Volatile Organic Compounds in the Atmosphere

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Preface

Every day, large quantities of volatile organic compounds (VOCs) are emitted into the atmosphere from both anthropogenic and natural sources. They are the 'fuel' that keeps atmospheric photochemistry running. Therefore, their sources, sinks and residence times are the subject of current research. In addition to influencing local, regional and even global photochemistry, several of these compounds have a potential impact on climate, both due to their properties as greenhouse gases and due to their ability to form aerosol particles on oxidation. The formation of gaseous and particulate secondary products caused by the oxidation of VOCs is one of the largest unknowns in the quantitative prediction of the earth's climate on a regional and global scale, and on the understanding of local air quality. To be able to model and control their impact, it is essential to understand the sources of VOC, their distribution in the atmosphere and the chemical transformations they undergo.

Furthermore, organic trace gases can be used as tracer compounds to investigate reactions that are not directly accessible to current measurement techniques or as probes to 'visualise' transport processes in the atmosphere or across atmospheric boundaries.

In recent years methods and techniques for the analysis of organic compounds in the atmosphere have been developed to increase both the spectrum of detectable compounds as well as the corresponding detection limits. New methods have been introduced to increase the time resolution of those measurements and to resolve more complex mixtures of organic compounds. New technical developments reducing weight and energy requirements made the use of these instruments on various platforms such as balloons or aircraft possible.

This book describes the current state of knowledge of the chemistry of VOC as well as the methods and techniques to analyse gaseous and particulate organic compounds in the atmosphere. Chapter 1 is an instructive chapter summarising the variety and the roles of VOC in the atmosphere. Chapters 2 to 9 cover the various compound classes, their distribution in the atmosphere, their chemical transformations and their budgets as well as a survey of currently used measurement techniques. Chapters 10 and 11 describe new methods to measure a large part of the VOC family at a glance and for investigating their stable carbon isotope ratios. In-depth references are provided, enabling each subject to be explored in more detail.

The aim is to provide an authoritative review to address the needs of both graduate students and active researchers in the field of atmospheric chemistry research. It may also serve as a desktop resource for experienced scientists in the field of atmospheric research.

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Chapter 1

Volatile Organic Compounds in the Atmosphere: An Overview

Jonathan Williams and Ralf Koppmann

1.1 Introduction

The aim of this overview is to highlight the importance of organic trace gases in the atmosphere and to introduce the themes of the chapters to follow. This work is suited to those new to the field and to those seeking to place related activities in a broader context.

Tens of thousands of organic compounds have been detected in the air we breathe, and the focus here is on the myriad carbon-containing gases present at mixing ratios of some 10 parts per billion (ppbv, 10^{-9} or nmol/mol) down to some parts per trillion (ppt, 10^{-12} or pmol/mol). This excludes the three most abundant, but generally less reactive, organic compounds: carbon dioxide (370 parts per million, ppmv, 10^{-6} or µmol/mol), methane (1.8 ppmv) and carbon monoxide (0.15 ppmv), which have been discussed in detail elsewhere. Unfortunately various terms have been used in the literature to describe the subset of diverse carbon-containing gases under circa 10 ppbv. One of the first was non-methane hydrocarbons (NMHC), which was employed originally to distinguish alkanes, such as ethane, propane and butane, from methane. However, strictly speaking the word 'hydrocarbon' indicates a molecule containing only carbon and hydrogen atoms, and therefore this term appears to exclude oxygenated species such as alcohols, carbonyls and acids as well as organic compounds containing other heteroatoms, such as nitrogen or sulphur. In an attempt to embrace all the species relevant to atmospheric chemistry, a further term 'volatile organic compound' (VOC) was coined, although there is no general quantitative definition of what VOCs are. The Environmental Protection Agency (EPA) in the United States has defined VOC as any compound that participates in atmospheric photochemical reactions; however, there have been subsequent attempts to give a more quantified definition. The result is that VOCs are considered to be those organic compounds having a vapour pressure greater than 10 Pa at 25°C, a boiling point of up to 260°C at atmospheric pressure, and 15 or less carbon atoms. The remaining compounds are designated as semi-volatile organic compounds (SVOCs). This segregation emphasises the volatile gas phase species from those that partition to the aerosol phase which is reasonable since the later undergo different transport and chemistry (see Sections 1.3 and 1.4). Recently, however, the definition has become blurred by the use of OVOCs to specifically identify the oxygenated VOCs. For this chapter we prefer not to draw a divide through the continuum of

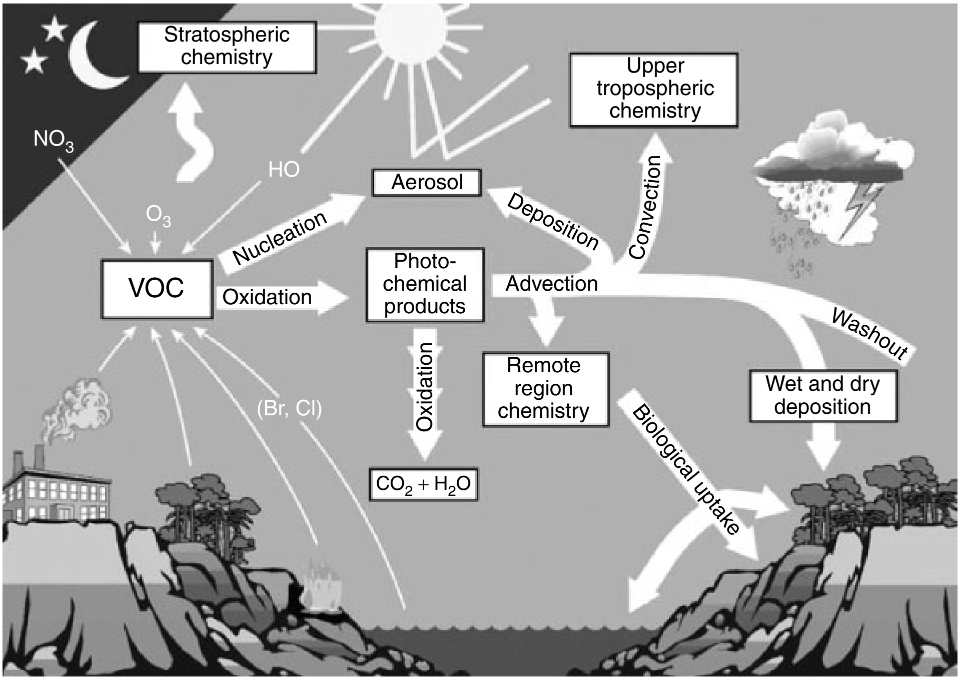

Figure 1.1 Sketch of the various processes which determine the fate of VOC in the atmosphere. The individual processes are discussed in the text and the individual classes of VOC in the following chapters of this book.

compounds and instead use the term 'trace organic compounds', referring to the dictionary definitions of organic (designating carbon compounds) and trace (an extremely small amount).

Despite being found at extremely low concentrations, trace organic compounds have profound effects in the atmosphere (see Figure 1.1). On the one hand, they are the 'fuel' which keeps oxidative atmospheric photochemistry running. Therefore, their sources, sinks and atmospheric residence times are the subject of much current research (see Sections 1.2–1.4). To investigate organic trace gases in the atmosphere it is essential that accurate concentration measurements and careful modelling studies are made (see Section 1.5). In addition to influencing local, regional and even global photochemistry, several such compounds have a potential impact on climate, both due to their properties as greenhouse gases and due to their ability to form aerosol particles on oxidation (see Section 1.6). Organic trace gases can be used as tracer compounds to investigate reactions which are not directly accessible to current measurement techniques or as probes to 'visualise' transport processes in the atmosphere or across atmospheric boundaries. Many open questions remain in this field of research, and some of the future challenges in the field are summarised in Section 1.7.

The intention here is to provide an up-to-date, referenced overview of the field emphasising 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. The authors would like to point out that the articles cited here represent a tiny fraction of a vast and widespread literature database. We hope that any omissions of particular works by colleagues will be forgiven in the interests of brevity.

1.2 Sources

Almost everything we do in daily life results in the release of organic species to the atmosphere. Driving a car (Fraser et al. 1998), painting the house (Fortmann et al. 1998), cooking (McDonald et al. 2003), making a fire (Andreae and Merlet 2001), cutting the grass (Fall et al. 1999; Kirstine et al. 1998) and even breathing (Barker et al. 2006; Phillips et al. 1999) – 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 this carbon leaks out in to the atmosphere, predominantly in highly reduced forms such as isoprene and terpenes (Fuentes et al. 2000; Guenther 2002; Kesselmeier et al. 2002). 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 the ambient temperature, moisture and light levels (Guenther et al. 1995; Kesselmeier and Staudt 1999). Both plants and invertebrates have been shown to use emission of specific organic species into the air for signalling (Greene and Gordon 2003; Krieger and Breer 1999). Examples of elaborate chemical mimicry have been found in have been found in insects (e.g. Cremer et al. 2002) and amongst plants to deter attack by herbivores (Kaori et al. 2002; Kessler and Baldwin 2001). While the natural world uses air as a communication medium, man often uses it as a repository for waste products. The emission rates and their associated uncertainties for VOCs from several source categories are summarised in Table 1.1.

The anthropogenic contribution to organic emissions in the atmosphere is dominated by the exploitation of fossil fuels (coal, oil and gas). Approximately 100 TgC/year was estimated to be emitted from 'technological' sources and 150 TgC/year from all anthropogenic sources including biomass burning (Müller 1992). Coal production mainly leads to methane emission, but minor emissions of ethane and propane are also present. Liquid fossil fuel production, storage and distribution result in a larger variety of organic gas emissions to the atmosphere. Crude oil production platforms are strong point sources of hydrocarbons such as methane, ethane, propane, butanes, pentanes, hexanes, heptanes, octanes and cycloparaffins (McInnes 1996). The major sources from processing liquid fossil fuels are catalytic cracking (0.25–0.63 kg/m^3 of feed), coking (about 0.4 kg/m^3 of feed) and asphalt blowing (about 27 kg of VOC/m^3 of asphalt) (Friedrich and Obermeier 1999). Furthermore, so-called fugitive emissions can occur from leaks and evaporation from all types of equipment and installations. Evaporative emissions are estimated to be 2.9 kg/t of fuel at service stations (McInnes 1996) and are familiar to anyone who has filled a car with gasoline/petrol. 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 (Schoenmakers et al. 2000). Major products of the complete combustion of fossil fuels are carbon dioxide and water. However, in practice, combustion leads to CO and organic gas by-products, mainly due to

Table 1.1 Overview of important sources and global annual emission rates of selected groups of VOC per year

	Emission rate	Uncertainty range
Fossil fuel use		
Alkanes	28	15–60
Alkenes	12	5–25
Aromatic compounds	20	10–30
Biomass burning		
Alkanes	15	7–30
Alkenes	20	10–30
Aromatic compounds	5	2–10
Terrestrial plants		
Isoprene	460	200–1 800
Sum of monoterpenes	140	50–400
Sum of other VOC	580	150–2 400
Oceans		
Alkanes	1	0–2
Alkenes	6	3–12
Sum of anthropogenic and oceanic emissions		
Alkanes	44	
Alkenes	38	
Aromatic compounds	25	
Terrestrial plants	1 180	
Total	1 287	

lack of oxygen, imperfect air/fuel mixing and inappropriate combustion temperatures. Tailpipe emissions from gasoline passenger cars with and without three-way catalyst are estimated, respectively, as 0.68 and 18.92 g of HC/kg of fuel, whereas passenger diesel cars (produced after 1996) emit about 1.32 g of HC/kg of fuel. Similarly, diesel heavy-duty vehicle emissions are estimated as 5.4 g of HC/kg of fuel. Exhaust gas emissions from motor vehicles strongly depend on parameters such as vehicle speed, motor load and engine temperature. The predominate emissions for gasoline and diesel combustion engines are paraffins (C_1—C_5 for gasoline cars and methane for diesel engines), C_2—C_5 olefins, ethyne, aromatic hydrocarbons (BTEX and C_9 aromatics), aldehydes (formaldehyde, acetaldehyde, acrolein, benzaldehyde, tolualdehyde), ketones (acetone) and others (mainly high molecular weight paraffins). A smaller emission contribution of anthropogenic gases comes from the solvents industry, and global inventories of these anthropogenic emissions have been compiled (Friedrich and Obermeier 1999; Olivier et al. 1999). These ‘anthropogenic’ emissions are discussed in detail in Chapter 2 of this book.

A further strong source of global emissions is from burning of biomass, and giant smoke plumes can nowadays be seen easily on satellite images, especially in the tropics during the dry season (September–October). These emissions are the most difficult to assess as sources, as they are highly dependent on fuel type, humidity and burn rate amongst other factors (Lobert et al. 1990). 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. Duncan et al. 2003). Most burning occurs during human-initiated land clearance but a large component also comes from the domestic use of biomass fuels (Levine 2003). A comprehensive summary of organic gas emissions from biomass burning relative to CO_2 has been made recently (Andreae and Merlet 2001).

On a global scale, the total amount of reactive biogenic emissions is not well established, although recent estimates indicate that c. 1300 TgC/year are emitted (Guenther 2002). The strongest biogenic emission is thought to be isoprene (C_5H_8), followed by the less specified so-called other reactive biogenic compounds that are mainly oxygenated compounds and monoterpenes. 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 (Guenther 2002; Muller 1992; Olivier et al. 1999). In comparison to terrestrial sources, emissions from the ocean are less well constrained although several important species are known to have a predominately marine source dimethyl sulphide (DMS, see Section 1.6) (Groene 1995) and methyl iodide (Lovelock 1975). A relatively small amount of organics is emitted from the ocean in the form of alkanes and alkenes, c. 5 TgC/year (e.g. Broadgate et al. 1997; Ratte et al. 1993). Recently global oceanic isoprene emissions have been estimated from satellite-derived chlorophyll map and laboratory studies 0.1 TgC/year (Palmer and Shaw 2005), that is, much smaller than the terrestrial source (c. 500 TgC/year). However, the surface ocean has been shown recently to be a massive reservoir for oxygenated organic species (Singh et al. 2003; Williams et al. 2004). Furthermore, a recent study of aerosols at a coastal site in Ireland (O'Dowd et al. 2004) showed that the organic fraction contributes significantly (63%) to the sub-micrometer particle mass of aerosols collected over the North Atlantic Ocean during phytoplankton bloom periods. Biogenic emissions in general are discussed in Chapter 3 of this book, while Chapter 4 includes a section concerning the biogenic formation of OVOCs.

From a global perspective, 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°N and 50°N. All these diverse organic emissions are broken down in the atmosphere into a wider array of partially oxidised species (Atkinson 1994; Atkinson and Arey 2003; Jenkin et al. 1997) and many thousands of gases have been detected in the atmosphere, from the tropics to Antarctica (Ciccioli et al. 1996; Zimmerman et al. 1988).

1.3 Sinks

Since the concentrations of organic trace species do not all simply increase with time there must logically be one or more removal processes (here termed sinks) acting on these compounds. The most important sink for organic trace gases in the atmosphere is chemical oxidation in the gas phase by the hydroxyl radical HO (or to a lesser extent O_3, NO_3 and halogen radicals) (Atkinson 1994; Jenkin et al. 2003; Saunders et al. 2003). Certain gas phase organic compounds in the air can absorb sunlight and thereby photolyse to smaller fragments. Some compounds can be efficiently removed physically by dry deposition to surfaces such as vegetation (Doskey et al. 2004; Muller 1992) or aerosol (Cousins and

Mackay 2001); or removed by wet deposition in rain (Fornaro and Gutz 2003; Kieber et al. 2002). The gas phase oxidation of organic compounds in air is mostly initiated by the HO radical, 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 oxidised 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 polarity 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 adsorbed onto solid particles (Bidleman 1988), but much smaller multi-functional organic compounds, such as oxalic acid, more readily adsorb and are commonly found on aerosols (Mochida et al. 2003). Further oxidative transformation of these species on the aerosol is also possible (Claeys et al. 2004a; Noziere and Riemer 2003).

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 section). 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 (http://www.iupac-kinetic.ch.cam.ac.uk/ and Mannschreck et al. 2002). Table 1.2 shows the atmospheric lifetime of several commonly measured VOCs with respect to OH, with lifetimes varying from months to minutes. Likewise, global photolysis rates can be calculated for many compounds from laboratory absorption cross section and quantum yield measurements (http://www. iupac-kinetic.ch.cam.ac.uk/). These rates can be profoundly influenced by clouds and this in turn can affect trace gas concentrations (Tie et al. 2003). 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 (Junge 1974). Relationships between the variability of organic gas measurements and their rate of removal by HO have been derived (Jobson et al. 1999; Williams et al. 2000) and exploited to derive HO trends. If a long-lived and hence well-distributed organic compound is known to react predominately with HO, and its emission and HO reaction rate are known, then the global HO concentration can be theoretically estimated. Initial attempts based on methyl chloroform indicated large changes in HO concentrations from 1978 to 2003 (Prinn et al. 2001, 2005) with a maximum in 1989 and a minimum in 1998, although other recent evidence suggests that uncertainty in the temporal and spatial emission pattern of methyl chloroform complicates such trend analysis (Krol et al. 2003).

Direct biological uptake can also be an effective atmospheric removal process for some organic species (Kesselmeier 2001; Kuhn et al. 2002). The rate of uptake is dependent on the ambient concentration, being strongest when ambient concentrations are high. Compensation points have been deduced for plants, which mark the crossover point between emission and uptake. A surprising recent discovery is that peroxy acetyl nitrate (PAN), an anthropogenic secondary oxidant like ozone, can also be taken up by plants (Sparks et al. 2003). This is an important development for the atmospheric nitrogen cycle as well as the organic species PAN.

Table 1.2 Overview of average tropospheric lifetimes of VOC compound groups and some selected VOCs as examples. Lifetimes are given for an average OH concentration of 6×10^5 per cm^3 and an average ozone concentration of 7×10^{11} per cm^3 (about 30 ppb)

Compound	Average lifetime
Alkanes	Months–days
Ethane	2.5 months
Propane	2.5 weeks
n-Pentane	4 days
Alkenes	Days–hours
Ethene	1.5 days
Propene	11 h
1-Butene	10 h
Cyclic compounds	Days–hours
Cyclopentane	4 days
Methylcyclohexane	2 days
Cyclohexane	3 h
Aromatic compounds	Weeks–hours
Benzene	2 weeks
Toluene	2 days
1,3,5-Trimethylbenzene	7.5 h
Biogenic compounds	Hours–minutes
Isoprene	3 h
α-Pinene	4 h
Limonene	30 min

1.4 Atmospheric distribution

Following emission, volatile organic species are distributed by atmospheric transport processes while undergoing the removal processes described in Section 1.3. The relationship between the atmospheric removal rate (lifetime) of the compound and the average mixing times for the various sections of the atmosphere together determine the extent to which a compound is globally distributed. Atmospheric mixing is physically impeded across the boundary layer temperature inversion (0.5–2 km), the tropopause (10–15 km) and the intertropical conversion zone (ITCZ, 10°S–10°N), and as a result strong gradients in organic species can develop across these atmospheric interfaces. Typical exchange times are 1–2 days for air to mix vertically out of the boundary layer, 2 weeks to a month for air to be advected zonally around the northern or southern hemisphere, about 1 year for interhemispheric exchange and 4–6 years for an exchange between troposphere and stratosphere. Chemical lifetimes, defined as the time for a chemical concentration to decay to $1/e$ of its initial value, varies from minutes to hours (terpenes and isoprene), through days to weeks (acetone, methanol, propane), years to decades (methyl chloroform, HCFC 134a), and up to hundreds of years for chlorofluorocarbons (CFC 11 and CFC 12) whose lifetime is determined by the mixing rate into the stratosphere. Short-lived compounds, such as the biogenic species isoprene ($CH_2C(CH_3)CHCH_2$), show strong atmospheric gradients within the boundary layer (0–2 km), whereas longer-lived compounds, such as CFC 113 (lifetime c. 8 years), are better mixed and only show strong gradients between the hemispheres (Boissard et al. 1996; Bonsang and Boissard 1999; Rudolph 1998). Some compounds are more or less uniformly distributed in the troposphere (CFC 12, lifetime 79 years, no remaining sources), only showing concentration gradients in the stratosphere. A large archive of aircraft measurements taken at various locations over the globe is available at http://www-gte.larc.nasa.gov/.

There are numerous examples in the literature of regional scale advection where organic pollutants found in remote locations have been linked to distant pollution sources by use of back trajectories (e.g. Blake et al. 1996; Traub et al. 2003). Intercontinental pollution events have been reported (Price et al. 2004; Stohl and Trickl 1999) and trajectories have even been used to track southern hemispheric biomass burning, through the ITCZ to the upper troposphere of the northern hemisphere (Andreae et al. 2001). Secondary photooxidants, such as ozone and PAN, that form en route have also similarly been identified in plumes emerging from urban centres (e.g. Rappengluck et al. 2003). Interestingly, there is growing evidence to suggest that migrating birds use chemical gradients as an olfactory aid to navigation (Wallraff 2001, 2003).

Where the atmosphere is in contact with the Earth, organic species can interact with the various surfaces, such as snow, soil and water (Ballschmiter 1992). Within these media further production or removal mechanisms may exist such as bacterial uptake, enhanced photolysis (Dominé and Shepson 2002; Klán et al. 2003) or biological production. Such processes will affect the lifetime of these species and hence their global distribution. Some higher molecular weight organics with considerably lower vapour pressures tend to partition predominantly to aerosols following release. When such a compound 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 compound. Examples of such compounds include polyaromatic hydrocarbons (PAHs, e.g. Mastral and Callén 2000), Polychlorinated 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 (Patton et al. 1991). The distribution of the long-lived semi-volatiles is markedly different to that of the volatiles, and with time through repeated volatilisation and adsorption, such compounds tend to concentrate in polar regions (Burkow and Kallenborn 2000) in a manner that could be likened to a global distillation (from the tropics to the poles). Some of these compounds are toxic (Walker 2001a) and can bioaccumulate through the food web (Tanabe et al. 1984), posing a risk to human health and the environment (UNEP 2001).

While the boundary layer (0–2 km) tends to be turbulent, the so-called free troposphere above is less well mixed. In addition to the slow process of diffusion, organic gases may be distributed in the atmosphere by meteorological events such as convection (Collins et al. 1999) and via lifting by frontal systems (Purvis et al. 2003). 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 (Bonsang and Boissard 1999; Singh and Zimmerman 1992). Certain photochemical products, such as organic nitrates (e.g. PAN or alkyl nitrates), have a hemispheric concentration that is maximum in the spring. This has been explained as the photochemical optimum between the high precursor source and low photochemical sink in wintertime, when PAN precursors are accumulated, and the high photochemical sink in summer (Penkett 1983).

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 NMHC, alkanes and alkenes (Singh et al. 2001, 2004). Similar high mixing ratios of oxygenates and compound diversity have been reported in other airborne studies (Crutzen et al. 2000), in urban centres (Lewis et al. 2000) and in continental outflow from Asia (Jacob et al. 2003; Lelieveld et al. 2001) and Europe (Salisbury et al. 2003). These results concur with earlier theoretical work on the oxidation of organic compounds (Calvert and Madronich 1987; Madronich et al. 1990). Our views about the distribution, sources and role of reactive organic species in the atmosphere are currently being revised rapidly.

1.5 Measurement tools

The human nose is particularly sensitive to several chemical groups (Cain 1979; Firestein 2001). Familiar examples include forests, which emit terpenes (e.g. Geron et al. 2000; Isidorov et al. 2000); oil refineries, which emit aromatic compounds and alkenes (e.g. Doskey et al. 1999); fish markets, which emit amines (Morita et al. 2003) and freshly cut onions, which emit sulphur compounds (e.g. Ferary and Auger 1996). While human subjects are widely used in odour identification studies (Ferreira et al. 2003; Walker 2001b), the nose's response is inherently subjective (Molhave et al. 1991) and difficult to quantify. Therefore, to investigate the atmosphere quantitatively, researchers have employed a variety of sensitive and specific sensors, including mass spectrometers, flame-ionisation detectors, electron-capture detectors, optical absorption, chemiluminescence and atomic emission detectors (e.g. Apel et al. 1998; Helmig 1999; Kormann et al. 2002; Sigrist 2003). In many cases such detectors are coupled to pre-separation devices, for example, a gas chromatograph so that individual gases may be isolated prior to detection and a single specific compound can be measured. 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 (e.g. Murlis et al. 2000) and elsewhere the leaves of plants have been analysed for long-term exposure statistics (Hiatt 1999). Ideally for air studies a detectors should also be capable of measuring the huge range of concentrations in the atmosphere. High mixing ratios of several tens of ppbv (nmol/mol) can be found for alkanes and aromatics in polluted urban areas urban areas (Derwent et al. 2000), while halons must be reliably measured at only 0.045 pptv (pmol/mol) (Fraser et al. 1999). The recently reported compound SF_5CF_3 was first detected at 0.005 pptv (Sturges et al. 2000). This means that if only 200 tonnes of such material would be emitted anywhere in the world it would, in time, be detectable by this instrument. Global networks of detectors are in currently place to routinely monitor changes in greenhouse gases (Prinn et al. 2000).

Much of our atmospheric knowledge to date has been driven by what can be reliably measured and how fast (Roscoe and Clemitshaw 1997). Although the first atmospheric research on organic trace gases (specifically PAN) was made using infrared spectroscopy (Stephens 1961; Stephens et al. 1956), the following 30–40 years of research on atmospheric organic gases have been dominated by gas chromatography (e.g. Darley et al. 1963; Helmig 1999) coupled to some form of detector. Samples have been either introduced directly into the instrument in the field or collected in pressurised steel canisters, absorbent packed cartridges or filters for later analysis in the laboratory. The alkanes (major components of fossil fuel) were one of the first and most widely investigated subset of the reactive organic species (Blomberg et al. 2002). 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 ionisation detection has allowed widely available quantitative analysis (Helmig 1999). Many oxidised gases are more difficult to quantify as they may stick to surfaces, thermally decompose or may even be produced in measurement systems (Bates et al. 2000; Helmig et al. 1996; Kelly and Holdren 1995; Lestremau et al. 2001; Li-Jones et al. 2001; Tanner 2003). These techniques are sensitive and specific, but due to the predetector sample separation, these are limited in sampling frequency.

Recently, several important new advances have been made in analytical techniques. These have permitted more organic species to be measured, such as high precision and sensitivity so as to enable δ^{13}C isotopic ratios to be determined in organics at mixing ratios below ppbv levels (Rudolph et al. 1997) (see Chapter 10 of this book). Higher frequency measurements have been made possible with chemical ionisation mass spectrometry (CIMS) through use of proton transfer reactions (Hewitt et al. 2003; Lindinger et al. 1998; Williams et al. 2001) (see Chapter 11 of this book), or by other chemical ionisation techniques (Heeb et al. 1999; Leibrock et al. 2003). Several of these high frequency methods have been further developed to measure emission fluxes directly (Bowling et al. 1998; Karl et al. 2004; Warneke et al. 2002). Furthermore, improvements in the field of gas chromatography (e.g. multi-dimensional gas chromatography or comprehensive chromatography, Phillips et al. 1985) have delivered considerable improvements in compound separation, identification and sensitivity (see Chapter 12 of this book). The physical separation of even enantiomeric monoterpenes, or optical isomers is also now possible from ambient air (Yassaa and Williams 2005). 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 planes, ships, balloons and ground sites to establish the global budgets of a wide range of organic species.

1.6 Modelling tools

A variety of numerical models is available today to simulate chemistry and transport in the atmosphere from the level of box models to three-dimensional chemistry and transport models. To simulate atmospheric chemistry in detail, models need to deal with VOCs which play a significant role in all reaction cycles in the atmosphere. In this regard the major input data they require are (a) the emission inventories describing the primary emission of VOC including their specific source compositions and their spatial and temporal variations, (b) the oxidation chemistry of VOC including the kinetics as a function of temperature and pressure and (c) for certain species a consideration of other significant loss processes such as dry and wet deposition. Understandably, due to the huge number of organic compounds in the troposphere, both a complete emission inventory of all possible compounds with the necessary resolution in time and space and a complete coverage of all possible chemical reactions including those of secondary reaction products will never be available.

There are only a few comprehensive emission inventories available and these cover the most important compounds relevant for atmospheric chemistry. The global distribution and source strengths of anthropogenic NMHC are usually taken from the Emission Database for Global Atmospheric Research (EDGAR V2.0) database (Olivier et al. 1996, 1999).

Detailed information on this database and access to the data is available on http://www.mnp.nl/edgar/. The EDGAR database details sources of fossil-fuel-related activities, biofuel combustion, industrial production and consumption processes (including solvent use) on a per country basis, land-use-related sources, including waste treatment, partially on a grid basis and partially on a per country basis; and natural sources on a grid basis. The database can be used to generate global, regional and national emission data in various formats. For all compounds the reference year is 1990, except for halocarbons, for which 1986 is the reference year. In 2001, version 3.2 was released which comprises emissions by region and source for the period 1990–5. However, organic compounds emissions given in the EDGAR database are known to have large uncertainties in both magnitude and distribution of the emissions.

An inventory of biomass burning and natural VOC emissions can be found in the Global Emissions Inventory Activity (GEIA) database. Details of this database can be found on http://www.geiacenter.org/. The biogenic VOC (BVOC) dataset consists of three files that cover isoprene, terpenes and 'other' NVOC data. This database provides BVOC emission measurements and modelling parameters and, in addition, an enclosure database that summarises information from literature and identifies the plant species and the BVOC studied, including enclosure and analytical techniques and other parameters. Presently, about 1 800 plant species from which BVOC emissions have been studied are documented.

As will be described in the following chapters, for individual VOC compound classes the chemistry of VOC can be quite complex. Two main approaches are used to simulate the complex chemistry of VOC using numerical models. One approach is to significantly reduce the number of organic compounds and hence the complexity of the corresponding reactions. Three methods are used to reduce the number of organic reactions, namely the carbon bond mechanism, the surrogate species method and the lumped species method. In the carbon bond mechanism, individual organic compounds are segregated into one or more bond groups that have a similar chemical reactivity (cf. Gery et al. 1988). With the surrogate species method all VOC of similar reactivity are grouped together. The rate coefficient of each of these compounds is then set equal to that of one particular compound (cf. Atkinson et al. 1982). In the lumped species method, VOC are grouped by their reactivity towards reactions with HO radicals. The rate coefficient is determined by taking the mole fraction weighted average of the reaction coefficient of each compound of the lumped group.

Currently the most widely used lumped mechanism is the Regional Acid Deposition Model (RADM) (Stockwell et al. 1990). This mechanism contains 158 chemical reactions and 63 gaseous compounds. Besides primarily emitted inorganic compounds and 16 organic compounds or compound groups, respectively, RADM also includes photochemically produced compounds. This mechanism has meanwhile been updated into a version named

Regional Atmospheric Chemistry Model (RACM) (Stockwell et al. 1997) and includes reaction schemes for isoprene and the group of monoterpenes. The RACM mechanism again has been improved (Regional Atmospheric Chemistry Model-Mainz Isoprene Mechanism, RACM-MIM) by implementing an explicit chemistry of isoprene (Geiger et al. 2003), the most important BVOC (see Chapter 3). Today RACM is widely used in a variety of mathematical models, ranging from box models to three-dimensional chemistry and transport models. However, the mechanism is also available as a stand-alone model for simulating tropospheric chemistry at typical ambient trace gas concentration levels.

The aforementioned methods of condensing VOC reactions have, of course, some disadvantages. The results of a model investigation of a single hydrocarbon oxidation are likely to be erroneous. Investigation of the RACM simulation showed, for example, that for a simulation of the oxidation of some individual VOC, such as branched alkanes, the error can be considerable. Therefore, other approaches have been developed that try to describe the complex chemistry of organics as explicitly as possible, leading to a vast number of chemicals and reactions which have to be taken into account. For example, the widely used Master Chemical Mechanism (MCM) is a detailed chemical mechanism containing 12 600 reactions and 4 500 chemical species (Jenkin et al. 2003). This mechanism includes the complete tropospheric oxidation of 124 VOC. The VOC which are degraded in this mechanism were selected on the basis of available emission data and provide approximately 90% mass coverage of the emissions of uniquely identifiable chemical species. The majority of the degradation schemes have been constructed using the methodology described by Jenkin et al. (1997). A review and update of the ideas behind the mechanism as well as recent developments can be found on the corresponding web page (http://mcm.leeds.ac.uk/MCM/).

1.7 How organic species affect the atmosphere

In the 1950s Haagen Smit and co-workers showed that the oxidation of organic species in the presence of NO_x and sunlight can form ozone (Haagen Smit 1952). Ozone, which is toxic to humans and plants, has become a major air quality problem in cities and larger areas such as the Mediterranean (Lelieveld et al. 2002) and the south-eastern United States (Solomon et al. 2000). Ozone control strategies adopted in the 1970s were initially unsuccessful due to an underestimation of natural organic emissions in the initial models (Trainer et al. 1987). However, more recent emission controls applied to cars (including NO_x and organic species reductions) have reduced regionally produced ozone (Derwent et al. 2003).

The capacity of the troposphere to oxidise emissions is also dependent on the amount of organic compounds present. Reaction with the main atmospheric oxidant, the HO radical, is the primary loss mechanism of organics from the atmosphere (see Section 1.3). While the initial reaction is a sink, subsequent oxidation steps may be a source of HO_x (HO and HO_2), making the global effect of organic species complicated. In cities where NO_x concentrations are high, increasing concentrations of organics increase 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 (Wang et al. 1998). 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 photolysed in the dry upper troposphere

(McKeen et al. 1997) and can lead to strong ozone formation. Similar effects are produced by organic peroxides and aldehydes (Jaeglé et al. 2000). At night the organics may also provide an important source of HO radicals (e.g. Platt et al. 2002) through the reactions of alkenes with ozone, and in oceanic regions, organohalogens can provide ozone-depleting halogen radicals such as Br (Platt and Honninger 2003), which can link with inorganic halogen cycles (Sander et al. 2003).

The global impact of organics on ozone and the hydroxyl radical have been investigated in models (Houweling et al. 1998; Wang et al. 1998). 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 oxidised in the presence of NO_x (Roberts 1990). 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 (Singh and Salas 1989). 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 and NO_2) concentrations acts to produce ozone; however in contrast, other trace organic gases can act to destroy ozone in the stratosphere. Prior to man's proliferation on the planet, long-lived naturally produced organohalogens, such as methyl chloride, represented the most important mechanism for chlorine transport to the stratosphere and hence ozone destruction (Anderson 1990). More recently man-made chlorinated, brominated and fluorinated hydrocarbons have been shown to deliver significant additional quantities of chlorine and bromine into the stratosphere (Rowland 1990) and be the cause of the 'ozone holes' observed over the polar regions (Molina 1988). As a result of legislation, the overall tropospheric abundance of halogen from halocarbons is now decreasing (Montzka et al. 1996). However, emissions of certain species (e.g. Halons) persist because of a lack of suitable substitutes for critical uses such as fire extinguishants (Butler et al. 1998).

In addition to the major organic greenhouse gases CO_2 and CH_4, certain other organic species have been implicated in long term or climate effects. Perhaps the best-known example is DMS, a compound which is naturally emitted from the oceans, and that has been proposed as a potential negative feedback to climate warming (Charlson et al. 1987). The hypothesis is that a long-term warming of the oceans would produce more DMS emission, which following oxidation to SO_2 and then sulphate would lead to more clouds 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 available water 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 (Feingold et al. 2003; Platnick and Twomey 1994). More recently certain oceanic alkyl halides have been linked to cloud formation and hence to possible climatic effects (O'Dowd 2002). While all organic species are infrared active to some extent, their influence on the global radiative forcing depends on their absorption spectrum and atmospheric abundance (Harries et al. 2001). 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, organic species may through chemistry also affect the radiation indirectly (Ramanathan 1998; Wigley et al. 2002). Due to the wide range of physical and chemical properties of organic compounds, 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 (Sanderson et al. 2003).

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 photoreactors within which complex proteins may build up (Tuck 2002; Vaida 2002). 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 (Nilson 2002). It has also been speculated that other organic species (nitriles) provided a source of nitrogen to photosynthesising marine organisms in the ancient oxygen-free atmosphere of the Earth (Bange and Williams 2000).

The trace organic species also have enormous potential for revealing the atmospheric chemical history of the Earth. The analysis of air trapped in ice cores for CH_4 and N_2O has provided atmospheric information of the past 120 000 year. Individual organic species can be more specifically attributed to sources than long-lived species such as CH_4 and N_2O. Early work on small cores dating back only c. 40 year have demonstrated this potential (Lee et al. 2003).

That gas phase organic compounds and atmospheric aerosols are strongly linked has been established for some time (Went et al. 1967), and organic atmospheric aerosols have recently been reviewed in detail by Seinfeld and Pankow (2003) and Jacobson et al. (2000). The blue hazes and reduced visibility over forests are the result of enhanced scattering of blue light by particles similar in size to the wavelength of light (Watson 2002). These particles can be produced from gaseous organic precursors, which condense from the gas phase to form aerosols (Kavouras et al. 1998). 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 (Bonn and Moortgat 2003; Claeys et al. 2004b; O'Dowd et al. 2002). Such nuclei may grow in size by coagulation with other particles and later through the condensation of other organic species onto the surfaces (Griffin et al. 1999; Kavouras and Stephanou 2002; Kulmala 2003). Recent evidence has shown that organic compounds absorbed into particles may undergo acid-catalysed reactions: oxidation, hydration, hemiacetal and acetal formation; polymerisation and aldol condensation (Claeys et al. 2004b; Iinuma et al. 2004; Jang et al. 2002; Kalberer et al. 2004; Tolocka et al. 2004) and chemical oxidation of organics such as isoprene can occur in the aerosol liquid phase through acid catalysed reactions with hydrogen peroxide (Claeys et al. 2004a). 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 (Roberts et al. 2002; Yu 2002). An organic layer has also been recently reported on marine aerosols (Tervahattu et al. 2002). In more polluted conditions, it has been shown that uptake of organic gases onto soot particles can change particle reflectivity (Saathoff et al. 2003), making light absorbing soot particles more reflective. The opposite can also be speculated, that organic species can make reflective ammonium sulphate 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 (Pruppacher and Klett 1997). However, in the presence of aerosols, condensation can occur at conditions more readily found in the atmosphere. Sulphate is a very effective cloud condensation nucleus and hence much research has been focused on DMS and its oxidation products (Pandis et al. 1994). A wide range of anthropogenic and biogenic compounds have been tested for their effect on ice nucleating properties (e.g. Szyrmer and Zawadzki 1997). Amino acids have been shown to be particularly effective in this regard (Milne and Zika 1993), and while long-chain alcohols in monolayers can also promote ice formation (Gavish et al. 1990), some organic acids appear to delay activation (Shantz et al. 2003). There is also some evidence that organic gases can influence the shape of ice crystals (Hallett and Mason 1958), a parameter that is predicted to have a large effect on snowfall rate (Lohmann et al. 2003).

In cities, organic aerosols and soot are also emitted directly, particularly from diesel exhausts. POPs such as PAHs (carcinogenic) and PCBs (toxics derived from burning plastics) are often associated with urban particles. Particles smaller than 10 μm (PM 10) can be effectively inhaled by humans, and correlations have been shown with mortality rates (Brunekreef et al. 1995). In the clean marine environment it has been shown recently that aerosols can be efficiently formed from iodine-containing organics, such as diiodomethane (Jimenez et al. 2003). 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 (Gill et al. 1983). The impact of ship emissions of organics on the atmospheric aerosol is also currently under investigation (von Glasow et al. 2003; Noone et al. 2000). A more detailed discussion of organic aerosols can be found in Chapter 9 of this book.

1.8 Open questions and future directions

The previous sections have outlined how huge emissions of organic gases enter the atmosphere and how oxidation, predominantly initiated by the HO radical, breaks down these gases to CO_2 and water. Determining how much reactive carbon is in ambient air and comparing it to the individually measured compounds is an important ongoing task. A similar budgeting process has been successfully performed for atmospheric nitrogen species (Fahey et al. 1986). For the carbon compounds this job 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 C_y by chromatographic separation and then conversion of all reactive species to CH_4 (Maris et al. 2003; Roberts et al. 1998). Comparisons to individually measured hydrocarbons are reasonable suggesting that most compounds making up the budget are being measured individually. However, the techniques adopted involve significant sample handling, where losses of some organic species could occur (Chung et al. 2003). Laboratory experiments and some as yet unpublished field studies have shown the potential of HO measurements to determine total reactivity (Jeanneret et al. 2001; Kirchner et al. 2001), but the size and complexity of the instrumentation used has until now precluded widespread use. Recently ground-based measurements made over a forest have shown that a considerable fraction of the measured reactivity could not be accounted for by speciated measurements and that the missing reactivity had a terpene-like emission profile (Di Carlo et al. 2004). Further forest-based ozone fluxes and possible unidentified photoproducts support this notion (Goldstein et al. 2004; Holzinger et al. 2005). Generally, global models have considerable difficulty simulating the chemistry over large forest areas (e.g. the Amazon rainforest) since the high fluxes from known reactive organic compounds, such as isoprene and monoterpenes, tend to consume the available HO radicals in the model. 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 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 (Fried et al. 2003), the difference being up to a factor of 3–4 in the upper troposphere (Kormann et al. 2003). Assuming this is not 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 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 (e.g. Calvert et al. 2002; Jenkin et al. 1997) 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 multi-phase 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 (Chung and Seinfeld 2002; Griffin et al. 2002).

The role of the ocean in the budgets of organic species is surprisingly poorly understood. Many organic species are reported to be emitted from the ocean (including sulphur-containing gases (Kettle et al. 2001), organohalogens (Carpenter et al. 2003), alkyl nitrates (Chuck et al. 2002)) while many other species are taken up (e.g. acetone, Warneke and de Gouw 2001; methanol, Galbally and Kirstine 2002). 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; Galbally and Kirstine 2002; Singh et al. 2003; Williams et al. 2004). The ocean is able