Compensation points are typically deduced for plants, which mark the crossover point between emission and uptake. A surprising recent discovery is that PAN (peroxy acetyl nitrate), an anthropogenic secondary oxidant like ozone, can also be taken up by plants.[93] This is an important development for the atmospheric nitrogen cycle as well as the organic species PAN.

Spatial Distribution

Following emission, volatile organic species are distributed according to the wind vector and the atmospheric chemical removal rate (lifetime) of the compound. The boundary layer inversion (0.5–2 km), the tropopause (10–15 km), and the inter-tropical conversion zone (ITCZ, 10°S to 10°N) all impede mixing of the air, and as a result strong gradients in organic species can develop across these atmospheric divides. Typical exchange times are one to two days for air to mix vertically out of the boundary layer, a month for air to be advected zonally around the northern or southern hemisphere, and about one to two years for interhemispheric exchange. Chemical lifetimes, defined as the time for a chemical concentration to decay to 1/e of its initial value, vary from minutes to hours (terpenes and isoprene), through days to weeks (acetone, methanol, propane), years to decades (methyl chloroform, HCFC134a), and up to hundreds of years for chlorofluorocarbons (CFC11, CFC12). Short-lived compounds, such as the biogenic species isoprene ($CH_2C(CH_3)CHCH_2$), show strong atmospheric gradients over the boundary layer, whereas longer-lived compounds such as CFC113 (lifetime of about 12 years) are better mixed and only show strong gradients between the hemispheres.[94] Some compounds are more or less uniformly distributed in the troposphere (CFC12, lifetime 79 years, no remaining sources) only showing concentration gradients in the stratosphere.

There are numerous literature examples of regional scale advection where organic pollutants found in remote locations have been linked to distant pollution sources by use of back-trajectories.[95,96] Intercontinental pollution events have been reported,[97] and trajectories have even been used to track southern hemispheric biomass burning through the ITCZ to the upper troposphere of the northern hemisphere.[98] Secondary photooxidants such as ozone and PAN, which form en route, have also similarly been identified in plumes emerging from urban centres.[99] Interestingly, there is growing evidence to suggest that migrating birds use chemical gradients as an aid to navigation.[100,101]

Where the atmosphere is in contact with the Earth organic species can interact with the various surfaces (e.g. snow, soil, water).[102] Within these media further production or removal mechanisms may exist such as bacterial uptake, enhanced photolysis,[103,104] or biological production. Such processes will affect the lifetime of these species and hence their global distribution. Some larger organics with considerably lower vapour pressures tend to partition predominantly to aerosols following release. When such a species is unreactive, as with persistent organic pollutants (POPs) which

are emitted through incomplete combustion or pesticide use, the lifetime of the transporting aerosol will then determine the distribution of this species. Examples of such compounds include polyaromatic hydrocarbons (PAHs),[105] polychlororinated biphenyls (PCBs), and polychlorinated dibenzo-*p*-dioxins (PCDDs). Whether in gas form or as particles, these compounds can be transported long distances from source regions.[106] The distribution of the long-lived semi-volatiles is markedly different to that of the volatiles, and with time through repeated volatilization and adsorption such compounds tend to concentrate in polar regions[107] in a manner that could be likened to a global distillation (from the tropics to the poles). Some of these compounds are toxic[108] and can bioaccumulate through the food web,[109] posing a risk to human health and the environment.[110]

While the boundary layer (<2 km) tends to be turbulent, the troposphere above is less well mixed and chemical lifetimes are longer. In addition to the slow process of diffusion, organic gases may be distributed in the atmosphere by meteorological events such as convection[111] and via lifting by frontal systems.[112] The overall distribution of the organic species varies with latitude and season as a function of the source and sink strengths, as well as prevailing meteorology.[94,113] Certain photochemical products, such as PAN, have a hemispheric concentration maximum in the spring. This has been explained as the optimum between the winter, when precursors are accumulated, and the maximum photochemistry in summer.[114]

In the early years of atmospheric research it was assumed that after several days to weeks the atmosphere would have effectively removed an organic pollutant, based on the atmospheric lifetime of alkanes. Recently however, from measurements made between 1 and 13 km over the remote Pacific Ocean, far from source regions, it was shown that volume mixing ratios of oxygenated organic species are some five times higher than those of the non-methane hydrocarbons, alkanes, and alkenes.[115,116] Similar high mixing ratios of oxygenates and compound diversity have been reported in other airborne studies,[117] in urban centres,[118] and in continental outflow from Asia[119,120] and Europe.[121] These results concur with earlier theoretical work on the oxidation of organic compounds.[122,123] Our views about the distribution, sources, and role of reactive organic species in the atmosphere are currently being rapidly revised.

Atmospheric Chemistry Relevance

In the 1950s Haagen Smit and coworkers showed that the oxidation of organic species in the presence of NO_x and sunlight can form ozone. Ozone, which is toxic to humans and plants, has become a major air quality problem in cities and larger areas such as the Mediterranean[124] and the south-eastern United States.[125] Ozone-control strategies adopted in the 1970s were initially unsuccessful due to an underestimation of natural organic emissions in the initial models.[126] However more recent emission controls applied to cars (including NO_x and hydrocarbon reductions) have reduced regionally produced ozone.[127]

The capacity of the troposphere to oxidize emissions is also dependent on the amount of organic species present. Reaction with the main atmospheric oxidant, HO, is the primary loss mechanism of organics from the atmosphere (see *Removal from the Atmosphere*). While the initial reaction is a sink, subsequent oxidation steps may be a source of HO_x ($HO + HO_2$), making the global effect of hydrocarbons complicated. In cities, where NO_x concentrations are high, increasing concentrations of organics increases the ambient HO. However, in most of the free troposphere HO production is not limited by organics but rather by NO_x, and increasing organic concentrations generally decreases ambient HO under these conditions.[128] In the upper troposphere, where water concentrations are low (<100 ppmv), organic species may provide the main source of HO_x radicals. For example, acetone is a source of HO_x when photolyzed in the dry upper troposphere[129] and can lead to strong ozone formation. Similar effects are produced by organic peroxides and aldehydes.[130] At night the organics may also provide an important source of HO[131] through the reactions of alkenes with ozone. In oceanic and arctic regions organohalogens can provide ozone-depleting halogen radicals such as Br,[132,133] which can link with inorganic halogen cycles.[134]

The global impact of organics on ozone and the hydroxyl radical have been investigated in models.[128,135] Sensitivity studies in global models indicate that removing hydrocarbon emissions gives modest decreases in global ozone ($<15\%$) and relatively small increases in global mean HO ($<20\%$). These studies highlight the role of organic nitrates such as PAN in the distribution of NO_x and hence HO_x. These nitrates form where hydrocarbons are oxidized in the presence of NO_x.[136] The most abundant nitrate, PAN, is a lachrymator and largely responsible for the sore eyes experienced in smog. Having a longer lifetime than NO_x, organic nitrates may be transported much further from the pollution sources before decomposing to release NO_x again. In this way these compounds function as a long-distance transport mechanism for NO_x and in so doing they influence the global oxidation budget.[137] The effect of organic species on the global distribution of ozone and HO is a key area of atmospheric research.

In the troposphere, photooxidation of organic gases in the presence of high NO_x ($NO + NO_2$) concentrations acts to produce ozone; however, other trace organic gases can act to destroy ozone in the stratosphere. Prior to human proliferation on the planet, long-lived naturally produced organohalogens such as methyl chloride represented the main mechanism for chlorine transport to the stratosphere and hence ozone destruction.[138] More recently, artificial chlorinated, brominated, and fluorinated hydrocarbons have been shown to deliver significant additional quantities of chlorine and bromine to the stratosphere[139] and be the cause of the 'ozone holes' observed over the polar regions.[140] As a result of legislation, the overall tropospheric abundance of halogen from halocarbons is now decreasing.[141] However, emissions of certain species (e.g. halons) persist because of a lack of suitable substitutes for critical uses such as fire extinguishants.[142]

Climate and Radiative Effects

In addition to the major greenhouse gases CO_2 and CH_4, certain organic species have been implicated in long term or climate effects. Perhaps the best-known example is DMS, a compound that is naturally emitted from the oceans and which has been proposed as a potential negative feedback to climate warming.[143] The hypothesis is that a long term warming of the oceans would produce more DMS emission, which following oxidation to SO_2 and then SO_4^{2-} would lead to more clouds (see *Organic Gases and Aerosols*) and hence more reflection of incoming sunlight. In polluted regions, where organic species can provide large numbers of condensation nuclei for clouds, then a further radiative consequence of organics emerges. The larger number of nuclei means that the water available in the cloud is more widely distributed, causing the average droplet size to be smaller and the cloud as a result to be more reflective.[144,145] More recently certain oceanic alkyl halides have been linked to cloud formation and hence to possible climatic effects.[146] While all organic species are infra-red active to some extent, their influence on the Earth's radiative forcing depends on their absorption spectrum and atmospheric abundance.[147] The CFCs and HCFCs are important in this regard. Therefore organic gases, or the particulate products thereof, can cause a direct effect on climate forcing by reflecting or absorbing incoming light, or an indirect effect through modification of cloud albedo and lifetime. By influencing global ozone (see *Atmospheric Chemistry Relevance* section) organic species may through chemistry also affect the radiation indirectly.[148,149] Due to the wide range of physical and chemical properties of organic species, it is extremely difficult to assess their overall climate feedback effects, especially when the emissions are likely to be also changing as a function of time.[150]

When considering the climate effects we may also consider possible roles of organic species on our past climate. Atmospheric organic species have also been implicated in the beginning of life, which has influenced our climate profoundly. Small micelles and reverse micelles resulting from high molecular weight organics and water coating on aerosol have been proposed as photo-reactors within which complex proteins may build up.[151,152] On a larger scale, primordial ocean oil slicks of organic species have also been proposed as a means of climate change and important in the formation of the first proteins.[153] It has also been speculated that other organic species (nitriles) provided a source of nitrogen to photosynthesizing marine organisms in the ancient oxygen-free atmosphere of the Earth.[154]

Trace organic species also have enormous potential for revealing the atmospheric chemical history of the Earth. The analysis of CH_4 in air trapped within ice cores has provided atmospheric information of the past 120000 years. However, individual trace organic species can be more specifically attributed to sources than long-lived species such as CH_4 and thus provide more detailed information about the past. Early work on small cores dating back only about 40 years have demonstrated this potential.[155]

Organic Gases and Aerosols

That gas-phase organic species and atmospheric aerosols are strongly linked has been established for some time,[156] and organic atmospheric aerosols have been reviewed in detail.[157,158] The blue hazes and reduced visibility over forests are the result of the enhanced scattering of blue light by particles similar in size to the wavelength of light.[159] These particles can be produced from gaseous organic precursors, which condense from the gas phase to form aerosols.[160] In this respect, oxygenated species with low vapour pressures are favoured; examples include the photochemical products of biogenic emissions such as isoprene (2-methyltetrols), terpenes (pinic and norpinic acid), and sesquiterpenes.[146,161,162] Such nuclei may grow in size by coagulation with other particles and later through the condensation of other organic species onto the surfaces.[163–165] Recent evidence has shown that organic species absorbed into particles may undergo acid-catalyzed reactions: oxidation, hydration, hemiacetal and acetal formation, polymerization, and aldol condensation[161,166–169] and chemical oxidation of organics such as isoprene can occur in the aerosol liquid phase through acid-catalyzed reactions with hydrogen peroxide.[81] As the particle grows, the hydrophilic and light scattering properties of the particle can be affected by condensing organic gases or oxidation processes. In pristine conditions over the Amazon it has been shown that hydrophilic organic species are a large fraction of wet-season aerosol mass and they are predicted to significantly contribute to particle growth into cloud condensation nuclei.[170,171] An organic layer has also been recently reported on marine aerosols.[172] In more polluted conditions it has been shown that uptake of organic gases onto soot particles can change particle reflectivity,[173] to make light-absorbing soot particles more reflective. The opposite can also be speculated, that organic species can make reflective ammonium sulfate particles darker and more light absorbing. The organics therefore play a critical role in determining the aerosol albedo.

As precursors of cloud condensation nuclei, organic gases can be important in the formation of clouds. Pure water requires extremely high relative humidities (400% or more) in order to produce clusters that provide nuclei for further condensation.[174] However in the presence of aerosols, condensation can occur at conditions more readily found in the atmosphere. Sulfate is a very effective cloud condensation nucleus and hence much research has been focussed on DMS and its oxidation products[175] (see *Climate and Radiative Effects*). A wide range of anthropogenic and biogenic compounds have been tested for their effect on ice-nucleating properties.[176] Amino acids have been shown to be particularly effective in this regard,[177] while long-chain alcohols in monolayers can also promote ice formation.[178] Some organic acids appear to delay activation.[179] There is some evidence that organic gases can influence the shape of ice crystals,[180] a parameter that is predicted to have a large effect on snowfall rate.[181]

In cities, organic aerosols and soot are also emitted directly, particularly from diesel exhausts. Persistent

organic pollutants such as PAHs (carcinogenic) and PCBs (toxic, derived from burning plastics) are often associated with urban particles. Particles smaller than $10\,\mu m$ (PM10) can be effectively inhaled by humans, and correlations have been shown with mortality rates.[182] In the clean marine environment it has been shown recently that aerosols can be efficiently formed from iodine-containing organics, such as diiodomethane.[183] Furthermore, following formation marine aerosol appears to be coated with organic fatty acids. This coating of organic surfactants could have important effects on the physical and chemical properties of the aerosol.[184] The impact of ship emissions of organics on the atmospheric aerosol is also currently under investigation.[185,186]

Current Open Questions

The previous sections have outlined how huge emissions of organic gases enter the atmosphere and how oxidation, predominatly initiated by HO, breaks down these gases to carbon dioxide and water. Determining how much reactive carbon is in ambient air and comparing it to the individually measured compounds is an important on-going task. A similar budgeting process has been successfully performed for atmospheric nitrogen species.[187] For the carbon compounds this task is made difficult by the presence of CO, CH_4, and CO_2, whose concentrations dwarf those of the more reactive species. Some initial attempts have been made to measure the total carbon, termed Cy, by chromatographic separation and then conversion of all reactive species to CH_4.[188,189] Comparisons to individually measured hydrocarbons are reasonable, but the techniques adopted involve significant sample handling, where losses of some organic species could occur.[190] Laboratory experiments and some as yet unpublished field studies have shown the potential of HO measurements to determine total reactivity,[191,192] but the size and complexity of the instrumentation used has until now precluded widespread use. From recent measurements made over a forest, it has been shown that a considerable fraction of the measured reactivity could not be accounted for by speciation measurements and that the missing reactivity had a terpene-like emission profile.[193] Clearly much more work must be performed to determine what fraction of the ambient organic trace gases are being measured by current techniques. If the total reactivity can be reliably determined, it can simplify photochemical modelling of organic species and aid the development of ozone control strategies.

A further open issue is chemical oxidation in the polluted atmosphere. How well we understand the oxidation process can be generally assessed from the agreement between values from a theoretical model and direct measurement. Formaldehyde concentration is considered a good parameter to compare since almost all organic species produce formaldehyde at some stage during gas-phase oxidation. While measured and modelled comparisons of formaldehyde show good agreement in clean environments, comparisons in polluted air have consistently shown an underestimate in model values,[194] the difference being up to a factor of three to four in the upper troposphere.[195] Assuming this not to be a result of transport or source strength errors in the model, this suggests that the organic chemistry in such circumstances is more complex than currently thought. The ozone-forming potential of the organic species (see *Atmospheric Chemistry Relevance*) is therefore not well understood. Needed are comprehensive field measurement datasets of organic compounds including precursor and oxygenated products. These must be compared with explicit chemistry models[28,196] to determine for which species real air oxidation chemistry differs from the theoretical oxidation pathways. A complicating factor in this research will be the determination of the gas-to-particle partitioning of the organic species and representation of multiphase chemistry in models. The next generation of atmospheric chemical transport models will require realistic but tractable mechanisms for organic oxidation and particulate formation and growth in order to calculate the radiative forcing of climate.[197,198]

The role of the ocean in the budgets of organic species also requires urgent investigation. Many organic species are reported to be emitted from the ocean (including sulfur-containing gases,[199] organohalogens,[200] and alkyl nitrates[201]) while many other species are taken up (e.g. acetone[202] and methanol[203]). In reality the ocean surface may be a highly variable source or sink for many compounds depending on the latitude, temperature, wind speed, and biological composition of the surface water. Ocean emissions may also be dependent on aeolian input of trace elements such as iron and phosphorous. It has been speculated that for some compounds the ocean surface layer represents a giant reservoir of organic species exceeding the amount in the troposphere (e.g. for methanol[203–205]). The ocean is able to assimilate CO_2 at rates per unit biomass five times greater than the largest terrestrial ecosystems, the rainforests, but oceanic organic trace gas production is not well understood. Considering its size and potential importance the ocean is surprisingly poorly characterized in terms of organic gases, although new measurement programs have recently been initiated.[206] Of particular importance to atmospheric chemistry is the characterization of tropical waters, as emission or uptake in these regions can affect air that is subsequently convected to the upper atmosphere in the ITCZ (see *Spatial Distribution*).

As new instrumentation is deployed in new locations, new compounds are discovered to be present in the air. Important sources and sinks of organic species are continuously being uncovered (e.g. methyl chloride from plants[207]). Compilation of global emission inventories is then by definition an open issue. Production of an emissions inventory is a long and laborious process, and the 'current' version is therefore out of date as soon as it is published, leading to large discrepancies between model and measurement even for anthropogenically emitted species.[208]

Future Prospects

From the last Section it is clear that an understanding of the sources, sinks, and chemistry of organic species in the

atmosphere is important in predicting future global change. If the Earth warms, as it is predicted to do, then we may expect the distribution of organics to be affected through concomitant increases in temperature and changes in convection and vegetation patterns. How biogenic emissions change as a function of the forecasted increases in CO_2 will be particularly important, and early indications are that biogenic emissions increase in elevated CO_2 conditions (e.g. monoterpenes[209] or methane[210]). However ozone is also expected to increase, which may also have an effect on these emissions.[211] Predictions based on the IPCC-recommended emission scenarios for organic and other species show increases in tropospheric ozone[212] and changing radiation budgets[149] which will lead to global air circulation change. These effects may in turn lead to changes in the hydrological and biogeochemical cycles.

To offset warming effects of CO_2, a number of proactive methods have been suggested to reduce directly the atmospheric CO_2 burden, that are relevant to organic species. Methods such as intensive tree planting and fertilizing the ocean with iron should be carefully vetted for side effects associated with organic emissions before implementation. For example, plantations of fast-growing trees such as black larch as carbon sinks can lead to extreme local terpene emissions with important consequences for regional pollution. In a sense this can convert a global problem into a regional one. A similar unexpected outcome can occur in the Amazon, where oil palms are often planted following tree clearance. Since the oil palm is a strong emitter of biogenic reactive compounds, it is conceivable that human interference can increase rather than decrease emission rates from a region. Similar effects have been noted in the United States, for example through proliferation of sweetgum in pine plantations, and it has been suggested that volatile organic carbon emissions are increasing at 6% per decade in the United States.[213] Experiments aimed at fertilizing the ocean with iron, in order to stimulate biological growth and hence CO_2 uptake, should be also carefully assessed for enhanced organic halogen or sulfur-containing emissions which can affect ozone chemistry and aerosol formation.[214]

In the future, the global population is expected to grow. Megacities will house greater proportions of an increasing population.[215] Therefore it will be increasingly important to control the local air quality in order to maintain human health.[216,217] This will have to be achieved in the face of a long-term global upward trend in background ozone.[218,219] Considerable effort is being made to reduce the organic emissions of automobile engines through use of alternative fuels such as CNG (compressed natural gas) and LPG (liquid petroleum gas) as well as new engine technologies.[220] Use of hydrogen fuel cell technology has been predicted to reduce CO and NO_x emissions by up to 50% but its impact on climate forcing is dependent of the technology used.[221] The use of filters in combination with diesel fuel has been predicted to significantly improve air quality in the short term.[158] Indoor pollution in cities is also likely to grow in importance. Increased use of terpene-based propellants and increasing background ozone combined with the construction of more airtight energy-efficient buildings all lead to greater exposure to organic chemicals.[222,223]

Concerns are already being raised by some nations that other nations situated upwind are responsible for their deteriorating air quality. This echoes the smaller scale situation in the 1980s when cities on the USA's east coast complained that they could not comply with national air quality standards due to pollution built up in the west. Similarly in the 1970s acid rain in Scandinavia was attributed to sulfur emissions in the United Kingdom. The issue of international pollution export (UNECE)[224] will almost certainly gain importance in coming years. Legal action is conceivable, where one country demands recompense from another for perceived health effects or tourism decline. Cost estimates for damage attributable to organic compounds have been made already: $1100 per Mg-VOC.[225] The monitoring of exported emissions from other countries may also be used as an indirect way of spying on the upwind country. In theory, in the future it could be possible to determine whether published economic figures are realistic by comparing trends with emissions or to determine whether certain processes are in operation. Emission trading has already been introduced for CO_2, despite the fact that the Kyoto Protocol has only just been ratified. Emission trading in other species is under discussion.[226] In theory limits could be imposed to trace organic species but this would require a much better understanding of emissions, and would logically entail policing, which considering the short lifetimes and small concentrations of many compounds seems unlikely. In the near future investigation of such compounds will remain a task for the atmospheric research community.

Data from a variety of new satellite platforms[227] is unlikely to contribute many new organic measurements in the near future because most of the organic species do not have unique optical properties and are at low concentrations. One exception is formaldehyde (CH_2O) and satellite measurements of this compound have been used elegantly to constrain the precursor isoprene emissions.[228] Some species, including CFC11, CFC12, CFC22, CCl_4, and ethane, have been measured from a balloon using a Michelson interferometer to 3-km resolution, giving hope for the next generation of satellite measurements. Further candidates for future measurement by satellite are PAN and acetylene. It may also be possible to use typical emission ratios in conjunction with CO measurements to improve estimates in inaccessible regions. Satellite data drive weather forecasts, which are increasingly likely to include ozone predictions in the future as air quality is increasingly recognized as a meteorological hazard.[216] However organic trace gas forecasts[229] are currently only of academic interest and available to the public only through a small number of internet sites.[230]

Over the past hundred years global anthropogenic emissions of organic species have increased by an estimated factor of seven[231] and in the future they can be expected to change still more as land use, vegetation patterns and industrial development alter rapidly.[232–234] Since the 1980s the growth in surface emissions in North America and Europe has lessened, although in other areas such as the Tropics strongly

increasing trends are expected in line with economical development. Emissions from air traffic, which affects cirrus clouds and thereby climate, are also predicted to increase in the future.[235,236] Control of anthropogenic organic emissions is politically difficult to realize both on regional[237] and on global scales (e.g. Montreal Protocol[238]).

To date most of our research on organics in the atmosphere has been passive. We have attempted to quantify emissions into the atmosphere and make deductions from there. On the other hand, deliberate emission of certain species has been proposed and practiced. One proposal was the deliberate emission of hitherto unused compounds, of known lifetime, in specific amounts into the Earth's atmosphere. Through regular measurements over a suitable time period it would then be theoretically possible to determine accurately the global HO strength.[239] Toxic compounds are also actively emitted into the environment as pesticides.[240] Less than 0.1% of these applied pesticides reach their target, raising important ethical questions.[241] It has been suggested that by actively injecting organics (ethane and propane) into the polar stratosphere, ozone depletions may be reduced.[242] Follow-up research suggested however, that this could have exactly the opposite effect,[243] which represents a stark warning against hasty experimentation. We may also be tempted to take active measures if, in the distant future, the planet begins to cool. Humankind may well consider dosing the atmosphere with some of radiatively active organic gases to offset ice ages or to adjust atmospheres of other planets. There is clearly an important role for organic species in the atmosphere long into the future.

Acknowledgements

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