

# TROPOSPHERIC CHEMISTRY AND COMPOSITION

## VOCs: Overview

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## Introduction

The troposphere, the region of the Earth's atmosphere in which we live and breath, is composed of many different kinds of gases. These components range from the abundant two-atom molecules O<sub>2</sub> and N<sub>2</sub>, to larger and more reactive chemicals, which include vast numbers of different volatile organic compounds (VOCs). Concentrations of VOCs can be as high as one part per million by volume (10<sup>-6</sup>, or ppmv) in source regions (cities and near fires) and below one part per trillion by volume (10<sup>-12</sup>, or pptv) in remote regions. Many VOCs are important in tropospheric reactions even at low pptv concentrations. A lot has been learned in the last few decades about VOC sources and their distributions. However, there is much still to be determined about this very important class of atmospheric gases.

Together with sunlight and nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>), VOCs undergo a complicated series of chemical and physical transformations over a whole range of spatial scales. Various classes of VOCs have a large impact on atmospheric chemistry, contributing to localized urban smog, regional scale photochemical ozone pollution, acid deposition, and particle formation/visibility degradation, and ultimately global changes in the oxidizing capacity of the troposphere. VOCs are also useful as diagnostic tracers for atmospheric transport, chemical pathways, and distribution of sources.

Photochemical smog has been detected in almost all of the world's major urban and industrial centers, at levels that often exceed internationally agreed threshold values set to protect human health. Detailed understanding of the mechanism of photochemical smog formation has developed from pioneering studies of Los Angeles smog in the 1950s through the

combination of laboratory studies, field experiments, air quality monitoring, and computer modeling studies. Man-made chlorinated hydrocarbons have reached the stratosphere, where the intense solar radiation activates their chlorine content into a potent depleting agent of the stratospheric ozone shield. Research into the important role played by VOCs in a range of environmental problems remains one of the most rapidly developing topics in the fast-developing field of atmospheric chemistry.

VOCs comprise a large variety of vapor phase carbon-containing atmospheric gases in the reduced form, with a wide range of physical and chemical behaviors. **Table 1** lists some important atmospheric organic species. Pure hydrocarbons containing only C and H, such as alkanes, alkenes, alkynes, and aromatics are, in turn a very important category of VOC and generally are referred to as nonmethane hydrocarbons (NMHCs). However, VOCs containing oxygen, chlorine, nitrogen, and other elements are also of significance. These gases include aldehydes, ketones, organic acids, alcohols (**Table 1**), and also ethers, esters, furans, nitriles, organic nitrates, chlorinated alkanes and alkenes, chlorofluorocarbons (CFCs), and hydrochlorofluorocarbons (HCFCs). Only carbon dioxide (CO<sub>2</sub>) and carbon monoxide (CO) are excluded. VOCs are typically classed as containing up to 12 carbon atoms per molecule, as those with more than 10 carbons tend to partition into atmospheric particles (aerosols).

VOCs are released into the atmosphere from numerous types of sources, both natural and from various human activities (anthropogenic). **Table 1** indicates that important source categories are combustion processes (e.g., vehicle exhausts and biomass burning); production, treatment, storage, and distribution of fossil fuels; and natural emissions from plants and the ocean. Other sources include organic solvents and landfills. In order to fully assess and control the effect that these gases have on our local, regional, and global air quality, it is important to compile detailed information on their emissions. However, the many types of sources, and their vast number, mean that preparing an inventory of emissions that includes all the diverse individual species is an extremely difficult task.

The diverse natural and anthropogenic VOC emission sources, together with their relatively short atmospheric lifetimes (**Table 1**), mean that VOCs show significant variation in their spatial (latitudinal and vertical), and temporal (diurnal and seasonal)

0422-T0001 **Table 1** Some important atmospheric organic species: typical sources, sinks and concentration ranges

Class and compound	Formula	Estimated atmospheric lifetime	Principal source types <sup>a</sup>	Principal sinks	Typical remote mixing ratios (ppb)
<b>Alkanes</b>					
Methane	CH <sub>4</sub>	10 years	Microbial natural gas, BB	OH <sup>•</sup> , Stratosphere	1.7–1.9
Ethane	C <sub>2</sub> H <sub>6</sub>	80 days	Natural gas, motor vehicles	OH <sup>•</sup>	0.2–2
Propane	C <sub>3</sub> H <sub>8</sub>	17 days	LPG, motor vehicles	OH <sup>•</sup>	0–1
n-Butane	C <sub>4</sub> H <sub>10</sub>	6 days	Motor vehicles	OH <sup>•</sup>	0–0.5
i-Pentane	C <sub>5</sub> H <sub>12</sub>	4 days	Motor vehicles	OH <sup>•</sup>	0–0.3
<b>Alkenes</b>					
Ethene	C <sub>2</sub> H <sub>4</sub>	1.7 days	Vehicle exhaust, BB, biogenic	OH <sup>•</sup> , NO <sub>3</sub> <sup>•</sup> , O <sub>3</sub>	0–0.1
Propene	C <sub>3</sub> H <sub>6</sub>	7 hours	Motor vehicles, BB, biogenic	OH <sup>•</sup> , NO <sub>3</sub> <sup>•</sup> , O <sub>3</sub>	0.01
Isoprene	C <sub>5</sub> H <sub>8</sub>	1.5 hours	Vegetation	OH <sup>•</sup> , NO <sub>3</sub> <sup>•</sup> , O <sub>3</sub>	0–1
α-Pinene	C <sub>10</sub> H <sub>16</sub>	3 hours	Vegetation	OH <sup>•</sup> , NO <sub>3</sub> <sup>•</sup> , O <sub>3</sub>	0–1
<b>Alkynes</b>					
Ethyne	C <sub>2</sub> H <sub>2</sub>	24 days	Vehicle exhaust, BB	OH <sup>•</sup>	0–1
<b>Aromatics</b>					
Benzene	C <sub>6</sub> H <sub>6</sub>	12 days	Motor vehicles, solvents	OH <sup>•</sup>	0–0.5
Toluene	C <sub>7</sub> H <sub>8</sub>	2.5 days	Motor vehicles, solvents	OH <sup>•</sup>	0–0.5
m-Xylene	C <sub>8</sub> H <sub>10</sub>	0.6 days	Motor vehicles, solvents	OH <sup>•</sup>	0–0.1
<b>Aldehydes</b>					
Formaldehyde	HCHO	4 hours	HC oxidation, vehicle exhaust, BB	OH <sup>•</sup> , NO <sub>3</sub> <sup>•</sup> , hν	0.1–0.5
Acetaldehyde	CH <sub>3</sub> CHO	11 hours	Vehicle exhaust, HC oxidation, biogenic	OH <sup>•</sup> , hν	0.1–0.2
<b>Ketones</b>					
Acetone	CH <sub>3</sub> C(O)CH <sub>3</sub>	16 days	HC oxidation, biogenic	OH <sup>•</sup> , hν	0.3–1
<b>Acids</b>					
Formic acid	HCOOH	~ 1 week	HC oxidation, BB, biogenic	Scavenging	0–5
Acetic acid	CH <sub>3</sub> COOH	~ 1 week	HC oxidation, BB, biogenic	Scavenging	0–2
<b>Peroxides</b>					
Methyl hydroperoxide	CH <sub>3</sub> OOH	2 days	HC oxidation	Scavenging, OH <sup>•</sup> , hν	0–1
<b>Alcohols</b>					
Methanol	CH <sub>3</sub> OH	16 days	Biogenic, HC oxidation	OH <sup>•</sup>	0.4–2.0
<b>Sulfur gas</b>					
Dimethyl sulfide	CH <sub>3</sub> SCH <sub>3</sub>	3 days	Oceans	OH <sup>•</sup> , NO <sub>3</sub> <sup>•</sup>	0–200 ppt

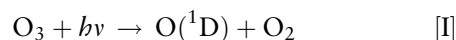
<sup>a</sup>HC, hydrocarbon; LPG, liquid petroleum gas; BB, biomass burning.

distribution patterns in the atmosphere. Therefore, direct observations of such patterns play an important role in assessment of emissions and their effect on atmospheric chemistry.

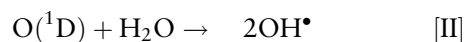
## Hydroxyl Radicals, Atmospheric Lifetimes, and Ozone Formation

0422-P0035 Even at relatively low tropospheric mixing ratios (ppbv to pptv levels, Table 1), the high reactivity of VOCs allows them to play a significant role in atmospheric chemistry. The main sink of most VOCs is through photooxidation, initiated typically by reaction with hydroxyl (OH<sup>•</sup>) free radicals. These

radicals are formed when ozone (O<sub>3</sub>) is photolyzed by sunlight of a particular wavelength range (denoted below as *hν*) to produce excited “singlet” (O(<sup>1</sup>D)) oxygen atoms (eqn [I]).



These then collide with a water molecule to produce two hydroxyl free radicals (radical species are here indicated by a ‘dot’ (•)) (eqn [II]).



The lifetime ( $\tau$ ) of a hydrocarbon species RH, as a result of reaction with the hydroxyl radical (eqn [III])

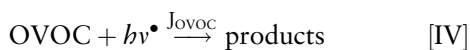
is given by eqn [1], where  $k$  is the laboratory determined reaction rate constant.



$$\tau_{\text{RH}_{\text{OH}}} = \frac{1}{k[\text{OH}^\bullet]} \quad \text{[1]}$$

Hydrocarbons, such as the alkenes, which contain C = C double bonds, also undergo addition reactions with ozone (Table 1).

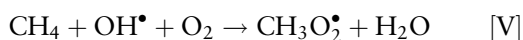
0422-P0040 Unlike most hydrocarbons, many nonmethane oxygenated VOC (OVOC) species such as formaldehyde (HCHO) can be photolyzed throughout the troposphere (Table 1). Their lifetime as a result of photolysis according to eqn [V] is the inverse of the photolysis rate constant ( $J_{\text{OVOC}}$ ) (eqn [2]).



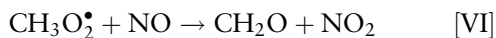
$$\tau_{\text{OVOC}_{h\nu}} = \frac{1}{J_{\text{OVOC}}} \quad \text{[2]}$$

0422-P0045 Ozone can be produced as a result of this oxidation of "atmospheric fuels" (CO, methane (CH<sub>4</sub>) and other VOCs) in the presence of nitrogen oxides and sunlight. The oxidation of a typical VOC is illustrated in Figure 1.

0422-P0050 In parts of the atmosphere remote from sources, the formation of ozone is dominated by the oxidation of CO and CH<sub>4</sub>. Methane reacts with hydroxyl radicals and subsequently oxygen to make methylperoxy radicals (CH<sub>3</sub>O<sub>2</sub>•) (eqn [V]).



Depending upon the relative concentration of nitric oxide (NO) and hydroperoxy radicals (HO<sub>2</sub>•), the methylperoxy radicals will yield formaldehyde (CH<sub>2</sub>O) or methylhydroperoxide (CH<sub>3</sub>OOH) (eqn [VI]).



Thus, CH<sub>4</sub> is the predominant parent hydrocarbon for formaldehyde.

0422-P0055 However, in the rural and urban atmospheres of industrialized countries, both biogenic and anthropogenic nonmethane VOCs (NMVOCs) frequently play an extremely important role in the formation of pollutants, including O<sub>3</sub> and other oxidants. As shown in Figure 1, the photooxidation reactions of VOCs leads to the formation of the highly reactive radicals HO<sub>2</sub>• and RO<sub>2</sub>• (alkylperoxy radicals), both of which species oxidize NO to NO<sub>2</sub> to produce O<sub>3</sub> and carbonyl molecules. These carbonyls are themselves

highly reactive VOCs and will be photolyzed or attacked by OH• radicals to produce more peroxy radicals (Figure 1) and subsequently more ozone. Therefore, under the right conditions, more than one molecule of ozone is produced for each NMHC oxidized. It is through this cycling of HO<sub>2</sub>• and NO<sub>2</sub> that VOCs such as NMHCs and other VOCs have an active role in HO<sub>x</sub> chemistry and in ozone production. In fact, organic compounds can be classified according to their atmospheric reactivity and consequently their photochemical ozone creation potential.

Other major products are organic nitrates, including peroxyacyl nitrates such as PAN and organic nitrates (RONO<sub>2</sub>) (Figure 1). PAN and O<sub>3</sub> are major surface level pollutants, especially in urban areas, and are responsible for many of the negative consequences for human health and crop damage associated with photochemical smog. Organic nitrates have substantially longer photochemical lifetimes than NO<sub>x</sub> and so can be effective temporary reservoirs, transporting reactive nitrogen far from the source and effectively expanding the spatial influence of the original emissions.

The production of tropospheric ozone is balanced by *in situ* photochemical destruction and by dry deposition at the Earth's surface. In the continental boundary layer, especially above forested regions and

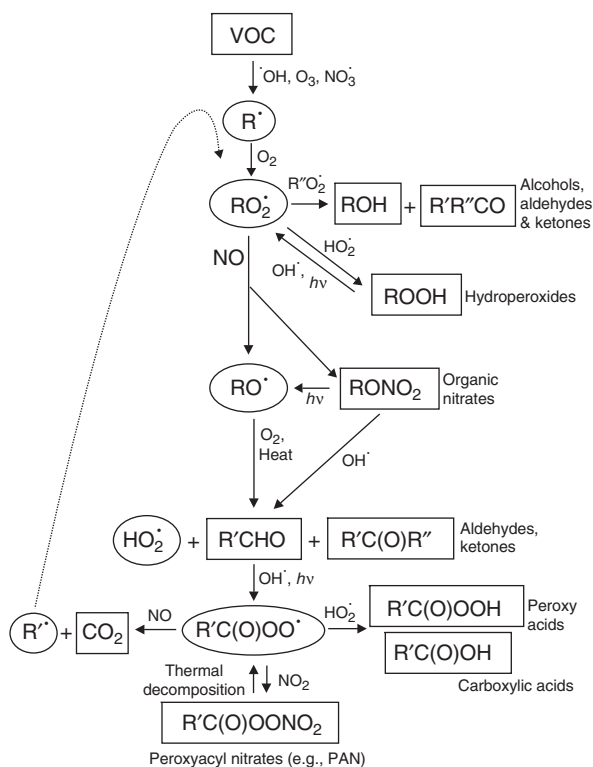


Figure 1 Organic radicals and products in the photooxidation of a typical VOC.

in urbanized and industrialized areas (where the level of biogenic or anthropogenic hydrocarbons can be high), similar cycles involving oxidation of VOCs become dominant mechanisms for the photochemical production of O<sub>3</sub>. Urban ozone generation is most efficient when the relative proportions are about 7 to 1 VOC to NO<sub>x</sub>. Because most areas of the world (even in remote areas) the atmospheric “fuels” are readily available, NO<sub>x</sub> very often the rate-limiting precursor of ozone formation. Biogenic emissions of VOCs are often abundant enough to have a critical influence on this ratio, especially in urban–suburban areas, such as Atlanta, Georgia in the United States, and must be taken into account when regulating emissions with the goal of reducing tropospheric ozone pollution.

### Sources and Sinks

0422-P0070 Fossil fuel production, industries, and automobiles all produce VOCs in varying amounts. Anthropogenic sources are a major source of VOCs, especially hydrocarbons. A recent estimate of anthropogenic nonmethane VOC emissions indicates a global source of about 140 Tg y<sup>-1</sup>, or (140 × 10<sup>6</sup> t y<sup>-1</sup>). However, natural sources make a significantly larger contribution to total emissions, with about 1150 Tg y<sup>-1</sup> of biogenic origin.

0422-P0075 Emissions from different types of sources will result in varying atmospheric distributions. Motor vehicles are a large source of VOC emissions in the United States and most of Europe. They are the result of both exhaust emissions and evaporation of the unburned fuel (evaporative emissions). Most VOCs are emitted over continental regions.

### Combustion Processes

0422-P0080 The major products of complete combustion of fossil fuels are carbon dioxide and water. However, in practice, actual combustion processes are less complete. One common reason is lack of oxygen; or the combustion temperature might be low; alternatively the residence time of the fuel in the burner zone may be too short. This incomplete combustion of fossil fuels leads to emissions of CO and VOCs. Hydrocarbons can be emitted in a partly oxidized form (e.g., aldehydes) or even in an unoxidized form (e.g., alkanes and aromatics). In addition, new hydrocarbons (e.g., alkenes, alkynes, and aromatics) may be formed by radical reactions. The more incomplete the reaction is, the greater the resultant VOC emissions. Exhaust emissions of VOCs from motor vehicles are strongly dependent on engine type, emission control technology, driving modes (open highway or heavy traffic),

and ambient temperature at cold start. For example, two-stroke engines of mopeds tend to have the highest VOC emissions per unit of fuel used, while gasoline engines equipped with three-way catalysts have relatively low emissions of noncombusted or partly combusted gasoline.

Another important global source is emissions from the combustion of organic material in oxygen-deficient fires, or biomass burning. The combustion of biomass material is a common practice, principally in the tropics during the dry season. Approximately 90% of all biomass burning events are thought to be initiated by human activities; it is done to clear forest land for agriculture and grazing, to burn agricultural by-products and dry savanna grasses, to maintain soil fertility, for weed control, to discourage insects and other pests, and in use as fuel for cooking and heating. This burning leads to the emission of methane, NMHCs, and a variety of partially oxidized organic compounds (Table 1), often consisting of a high proportion of medium- and high-molecular weight gases, in addition to carbon monoxide and particulate species. Biomass burning accounts for global NMHC emissions of about 40 Tg y<sup>-1</sup>.

About 80% of biomass burning is thought to occur in the tropics, with the majority taking place in Africa, South America, and Asia. These emissions contribute significantly to the local and sometimes regional budgets of organic trace gases and the formation of ozone.

### Methane

Methane is the most abundant hydrocarbon in the atmosphere. Its global sources total about 540 Tg y<sup>-1</sup>, with about 160 Tg y<sup>-1</sup> from natural sources (mostly wetlands), and about 380 Tg y<sup>-1</sup> from anthropogenic sources (principally fossil fuels, livestock, and rice paddies). Of this, emissions from landfills, tropical swamps, rice fields, biomass burning, and termites total about 300 Tg y<sup>-1</sup>. Annual methane destruction rates total about 515 Tg y<sup>-1</sup> with approximately 445 Tg by OH• oxidation, 40 Tg by loss to the stratosphere, and 30 Tg by soil absorption. This implies that identified total sources exceed sinks by about 20 Tg y<sup>-1</sup>. However, recent temporal increases illustrated in Figure 2, are more consistent with sources exceeding sinks by about 35–40 Tg y<sup>-1</sup>.

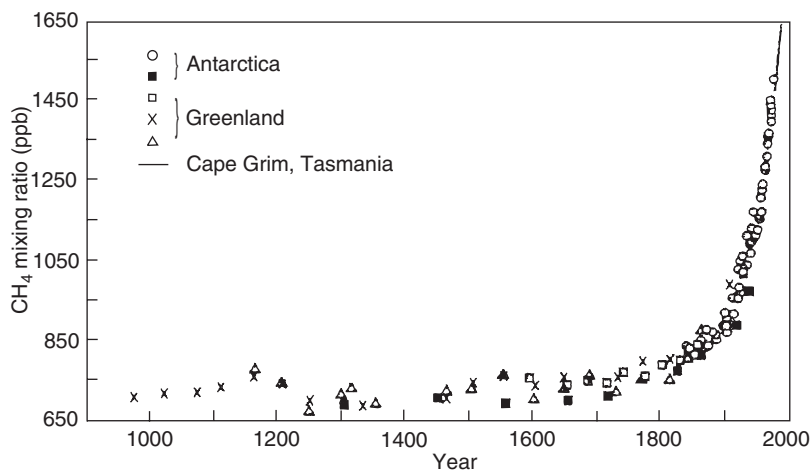
Methane levels began to increase rapidly about 1800 and have more than doubled over the past 200 years (Figure 2) as a consequence of modern industrial, agricultural, and residential activities. For example, since about 1800, the number of domestic ruminants (which produce methane by enteric fermentation of

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0422-F0002 **Figure 2** Methane mixing ratios over the last 1000 years as determined from ice cores from Antarctica and Greenland. (Reproduced from Intergovernmental Panel on Climate Change (IPCC) (1955) *Climate Change 1994: Radioactive Forcing of Climate Change and an Evaluation of the IPCC IS92 Emission Scenarios*. Cambridge: Cambridge University Press. 1995.)

grasses) has increased dramatically, accounting for about 15% of the total methane emitted annually.

## Biogenic Sources

0422-P0105 Large quantities of organic compounds are emitted from vegetation. As stated earlier, current global emission estimates of biogenic hydrocarbons total about  $1150 \text{ Tg y}^{-1}$ . The most common NMHC, isoprene ( $\text{C}_5\text{H}_8$ , 2-methyl-1,3-butadiene), alone is estimated to be emitted at a rate of about  $500 \text{ Tg y}^{-1}$ , mostly from deciduous vegetation in the presence of photosynthetically active radiation. In addition, plants are known to emit a range of monoterpenes ( $\text{C}_{10}\text{H}_{16}$ , including  $\alpha$ - and  $\beta$ -pinene, camphene, carene, *d*-limonene, and terpinolene), sesquiterpenes ( $\text{C}_{15}\text{H}_{24}$ ), various alcohols (e.g., methanol, ethanol, and 2-methyl-3-buten-2-ol), aldehydes (e.g., acetaldehyde), ketones (including acetone), ethene ( $\text{C}_2\text{H}_4$ ), esters, and furans. Many of these hydrocarbons contain  $\text{C}=\text{C}$  double bonds, which makes them susceptible to attack by  $\text{O}_3$  as well as  $\text{NO}_3^\bullet$  (nitrate radical) and  $\text{OH}^\bullet$  radicals (see **Table 1**).

0422-P0110 Reactive hydrocarbons, therefore, have long been a standard feature of Earth's atmosphere. Thus, it is often the presence or absence of  $\text{NO}_x$  that will determine whether ozone will be generated in the troposphere. Before the industrial era,  $\text{NO}_x$  was produced from atmospheric  $\text{N}_2$  and  $\text{O}_2$  only occasionally, for example, during forest fires and lightning. Now sources such as cars are all too common. This makes natural VOC sources very important in determination of the human impact of atmospheric pollution on the troposphere.

## Oxygenated VOCs

The fact that many oxygenated species can be photo- 0422-P0115  
lyzed throughout the troposphere means that their influence on tropospheric chemistry and ozone-formation potential is somewhat different from that of pure hydrocarbons. For example, carbonyls (including acetone and formaldehyde) and peroxides are important as sources of reactive odd oxygen ( $\text{HO}_x^\bullet$  free radicals) in the global-regional troposphere and in smoke plumes (**Figure 1**). Molecules such as acetone can form PAN in the upper troposphere, thus promoting the long-range transport of active nitrogen.

Formaldehyde ( $\text{CH}_2\text{O}$ ) has an extremely short 0422-P0120  
atmospheric lifetime (a few hours) compared to acetone (**Table 1**), and is principally a secondary photochemical by-product of methane and other hydrocarbon oxidation. It is an integral component of atmospheric photochemistry and air pollution. The photolysis of formaldehyde, its reaction with  $\text{OH}^\bullet$ , or its reaction with the  $\text{NO}_3^\bullet$  radical at night leads to peroxy radical ( $\text{HO}_2^\bullet$ ) formation and subsequently (and more importantly) to stronger oxidants like  $\text{OH}^\bullet$  and ozone. Formaldehyde photolysis is also a significant source of molecular hydrogen,  $\text{H}_2$ . Formaldehyde is directly emitted into the atmosphere by combustion of fossil fuels and biomass; however, these sources are small ( $<5\%$ ) in comparison with the global photochemical production from methane alone (approximately  $10^3 \text{ Tg}$ ).

Formic acid and acetic acid are ubiquitous tropo- 0422-P0125  
spheric trace gases and contribute a large fraction of the free acidity in precipitation in remote areas. Known sources include primary emissions from terrestrial vegetation and from automobile exhaust and

biomass burning. They are also formed as secondary products of photochemical gas phase reactions of ozone with alkenes and liquid phase cloud-water reactions. Neither photolysis nor reaction with OH• represent a significant sink, but organic acids are quickly removed from the atmosphere by scavenging out of the gas phase by coming into contact with atmospheric water and aerosol particles (Table 1). However, their chemistry is at best highly uncertain.

In general, measurements of organic oxygenated species in the remote troposphere are extremely sparse and often limited to a few species. However, a large number of oxygenated organic chemicals, including PAN, alkyl nitrates, acetone, formaldehyde, methanol, methylhydroperoxide, acetic acid, and formic acid, were measured during the October/November 1997 NASA SONEX (SASS Ozone and Nitrogen Oxide Experiment) mission over the North Atlantic region. SONEX revealed that the total atmospheric abundance of these oxygenated species nearly equals that of total NMHCs.

### Sampling and Analysis

Accurate measurements of the spatial distributions of VOCs on both a local and global scale can reveal a great deal about the magnitude and distribution of their sources and sinks, and provide essential insights into the origin of tropospheric ozone. Halocarbon and NMHC gases are useful tracers of anthropogenic and biogenic emissions, and for characterizing marine boundary layer (MBL) air.

With their relatively short atmospheric lifetimes (Table 1), the number of VOCs that can be found in the atmosphere, often at low but relevant levels (Table 1), is very substantial. Depending on the measurement site, thousands of individual VOCs can be detected in ambient air. The analysis of such a wide range of compounds requires a variety of different approaches and techniques with high separation power or highly specific detection methods. Measurement of any single class of organic compound often presents unique problems associated with sampling, standardization, analysis, and detection. These problems are multiplied when the simultaneous measurement of different compound classes is desired.

There has been tremendous progress in measurement techniques for atmospheric VOCs over the past 10–15 years, and existing techniques allow measurement of a broad range of VOCs in concentrations ranging down to a few pptv and even below. VOCs have been measured in a wide variety of atmospheric environments, from urban to the most remote locations over the tropical oceans and polar regions.

Nevertheless, the organic chemical composition of the troposphere is far from adequately characterized and the comprehensive determination of tropospheric VOC concentrations is still a challenging and evolving field.

### Sampling Methods

In situ instrumentation is often unavailable or impractical for use in the field to measure the range of VOCs of interest. There are numerous sampling techniques, the most popular of which are whole air sampling into a container, and sampling on solid adsorbents. The combination of sampling on solid adsorbents, followed by solvent extraction and subsequent analysis, — for example, by high-pressure liquid chromatography (HPLC) or gas chromatography – mass spectrometry (GC–MS) — is the most widely used, but a high incidence of sampling artifacts have hitherto confined them principally to studies in urban areas or studies of indoor pollution, rather than clean background conditions. The costly practice of collecting whole air into evacuated stainless steel canisters (either at ambient pressure or above, employing a sampling pump) has proved successful for the sampling of low- to medium-weight VOCs, particularly NMHCs and halocarbons, down to very low mixing ratios in air. However, compounds greater than about C<sub>10</sub> are likely to adsorb onto the walls of the canister during storage, leading to an underestimation of their ambient concentrations.

A substantial number of atmospheric VOCs are either highly polar (such as aldehydes and ketones) or thermally unstable (e.g., PAN). This limits the use of the conventional sampling techniques described above.

### Analytical Methods

Because of the typically low ambient VOC mixing ratios, some kind of preconcentration or sample enrichment step is needed prior to sample analysis. Most commonly, whole air samples are passed through a cold trap where the VOCs are condensed cryogenically, then warmed and flushed from the trap to a gas chromatographic (GC) column for separation of the complex mixture of components. Flame ionization detection (FID), electron capture detection (ECD) and mass spectrometry (MS) are the most widely used detection methods for whole air samples.

### Distributions

Trace gas distributions provide information crucial to establishing the extent of continental influence on the chemical environment of the remote troposphere. The

average atmospheric lifetimes of ethane, ethyne, and  $C_2Cl_4$  are much less than the 1-year average inter-hemispheric exchange time. However, they are comparable to mixing times within a hemisphere (about 2–6 weeks depending on latitude and season). Therefore, the NMHCs and  $C_2Cl_4$  show significant latitudinal, seasonal, and vertical gradients in the atmosphere.

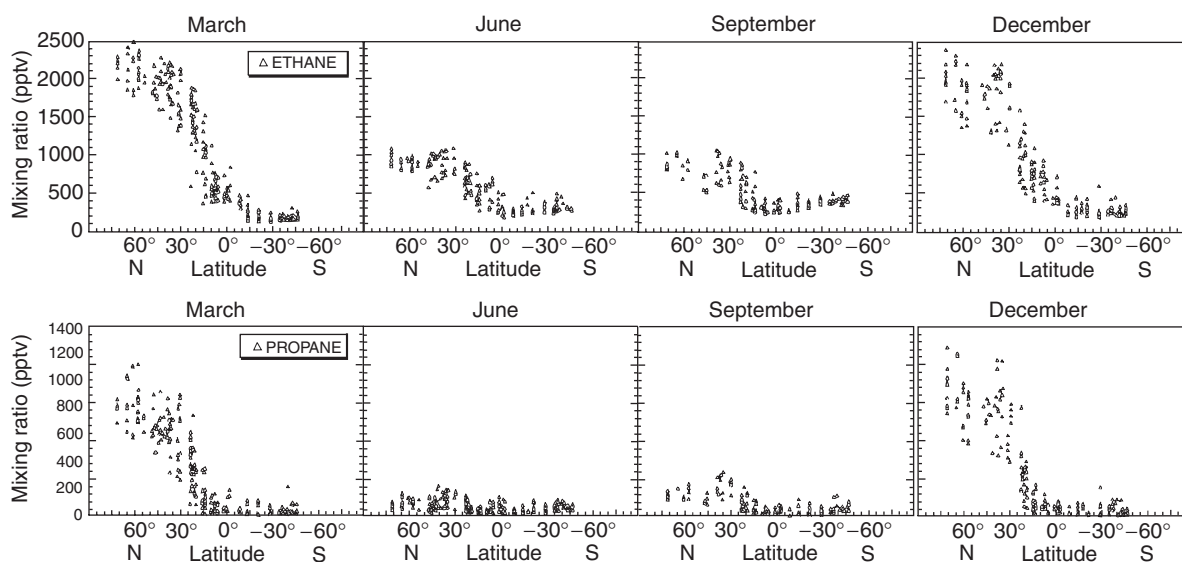
Because  $OH^\bullet$ , the main sink of VOCs is generated photochemically during daylight (see above), the strength of this sink varies diurnally and seasonally. Minimum OH levels at high latitudes are found in winter, resulting in significantly reduced removal rates for many trace gases. In the remote atmosphere, the most abundant NMHC compounds are the longest-lived group of light hydrocarbons (i.e., ethane, ethyne, and propane). **Figure 3** shows sharp latitude gradients in ethane and propane, with higher mixing ratios in the Northern Hemisphere during the winter months of March and December **Figure 4** illustrates how these same samples fit to a seasonal cycle, with much higher mixing ratios of ethane in the Northern Hemisphere, close to the major anthropogenic source regions compared to the maximum ethane levels reached in the Southern Hemisphere winter.

VOCs have been used in the study of the dynamical structure of such regions as the intertropical convergence zone (ITCZ). The ITCZ is a zone of convective air near the Equator, which forms a barrier to mixing between the air of the Northern and Southern Hemispheres. In addition, VOCs are useful probes with which to constrain atmospheric concentrations of  $OH^\bullet$  and atomic chlorine ( $Cl^\bullet$ ) radicals. Speciated sources, sinks, and distributions of VOCs are crucial

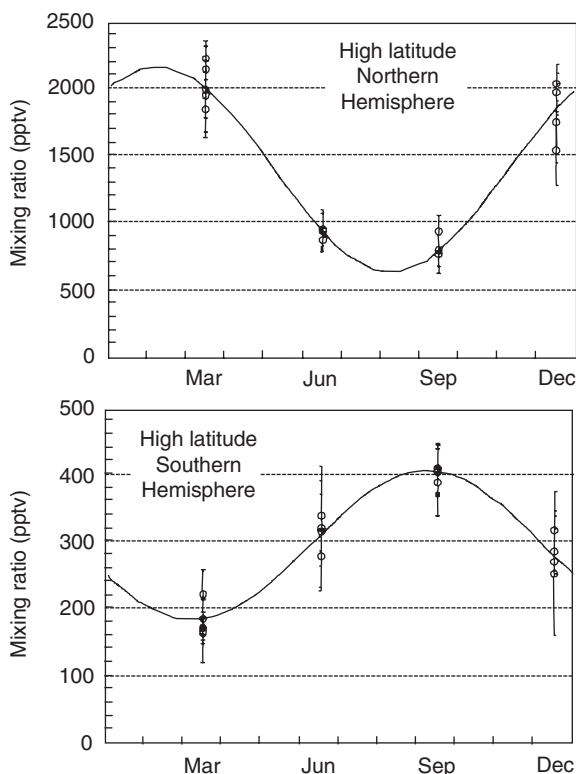
inputs into computer models of atmospheric chemistry. Such calculations test our understanding of the fate and impact of VOCs on the photochemistry in the troposphere.

Tropospheric  $O_3$  has two predominant sources, *in situ* photochemical production from its precursors ( $CO$ , NMHCs, and  $NO_x$ ) as outlined above, and downward mixing from the stratosphere. When combined with meteorological trajectory analysis, the contributions of different combinations of VOCs associated with the different source types discussed above enables the use of VOCs as chemical tracers playing a crucial role in establishing the most likely origin of  $O_3$ -enriched layers. For example, incomplete combustion, including urban fossil fuel use and biomass burning, is the principal global source of ethane ( $C_2H_6$ ), and ethyne ( $C_2H_2$ ); however, some gases such as  $C_2Cl_4$  are specific to industrial/urban activities, and serve as markers for such urban effluents. Biomass burning is an important global source of  $CH_3Cl$  (approximately 25–50%) and mixing ratios of  $CH_3Cl$  typically are not elevated in northern cities (i.e., those that do not rely heavily on biomass fuels), consistent with  $CH_3Cl$  having no significant urban/industrial origins. This makes  $CH_3Cl$  a particularly useful diagnostic for biomass burning emissions.

The most comprehensive speciation, combined with spatial coverage to date has been achieved by sampling aboard specially modified aircraft. In particular, the NASA Global Tropospheric Experiment (GTE) field campaigns have examined specific aspects of the tropospheric ozone budget and have amassed a



**Figure 3** Latitude distribution of ethane and propane mixing ratios near the surface of the Pacific during March, June, September, and December for samples collected and analyzed quarterly by the University of California, Irvine between March 1994 and March 1999.



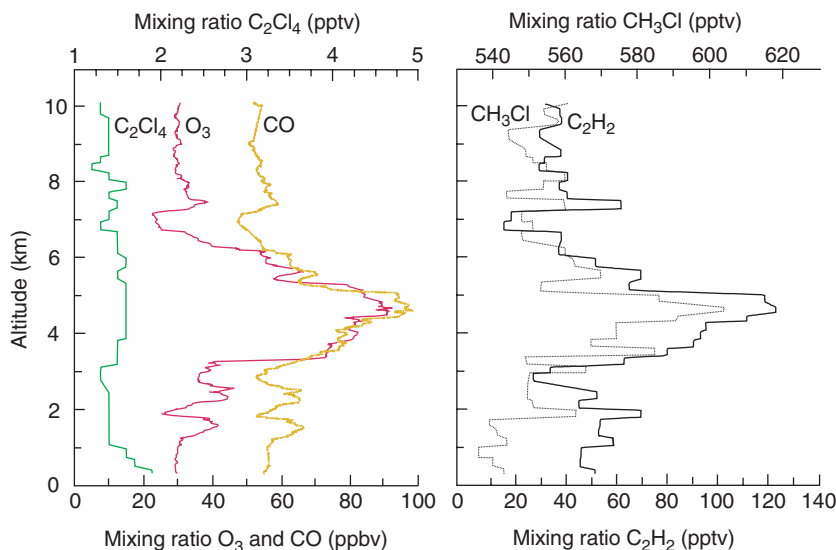
0422-F0004 **Figure 4** Composite seasonal cycle of average ( $\pm 1$ SD) ethane mixing ratios for high northern ( $30^{\circ}$ – $71^{\circ}$  N) and southern ( $14^{\circ}$ – $48^{\circ}$  S) latitudes for samples collected quarterly by the University of California, Irvine between March 1994 and March 1999.

significant database of tropospheric VOC measurements, including, NMHCs, dimethyl sulfide, halocarbons, formaldehyde, methyl peroxide, and acetone distributions (see <http://www-gte.larc.nasa.gov>). Be-

cause of their cost, these field campaigns are not numerous and they are limited in time. However, remote measurements of tropospheric trace gases from satellite platforms are still very limited in the range of gases that can be quantified. They are also associated with reduced accuracy and poor altitude resolution. Thus, *in situ* aircraft measurements presently offer the only way to sample with good resolution on large horizontal and vertical scales many of the VOCs that are present at low abundance in the atmosphere.

Most of the removal of long-lived oxidizable gases (e.g.,  $\text{CH}_4$  and methylchloroform,  $\text{CH}_3\text{CCl}_3$ ) takes place in the tropical troposphere, where abundant sunlight and high humidity enhance the formation of  $\text{OH}^{\bullet}$  from the photolysis of  $\text{O}_3$ . The composition of the tropical troposphere is particularly important because this is the predominant region from which the surviving gases and aerosols are transported upward into the lower stratosphere. Therefore, understanding the influence of tropical sources, such as biomass burning, on the production of  $\text{O}_3$  is necessary for assessing the impact of tropical fires both on the global oxidizing capacity of the atmosphere and on the radiative forcing of  $\text{O}_3$  in the upper troposphere.

It was reported above that burning of the world's forests, grasslands, and agricultural lands has a strong influence on VOC emissions. It therefore affects global atmospheric chemistry and is associated with climate change. Regional pollution episodes are known to have a significant impact on South East Asian air quality. Aircraft investigations such as the NASA GTE experiments TRACE-A (Transport and Atmospheric Chemistry near the Equator – Atlantic) and PEM-Tropics A (Pacific Exploratory Mission – Pacific)



0422-F0005 **Figure 5** Vertical profile through a layer of biomass burning pollution sampled by the NASA DC-8 aircraft near Tahiti on September 5, 1996. Mixing ratios of selected VOCs, CO, and ozone are shown.



encountered high levels of tropospheric ozone transported in fire plumes over large regions of the Southern Hemisphere. TRACE-A confirmed that biomass burning profoundly affects the chemical composition of the troposphere over the tropical South Atlantic during the Southern Hemisphere dry season, resulting in a seasonal enhancement by a factor of two in tropospheric ozone mixing ratios.

0422-P0200 The South Central Pacific region is very far from large-scale agricultural and industrial activities. Nevertheless, a variety of observations made during PEM-Tropics A have established the surprisingly ubiquitous influence of biomass burning emissions on the troposphere in this remote region. For example **Figure 5** shows a vertical profile through a thick pollution layer observed between 3 and 7 km, sampled by the NASA DC-8 aircraft near Tahiti on 5 September 1996. This layer exhibited high mixing ratios of O<sub>3</sub>, CO, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>2</sub>, and CH<sub>3</sub>Cl<sub>2</sub>, but C<sub>2</sub>Cl<sub>4</sub> remained at background levels (**Figure 5**). The lack of enhancement of C<sub>2</sub>Cl<sub>4</sub> in the plume indicates that urban pollutants did not contribute substantially. Instead, the observed signature of pollution tracers reveals distant biomass fires to be the source. Winds at the plume altitude were predominantly from the west and calculated indicated meteorological trajectories indicated that the plume air was over a region of Southern Africa where seasonal burning was taking place 9–10 days prior to being sampled near Tahiti.

## See also

**Chemistry of the Atmosphere:** Chemical Kinetics (0099). **Tropical Meteorology:** Intertropical Convergence Zones (ITCZ) (0417). **Tropospheric Chemistry and Composition:** Aerosols/Particles (0438); Aliphatic Hydrocarbons (0423); Aromatic Hydrocarbons (0424); Biogenic Hydrocarbons (inc. isoprene) (0425); Oxidizing Capacity (0437).

## Further Reading

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