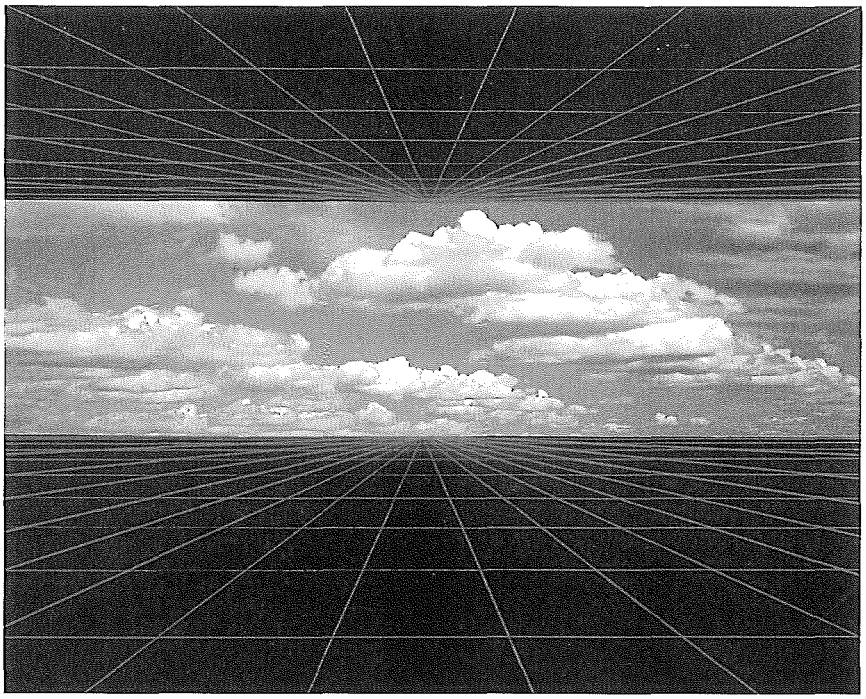
Forschungszentrum Jülich

Ralf Koppmann and Dieter H. Ehhalt (Editors)

Volatile Organic Compounds in the Troposphere



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Ralf Koppmann and Dieter H. Ehhalt (Editors)

Volatile Organic Compounds in the Troposphere

Proceedings of the Workshop on
Volatile Organic Compounds in the Troposphere
held in Jülich (Germany) from 27 – 31 October 1997.

In Cooperation with

Stiftung Deutsch-Amerikanisches Akademisches Konzil
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Network of Young Scientists in the Field of Atmospheric Chemistry

and

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PREFACE

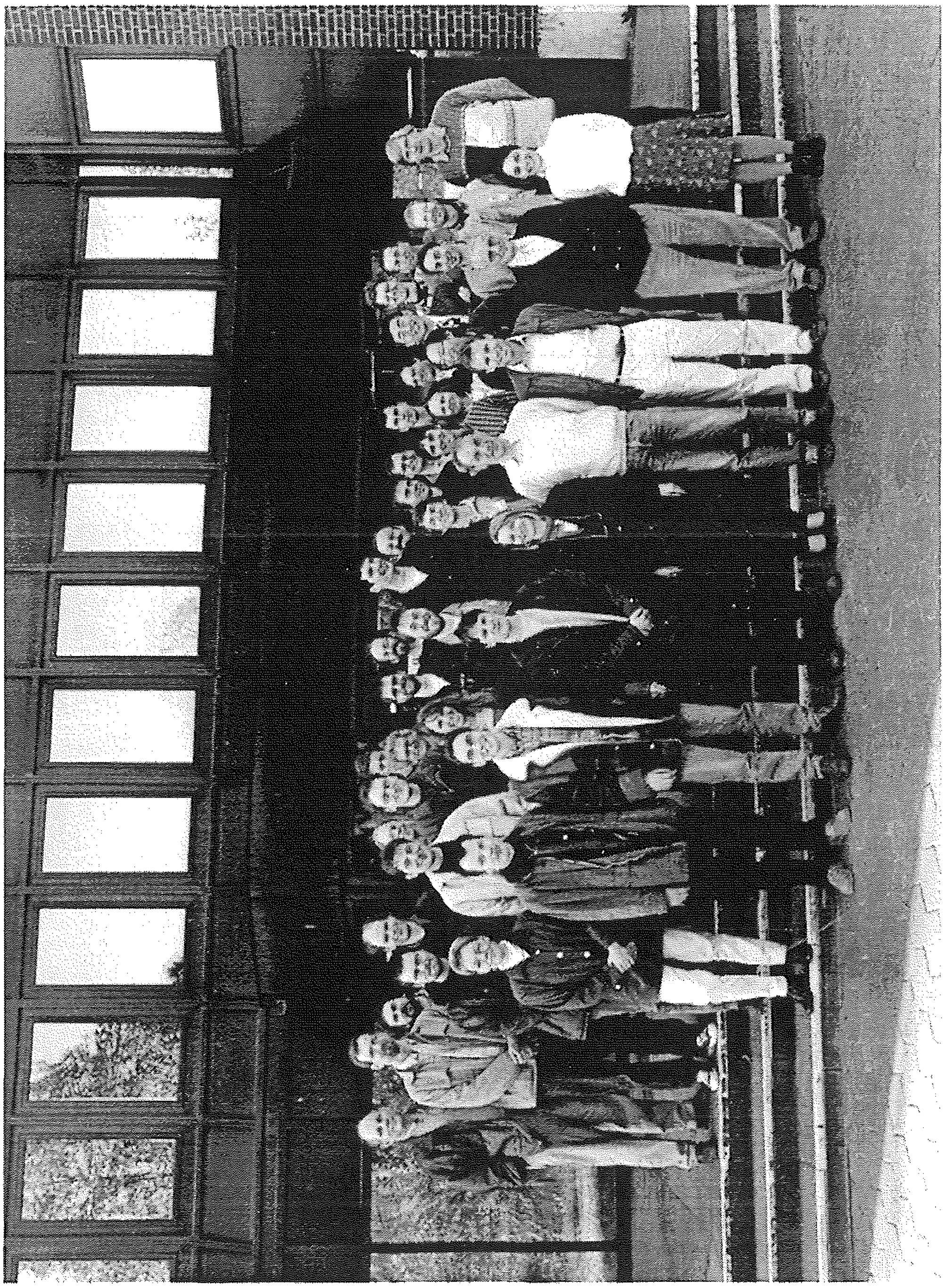
Atmospheric chemistry is a fast developing field. One of the fastest developing components within it is the research on volatile organic carbon, VOC. The large impact of VOC on atmospheric chemistry, their usefulness as diagnostic tracers for transport, chemical pathways and distribution of sources, along with the need for highly interdisciplinary research make the VOC a very attractive topic for young scientists in our and neighboring fields.

Because of the multitude of efforts going on in the different disciplines it is difficult to keep track of all the developments. The idea of this workshop was to provide a forum for young scientists to learn about the concepts and techniques in the neighboring disciplines, and even more important, to develop new ideas which would lead to future cooperations. I am happy to report that the workshop succeeded in both aspects as evidenced by a lively exchange of graduate students and post docs between the two countries resulting in a number of cooperations and joined papers.

The proceedings present the lectures introducing the various subject areas of VOC research at the workshop. It also includes the reports of three study groups, in which the young scientists, with some help from the more established attendees, tried to summarize some of the current issues and open questions in the field of VOC research.

D. H. Ehhalt

Dieter H. Ehhalt



FOREWORD

To an ever greater extent science and research are being judged on their ability to incorporate their results into questions of international relevance. This is particularly true of atmospheric chemistry which is faced with the global consequences of anthropogenic emissions and which sees its results channelled into far-reaching political decisions. In this, as in all scientific fields, a wide-ranging but equally closely-knit network of scientists is the way to guarantee the best possible approach to dealing with urgent questions.

In order to foster and develop scientific cooperation it is essential to integrate young scientists into this network at an early stage. The Research Center in Jülich and the National Center for Atmopheric Research (NCAR) in Boulder, Colorado, have been working together intensively for a long time. By way of workshops entitled „Networks of Young Scientists in the Field of Atmospheric Chemistry and Global Change" they have successfully realized the idea of fostering contacts amongst the younger generation of academics.

The participation of the greatest possible number of young scientists from Germany and the USA working on the topic of the first workshop, „Volatile Organic Compounds in the Troposphere", led to the establishment of a new „network" and extended the existing one. Apart from exchanging ideas on the subject, both in plenary sessions and small groups, it was possible to discuss the issues currently commanding the attention of the young participants, which they summarized as follows: „The greatest hurdles [the young scientists] face include a broad perception of their research fields, identifying the significant and relevant research questions, and developing the network of contacts needed to successfully investigate these questions [...]. The contacts [established] provide a linkage between names and faces which will be very helpful in continuing these relationships [...]"

One of the tasks of the German-American Academic Council Foundation (GAAC) is to stimulate and support projects which promise to create lasting contacts between young academics in both countries. The first workshop run by the FZ Jülich and the NCAR has proved most convincingly how this task can be tackled. On behalf of the GAAC I should like to wish the organizors every success in continuing their work in future.

Dr. Johannes Belz

German-American Academic Council Foundation, Bonn, Germany

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Invited Papers

MEASUREMENT OF NONMETHANE HYDROCARBONS IN THE ATMOSPHERE

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Today nearly all measurements of atmospheric nonmethane hydrocarbons are made by gas chromatography in combination with a preconcentration step. Depending on measurement location, number and frequency of measurements and compounds to be analyzed in-situ analysis or sample collection and analysis in the laboratory are applied. State of the art techniques allow measurements with detection limits in the lower ppt range and reproducibility of a few percent for mixing ratios of a fraction of a ppb. The comparison of different instruments show that accuracy of NMHC analysis (not including errors of absolute calibration) at mixing ratios above 0.1ppb is better than 10% for most NMHC.

In this paper an overview of the most widely used methods for NMHC measurements is given and the different steps in the procedure are discussed. The two steps with the largest contribution to overall uncertainty of NMHC measurements are sample collection and removal of water, carbon dioxide and ozone from the sample. But also separation efficiency is of key importance for reliable and correct measurements, especially for components with low mixing ratios in complex samples, e.g., urban or semi-urban air. Overlapping peaks with other minor components and tailing of major components often limit the accuracy of analysis of minor constituents in atmospheric samples.

1 Introduction

Volatile organic compounds (VOC) are important constituents of the atmosphere. They directly and indirectly affect the oxidative capacity of the atmosphere and thus influence the atmospheric residence times of many other important atmospheric trace constituents. They are precursor for environmentally harmful photo-oxidants, especially ozone. Some VOC have a direct adverse impact on the environment. However, the most important environmental impacts of VOC, including ozone formation, results from complex chemical reactions in the atmosphere. Consequently, the relationship between VOC emissions, atmospheric VOC concentrations and photo-oxidant levels is quite complex. Thus reduction and control strategies for ozone and other photo-oxidants require a detailed understanding of the relevant processes.

The actual levels of VOC and photo-oxidants in the atmosphere are the result of complex interactions between emissions, atmospheric transport and dilution, and chemical reactions. Thus understanding the distribution and chemistry of atmospheric VOC and photo-oxidants is inherently linked to thorough insight into atmospheric chemistry, including transport processes.

Currently the high ozone levels observed over many heavily industrialized and densely populated areas as well as the significant ozone increase at many remote locations in the Northern Hemisphere since the turn of the century are major concerns. Furthermore, it has to be remembered that understanding the distribution and chemistry of hydrocarbons in the atmosphere is important beyond these immediate problems. As consequence of the direct and indirect participation of VOC in most of the relevant reaction cycles it is impossible to understand the chemistry of

the troposphere without detailed, quantitative knowledge of the chemistry, distribution and budgets of VOC. For similar reasons studies of atmospheric VOC can also extremely valuable to gain insight into important atmospheric chemical and transport processes.

Up to the early eighties systematic studies of nonmethane hydrocarbons were, with few exceptions (Rasmussen *et al.*, 1974, 1983; Rudolph *et al.*, 1979; 1980; 1981 a and b; 1982 a and b; Cronn *et al.*, 1979; Rudolph and Ehhalt, 1981; Cronn and Nutmagul, 1982; Rasmussen and Khalil, 1982, 1983; Singh and Salas, 1982; Rudolph and Jebson, 1983, Roberts *et al.*, 1983), mainly limited to urban and semi-urban areas. During the past years the recognition of the importance of ambient VOC measurements has resulted in a tremendous increase of the number of studies of VOC in the atmosphere. During this period, a large number of different measurement techniques have been developed, although most of these methods still are in principal quite similar to the methods used 15–20 years ago. The availability of measurement techniques for VOC with high accuracy are a key prerequisite for studies of NMHC in the atmosphere. However, in spite of the numerous developments in the past years, NMHC measurements are still plagued with a number of problems.

Many details of the analytical method will depend on the purpose and type of study, e.g. number and frequency of the measurements, location, needed detection limit, reproducibility and accuracy, and of course on the compounds or groups of compounds to be analyzed (cf. Rudolph and Khedim, 1985; Rudolph *et al.*, 1986, 1989, Singh and Zimmerman, 1992). The number of varieties of different methods for the analysis of VOC in air reflects the many different intentions behind such measurements. Although it is not feasible and cannot be recommended to always develop a method specific for a given purpose, a detailed consideration of the actually needed instrument performance prior to selecting a measuring method can substantially increase the quality of the study and reduce the needed resources. This results from the conflict between different requirements, e.g., a low detection limit is not always compatible with a high reproducibility and the selection of sampling location has direct consequences for acceptable measurement or sampling techniques.

It is far beyond the scope of this presentation to discuss all the numerous varieties of VOC measuring methods in detail. Instead, a brief overview of the most widely used methods will be given and considerations to select analytical methods as well as limitations and problems of VOC measurements will be discussed on the basis of a few selected examples. The focus will be on measurements of C_2–C_{10} hydrocarbons.

2 Applications for measurements of VOC in air and consequences for the measurement technique

VOC measurements in air are made for a variety of reasons and the best suitable measurement technique strongly depends on the purpose of the study. It is tempting to introduce the two main measurement categories "regulatory" or "monitoring" and "scientific". However, the borders between these two have become rather diffuse in the past years and often a given series of measurements can be used both for regulatory and scientific purposes. A simple example is the climatology (e.g. representative seasonal or diurnal cycles) of hydrocarbons. Such data sets can serve as tools to better understand basic atmospheric processes, but they can also be used to check compliance with regulatory air quality standards, e.g. for benzene or for ozone precursors in general.

For the practical purpose of selecting the most suitable measurement technique it is more useful to consider the type of study and its intention. Examples for different types of studies are:

- Monitoring (for regulatory purposes, e.g. compliance with air quality standards or simply to establish a "hydrocarbon climatology")
- Source studies and emission measurements
- Field investigations centering around the chemistry of the atmosphere
- Tracer and diagnostic applications of hydrocarbon measurements
- Laboratory studies (reaction kinetics, simulation or smog chambers)

It is beyond the scope of this presentation to discuss the numerous different possible measurement techniques for each type of study. Instead, a few guidelines will be given which criteria to consider for the selection of an analytical method.

The first but by no means simplest step is to define the compounds or groups of compounds to analyze. Unfortunately, generalizing terms such as VOC or NMHC etc. are in this context not particularly helpful. The extremely large number of compounds and the wide range of concentrations require a specific selection of compounds based on the purpose of the measurements. As a rough guideline, we can differentiate between three different selection criteria:

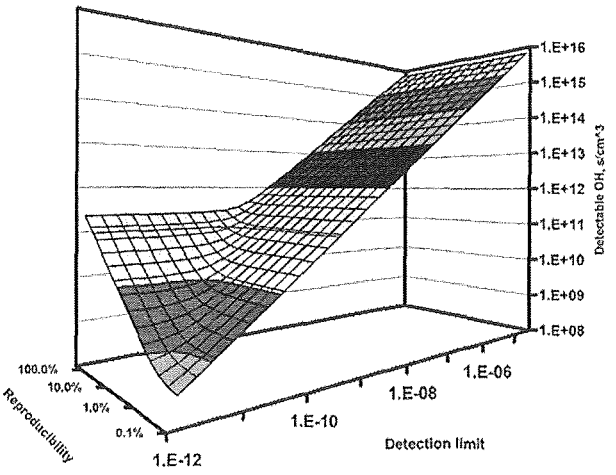
i) Monitoring of specific substances (or groups of compounds) for regulatory or health effect purposes, e.g. measurements of toxic substances such as benzene, PAN or formaldehyde. In this case both the compound selection criteria and the relevant concentration levels are directly linked to and easily deduced from the purpose of the investigation.

ii) Effect oriented investigations. For these type of studies the compounds to be analyzed are identified from considerations of their impact. For hydrocarbon this most frequently is their effect on the formation of photo-oxidants. Here a realistic definition of the compounds to be analyzed and the needed detection limits requires already a reasonable amount of knowledge about the situation to be studied.

iii)The use of trace gas measurements to deduce information about processes. In this case the selection of specific compounds and compound groups is very difficult. The amount and type of information deducible from concentrations and concentration distributions of different VOC is very difficult to assess. Moreover, very often concentration patterns for a larger group of compounds are needed to deduce useful information from hydrocarbon measurements. A number of applications has evolved during the past years, but the number of systematic studies is still very limited.

Evidently, increasing complexity of the application also results in increasingly complex relations between compounds to be analyzed, needed accuracy and detection limit. For (i) as well the relevant compounds as the needed detection limit and accuracy can be directly deduced from information such as regulatory thresholds, toxicity levels etc. For applications of type (ii) the definition of the analytical problem is less obvious, but based on a few general considerations, reasonably well defined criteria for the measurement methods can be established. E.g., a reasonable estimate of relevant compounds, detection limits and accuracy needed to study the formation of photo-oxidants or the impact of VOC on atmospheric chemistry can be based on the reactivity (e.g. rate constants for the reaction with OH radicals) of the individual hydrocarbons. Once a threshold for relevant contributions from individual compounds is defined, the needed detection limit, accuracy and the potentially relevant compounds can be deduced from this threshold. Such a threshold is to some extent arbitrary, however a reasonable value can be estimated based on the needed accuracy for the total VOC reactivity.

(a)



(b)

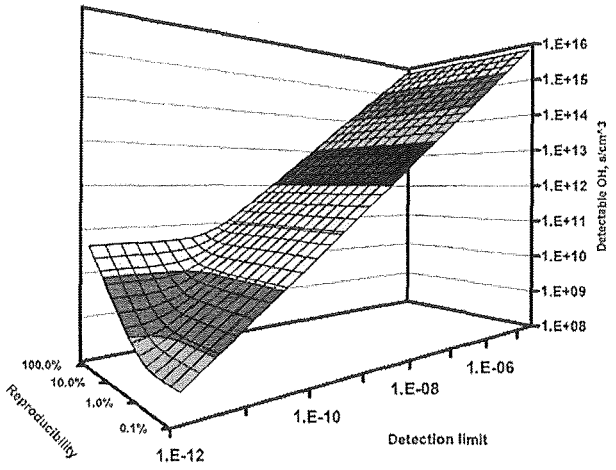


Figure 1. *Dependence of the indirectly detectable time integrated* OH *radical concentration (*∫[OH] *dt, cm*$^{-3}$*s) for a smog chamber study on detection limit and reproducibility of hydrocarbon measurement. The hydrocarbon levels are kept low in order to minimize the interference of the indicator compounds with the studied system.* ***(a)*** *"Indicator hydrocarbon" is methylcyclohexane (*k_{OH}*=1.1x10*$^{-11}$ *molecule cm*$^{-3}$*s*$^{-1}$*) with a mixing ratio of about 0.4 ppb, corresponding to an* OH *lifetime (for reaction with methylcyclohexane) of 10 s.* ***(b)*** *"Indicator hydrocarbon" is 1,3,5 trimethylbenzene (*k_{OH}*=6.1x10*$^{-11}$ *molecules cm*$^{-3}$*s*$^{-1}$*) with a mixing ratio of about 0.07 ppb, corresponding to an* OH *lifetime (for reaction with 1,3,5 trimethylbenzene) of 10 s.*

Measurements for the purpose of studying mechanisms in atmospheric chemistry and the use of VOC measurements as diagnostic tools for atmospheric processes require a completely different approach. The usefulness of a given substance as tracer in a general sense depends on the type of processes studied, the general level of understanding of the sources and sinks of such a compound and accuracy and sensitivity of available analytical techniques. One of the best known applications of VOC to study atmospheric key processes is the use of atmospheric 1,1,1,-trichloroethane measurements to calibrate global average OH concentration fields (Singh, 1977; Prinn *et al.*, 1987, 1992). More recent examples are the indirect estimates of Cl-atom concentrations based on changes in the patterns of hydrocarbon concentrations (Jobson *et al.* 1994; Rudolph *et al.*, 1996, 1997; Ramacher *et al.* 1997). There is no simple guideline to determine the required detection limit, reproducibility, or accuracy for such measurements. However, from all experience it is evident that the quality of such measurements is one of the key prerequisites for the use of VOC as diagnostic tools.

Finally, a specific application of VOC measurements should be mentioned, the use in laboratory kinetic studies to determine the concentrations of reactive radicals such as OH, Cl, or NO_3. This is a rather well established method and has been used in the past indirectly in the form of relative rate constant measurements. At present, the availability of NMHC measurement methods with very low detection limits and good reproducibility allows the determination of radicals in lab kinetic studies with very high sensitivity. E.g., an optimized technique should allow the detection of an OH-radical concentration of $10^5 cm^{-3}$ in less than half an hour (Figure 1). This is comparable with the presently available most advanced direct OH measurement methods.

One important point in designing a VOC measurement technique is the decision between online techniques (in situ instrumentation) and offline methods (field sampling and laboratory analysis). This is a rather complex question and often the decision is somewhat arbitrary. Nevertheless, there is a number of relevant criteria which have to be considered (cf. Rudolph *et al.*, 1989):

- Most important is the question whether there exists a *sampling procedure* of adequate quality and reliability. If not, the choices are to develop a new or modified sampling technique, or to use in-situ instruments. For some compounds, the present state of the art does not allow sampling at low concentrations without compromising the sample integrity. An important example is the measurement of light alkenes at concentrations below 0.1ppb. The presently used sampling methods result in the formation of artifacts in the range of several 10ppt, even if extreme care in the preparation of the sampling devices is taken (see below).

- *Sampling location and available logistics.* In general for in-situ instruments a higher amount of logistic support such as electrical power, cryogenic liquids etc. is required than for sample collection.

- *Sampling frequency, number of samples, and duration of the measurement series.* As a rule of thumb in-situ instruments are more suitable for longer, quasi-continuous measurement series with a large number of measurements at the same location. In-situ instruments can also be very suitable for mobile platforms (ship, trailer, airplane). However, in-situ measurements of VOC often have a limited time resolution, seldom better than 30 minutes per analysis, often more than 1h. For fast moving platforms such as airplanes this reduces the spatial resolution considerably. Many techniques allow collection of samples within a few minutes or less.

- *Required accuracy and reproducibility.* Use of in-situ instruments avoids the potential sample deterioration during sampling and sample storage. Moreover, the amount of samples that can be used for in-situ measurements is only limited by the method itself, not by the sample collection technique. This can be a substantial advantage for measurements at low concentra-

tions. However, many state of the art techniques for VOC measurements have sufficient sensitivity even if only relatively small sample volumes (several hundred cm^3 to some dm^3) are available. Laboratory measurements can be made under optimum conditions and several sampling techniques allow repeat analysis of aliquots of one sample.

3 Overview of VOC measurement procedure

The by far most widely used methods for NMHC measurements in air are based on gas chromatography in combination with a preconcentration step. As mentioned above, the following overview cannot include all existing varieties of NMHC measurement techniques but will consider those methods which are widely used, covering probably more than 95% of all presently used VOC measuring methods. The steps for NMHC analysis by gas chromatography are:

- *Sample collection and transport to laboratory.* (in case of in situ measurements this step is eliminated, but of course the instrument has to be set up at the measurement site).
- *Connection of sample (adsorbent tube, canister) to instrument (manifold or single sample inlet, manual or automatic changing of samples).* For in situ instruments sampling is done via an inlet line (generally flushed at a high flow rate, made of stainless steel, glass, Teflon).
- *Water/CO2 removal.* For nearly all applications water is removed, or at least substantially reduced either prior to or after the preconcentration step, in some cases also before or as part of the sampling procedure. It should be remembered that for very large samples it might be necessary to apply two drying steps, e.g., before preconcentration and after sample desorption. The amount of carbon dioxide in air is generally lower than that of water; therefore many applications do not remove carbon dioxide from the air. However, for larger samples and the use of capillary columns it is advisable to remove carbon dioxide to avoid split injections and peak broadening.
- *Sample preconcentration (cryogenic, adsorptive).* Sample preconcentration is needed for nearly all NMHC measurements, presently available detectors generally are not sufficiently sensitive to allow detection of the extremely small amount of substance in the low sample volumes which can be injected directly onto gas chromatographic columns.
- *Sample desorption.*
- *Focusing (on column, separate unit).* Often the desorbed sample is focused prior to separation to achieve a very narrow sample injection profile.
- *Desorption/injection.*
- *Separation.*
- *Detection.*

4 Discussion of the individual steps involved in VOC analysis

In this chapter, we will go backward, starting with the detection step. The rational behind this is, that the selection of the detection method to a considerable extend determines many of the other step in the analysis of VOC in air. E.g., the sensitivity of the detector determines the amount of sample needed and thus has a strong influence on the preconcentration step; the selectivity of the detector determines the needed resolution of the separation etc.

4.1 Detection

The most widely used gas chromatographic detector for VOC analysis is the flame ionization detector (FID). The required amount of sample is in the range of some 10^{-11} g. Advantages are reliability, stability, costs, easy operation, and the very high linear range of roughly six orders of magnitude. The FID is suitable for essentially all compounds containing C-C or C-H bonds. As a first approximation, the FID response does not depend on details of the chemical structure of the detected substance. This facilitates quantitation but at the same time the lack of specificity can cause serious problems due to overlapping peaks, incorrect peak identification etc. As a consequence FID detection should generally combined with high-resolution separation.

Mass spectrometry in combination with gas chromatography (GC-MS) is highly selective, yet it allows determination of a very broad range of substances in a single run. Moreover, the structural information from mass spectrometry in combination with the retention time is extremely valuable for the identification of unknown chromatographic peaks. For state of the art bench top GC-MS instruments the required sample size is in the range of 10^{-10}–10^{-12}g. Specific operating conditions such as Selective Ion Monitoring (SIM) and chemical ionization allow detection limits for individual substances well below 10^{-12} g. The disadvantages of mass spectrometric detection are the still rather high costs and the, compared to many other GC-detectors, rather demanding operation, including the evaluation of the mass spectra. Furthermore, the response of mass spectrometers is highly substance specific. Therefore quantitation requires substantially more effort for GC-MS detection than for e.g. GC-FID. For this reason, mass spectrometric detection is sometimes combined with other detection methods (see below).

Photo ionization detectors are occasionally used for substances with high photo ionization cross sections such as aromatics and aldehydes or many of the alkenes and dienes. Under optimum conditions the required amount of a substance suitable for GC-PID analysis can be below 10^{-12} g. Moreover, the selectivity of photo ionization detection can be tuned by varying the photon energy, i.e. change of the type of lamp. However, the presently available photo ionization detectors are not very stable in their response and require substantial maintenance and frequent calibrations if used for quantitative analysis. Today photo ionization detection is mainly used for a few specific measurement problems but should not be considered as a general-purpose detector such as FID or MS.

The reducing gas analyzer (RGA) belongs also into the category of detectors that are useful for specific applications but cannot be recommended for VOC analysis in general. In principal, the RGA detects all gases which reduce HgO to elementary Hg. The mercury vapor is detected by atomic absorption spectroscopy. Reduction efficiency towards HgO depends for most trace gases strongly on temperature, this allows to some extent tuning of the sensitivity of the RGA. RGA sensitivity for aldehydes, many alkenes, dienes etc. is comparable to flame ionization detection, for strongly reducing compounds substantially lower, down to some 10^{-12}g. As far as

stability and linearity is concerned, the presently available RGA is by far inferior to the FID. Furthermore, the RGA is one of the more expensive GC-detectors, although less expensive than mass spectrometry.

Electron capture detectors have a remarkable sensitivity, for many halogenated compounds detection limits in the range of some 10^{-13} to 10^{-14} g can be achieved. Disadvantage of the ECD is the limited linear range and the extremely compound specific sensitivity. Although not suitable for VOC analysis in general, its high sensitivity makes the ECD the detector of choice for measurements of many halogenated compounds and other VOC with highly electron attracting functional groups, e.g. peroxyacetyl nitrates.

There is a number of detectors that are specific for hetero-atoms or certain functional groups, e.g. nitrogen, halogen, sulfur, and phosphorous specific detectors. Other detection methods combined with GC are flame photometry and atomic emission spectroscopy. These detectors are very useful for a number of specific applications. However, as result of the decreasing cost of MS detection and the increasing sensitivity of bench top GC-MS systems, MS detection becomes more and more competitive with many of the selective detectors.

Finally, it should be mentioned, that several applications use more than one detector. Generally with the intention of more specific peak identification or to increase sensitivity by use of highly specific detection. However, again a result of the decreasing costs and increasing sensitivity of MS detection, such combinations are at present only rarely used. One of the most useful detector combinations is the coupling of MS and FID. The MS provides very detailed qualitative (structural) information for each peak, whereas the FID allows reasonable first order quantitation, even for unidentified peaks.

4.2 Separation

The most widely applicable columns for VOC separation are wall coated open tubular (WCOT) columns. Generally, they are used for compounds with boiling points comparable or higher than butane, but there are also a few applications of WCOT columns for analysis of C_2 and C_3 hydrocarbons. The wide range of commercially available capillary columns (diameters: 0.1–0.5mm, film thickness from 0.05–3µm, length typically between 15m and 120m) of high quality allows to select a suitable column for nearly all specific separation problem. However, due to the problems connected with interfacing the preconcentration step (see below) and the capillary column with minimum peak broadening, separation of low boiling substances generally is done on wide bore (0.32mm i.D.) columns with relatively thick films of stationary phase. Most widely used as general-purpose columns are cross linked stationary phases of low polarity, e.g. Rtx-1, DB-1, or HP-1 and Rtx-5, DB-5 and HP-5.

For the separation of low boiling VOC, very often porous layer open tubular columns (PLOT) are applied, e.g., GS-Q, GSC or various types of modified aluminum oxide columns. i.D. is generally 0.32mm or sometimes 0.5mm, typical length 15–30m, sometimes 60m. Although these columns do generally not have as good resolutions as WCOT columns, there high retention for very low boiling VOC at reasonable temperatures and their high specificity make them very useful for measurements of light VOC.

Support coated open tubular columns (SCOT), micro-packed and conventional packed columns are nowadays only seldom used, mostly for special applications or as precolumns e.g. for water or CO_2 removal.

Atmospheric concentrations of most VOC seldom exceed levels of several ppb, often relevant levels of VOC are only a few ppt, occasionally even less. In order to have sufficient amount of sample for detection, quantification or, in the case of GC-MS, also identification, generally sample volumes ranging from some cm^3 to some dm^3 are needed. Since most gas chromatographic methods, especially those using high resolution capillary columns, do not allow direct injection of such large air volumes, some kind of preconcentration step is needed. This preconcentration step can range from "on column enrichment" for small samples of a few cm^3 to multi-step preconcentrations of several dm^3 of air. For some applications the preconcentration step is integrated into the sample collection procedure (adsorptive sampling).

Preconcentration is usually done on small, packed columns (length 5–30cm, i.D. 1–5mm) generally made of stainless steel, glass or Teflon tubing, but also short pieces of capillary column, especially PLOT columns can be used. The dimension of the preconcentration columns depends on sample volume, sampling rate, type of sorbent, temperature and compounds or range of compounds to be analyzed. Most often used sorbent materials are glass beads at low temperatures (generally liquid N_2- or Ar-temperatures), porous polymers (e.g. TENAX), or carbonaceous sorbents (e.g. Carbosorb or Carbotrap).

Preconcentration on glass beads at low temperature has the advantage that desorption can be made at moderate temperatures thus minimizing sample decomposition. Moreover, glass beads only contribute marginally to blank values. The disadvantage of this preconcentration method is not only the need of cryogenic liquids, but also the very unselective preconcentration, i.e. apart from oxygen, nitrogen, methane, and the lighter rare gases nearly all other constituents of air, including carbon dioxide and water, are enriched together with the VOC.

Preconcentration on porous polymers and carbonaceous sorbents can be more selective. Often the sampling of water and carbon dioxide can be avoided, which eliminates the need for other steps to remove these substances from the sample (see below). Another advantage of these sorbents is the possibility to collect many VOC, with the exception of some very volatile compounds, at room temperature. For this reason, these types of sorbents are very often used for adsorptive sampling in the field. The main disadvantage of porous polymers and carbonaceous sorbents is the formation of substantial amounts of artifacts during sampling, storage and desorption. These artifacts strongly depend on the type of sorbent and the desorption conditions. There is a substantial number of compounds which are not influenced by the artifact formation, but one has to be aware that type and magnitude of potentially interfering artifacts can only be determined by testing the complete procedure, including sampling, eventual storage and desorption.

Samples are usually desorbed by increasing the temperature of the preconcentration column and simultaneously flushing the column with an inert gas to transfer the desorbed substances onto the separation column or a "focusing" unit (see below). Generally, the flow direction during desorption is reverse to the flow direction during preconcentration. Otherwise, substances trapped at the head of the trap during preconcentration have to migrate through the complete adsorption column which might result in extreme peak broadening for strongly adsorbed compounds during sample desorption.

Coupling of the preconcentration column and the separation column in a way that sample desorption and transfer does not result in peak broadening presents several problems. Sample desorption, and thus the heating rate of the preconcentration column, has to be fast enough to ensure quasi-instantaneous injection. For some applications, the gas flow is stopped during desorption to minimize the gas volume into which the sample is desorbed. However, the general

problem of interfacing preconcentration units with high-resolution capillary columns is the incompatibility of the dimensions of preconcentration and separation column. In order to allow the preconcentration of a sample of several hundred cm^3 within a reasonable time, the diameter of the preconcentration column has to be at least a few mm. Any sample eluting from such a column will be spread into a volume that is too large for injection onto a high resolution capillary column without a focusing step. For some applications only part of the gas flow from the preconcentration column is transferred to the separation column (split). This reduces the injection volume. However, the amount of sample injected is reduced by the same factor and the lower limit of detection is increased accordingly.

Today, for most applications the desorbed samples are focused either on a very small column with a diameter compatible with the separation column. Otherwise, the focusing step can be very similar to the preconcentration step. Another possibility is to focus the desorbed sample at the head of the separation column. Either a small part of the column is cooled to temperatures where migration of analyte is negligible, or the starting temperature of the temperature-programmed separation is kept sufficiently low to focus the complete sample at the head of the column.

The interfacing between preconcentration and separation column is presently one of the main problems which limit the use of narrow- or micro bore columns for the analysis of atmospheric NMHC. This problem is extreme for the analysis of low and medium molecular weight VOC, whereas for heavier VOC on column focusing on narrow bore columns is feasible.

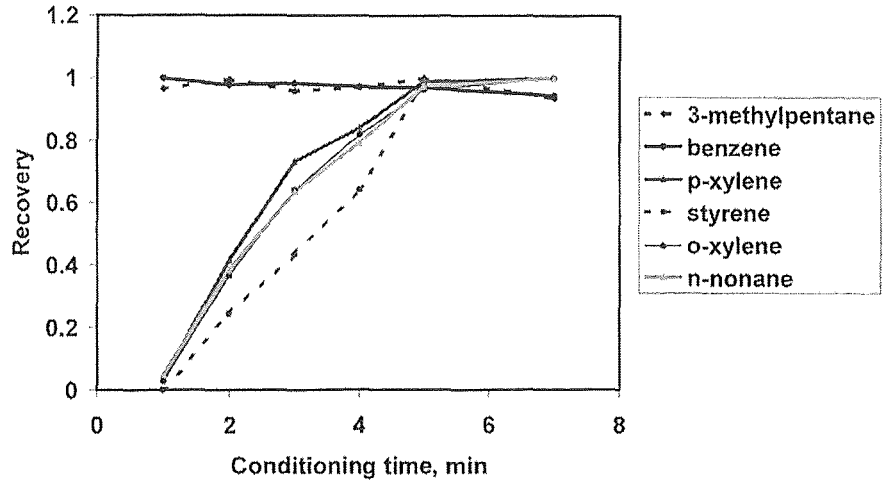
4.4 Water and carbon dioxide removal

An air sample of 1 dm^3 contains up to some ten cm^3 of water vapor and 0.35 cm^3 of carbon dioxide. In order to reduce the sample size sufficiently for separation on a capillary column, water and, in most cases, also carbon dioxide has to be removed from the sample. Several different methods are used to remove water from the samples:

- *Chromatographic separation.* The most widely used and simple method is the combination of adsorptive sampling with a preseparation of VOC and water (see above). As pointed out, this method is not suitable for the analysis of VOC with extremely high volatility. There are a few applications which combine cryogenic preconcentration with a chromatographic preseparation step to remove water and carbon dioxide from the sample (cf. Rudolph et al 1989).
- *Freeze out of water.* The water content of a sample can be reduced by passing air through a tube kept at low temperatures. If the dimensions of the tube and the flow rates are properly matched, the water content of the air can be reduced to roughly the equilibrium water vapor pressure at the temperature of the water trap. The main problem is to avoid the loss of analyte due to adsorption on the surface of the water trap. Preconditioning of the trap with some hundred cm^3 of sample air can reduce this problem substantially (Figure 2). Furthermore, the surface of the cooling trap should be as clean and inactive as possible. Under these conditions the reduction of the dew point of air samples to –40°C is possible without loss of hydrocarbons of up to 10 C-atoms (cf. Figures 3a and b). However, it is important to test such water traps regularly since even minor changes in the surface properties of the trap can have a substantial impact on the accuracy and reproducibility of the measurements.

Selective adsorption or chemisorption (drying agents). The use of drying agents is limited both by the risk of contamination and of loss of substance on the drying agent. Precleaning and conditioning of the drying agents can sometimes avoid contamination problems. Increasing the temperature of the drying agent can reduce the loss of analytes. However, there

(a)



(b)

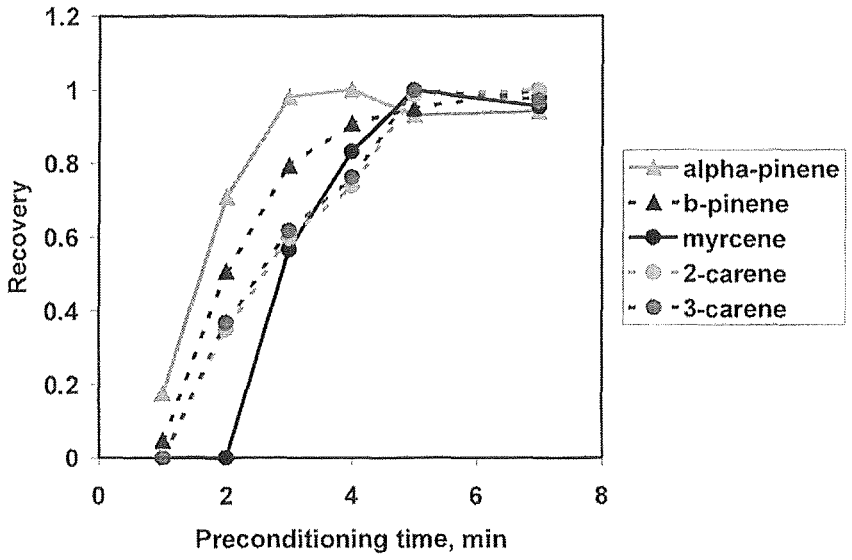
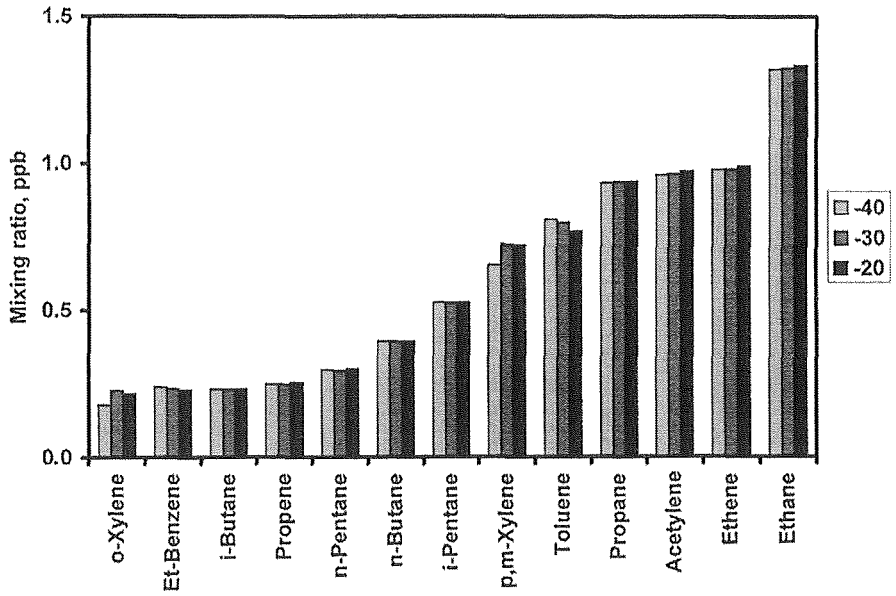


Figure 2. Sample recovery as function of conditioning time for a water trap at –40°C. Flow rate during conditioning is 30ml/min.

(a)



(b)

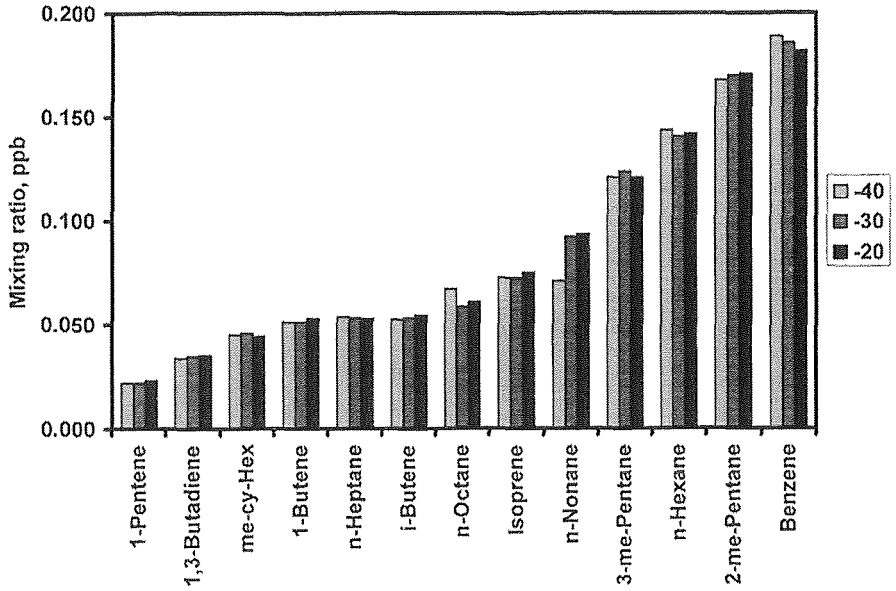


Figure 3. *Dependence of measured mixing ratio from temperature of water trap.*

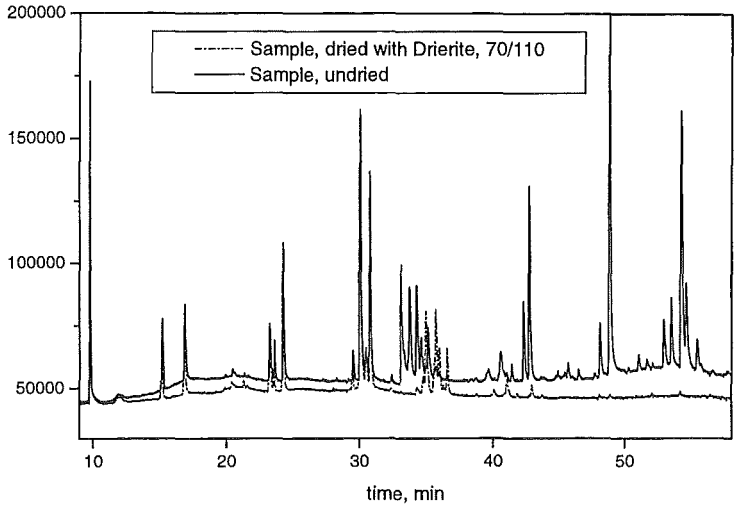


Figure 4. Comparison of chromatograms of air dried with drierite and undried air (K. von Czapiewski, private communication).

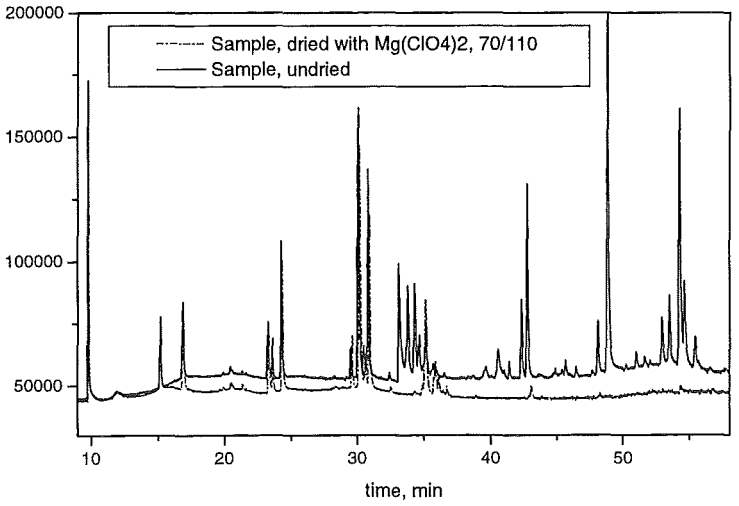


Figure 5. Comparison of chromatograms of air dried with magnesium perchlorate and undried air (K. von Czapiewski, private communication).

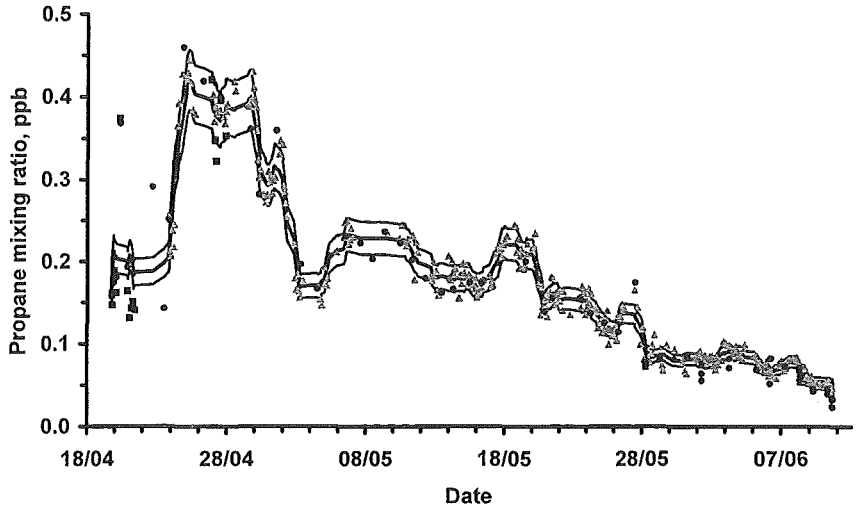


Figure 6. Time series of propane *mixing ratios measured in spring 1995 at Ny Alesund (Spitzbergen). Triangles and squares show the results from in-situ instruments, circles from canister sampling and analysis in the laboratory. The solid line are the mean of the in-situ measurments and the mean +/– the standard deviation (B. Ramacher, private communication).*

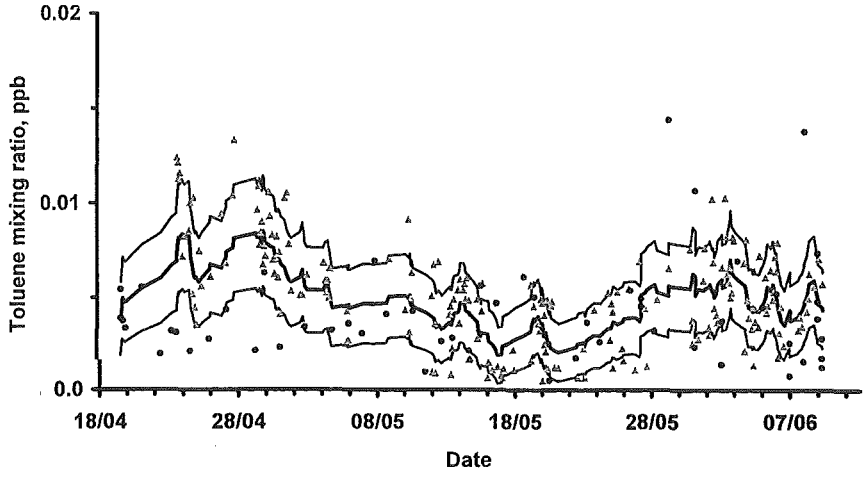


Figure 7. Time series of toluene *mixing ratios measured in spring 1995 at Ny Alesund (Spitzbergen). Triangles show the results from in-situ instruments, circles from canister sampling and analysis in the laboratory. The solid line are the mean of the in-situ measurments and the mean +/– the standard deviation (B. Ramacher, private communication).*

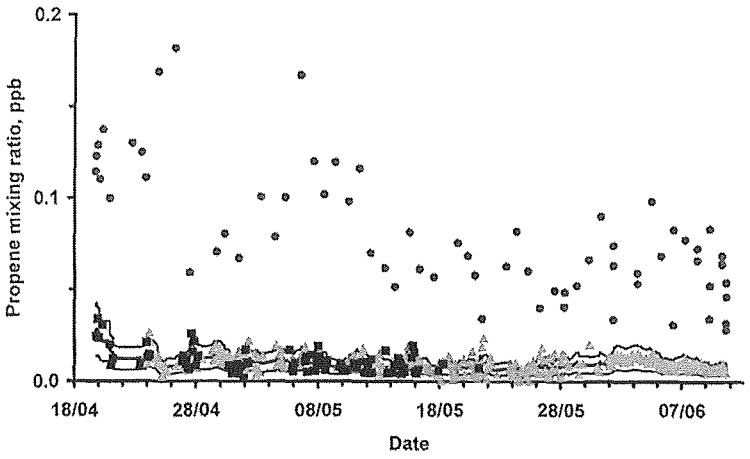


Figure 8. *Time series of* propene *mixing ratios measured in spring 1995 at Ny Alesund (Spitzbergen). Triangles and squares show the results from in-situ instruments, circles from canister sampling and analysis in the laboratory. The solid line are the mean of the in-situ measurments and the mean +/– the standard deviation (B. Ramacher, private communication).*

- are obvious limitations of acceptable temperatures and nearly all drying agents cause losses of heavier hydrocarbons (roughly above C_8 or C_7) and highly polar substances. Some examples for the possibilities and limitations of the use of drying agents are given in Figures 4 and 5.
- *Diffusion dryers.* In the past years drying of air samples by diffusion through a semi-permeable membrane (NAFION type membranes) has been used for a number of applications. The advantage is the suitability of this method for continuous operation and the ease of operation. Disadvantage is the high risk of sample loss and contamination. If large volumes of sample air are available (e.g. in-situ instruments) conditioning of the dryer can reduce sample losses and contamination.

For smaller samples (roughly below $100cm^3$), removal of carbon dioxide is less essential than water removal. However, in case of large sample volumes or narrow bore columns carbon dioxide can cause severe chromatographic problems. Carbon dioxide is either removed by chromatographic methods or by chemisorption (e.g. hydroxides on supports with high surface areas). Similar to drying agents, reagents reacting with carbon dioxide may also cause loss of sample or contamination. Good results are obtained with potassium carbonate at roughly 70°C.

4.5 Ozone removal

In most air masses substantial concentrations of ozone can be found. During preconcentration of a sample, ozone can either react with the packing of the preconcentration column causing artifacts or with adsorbed sample causing losses of unsaturated compounds.

Some sampling and preconcentration methods by themselves reduce ozone concentrations without any specific, additional steps. In stainless steel sampling cans ozone rapidly decays

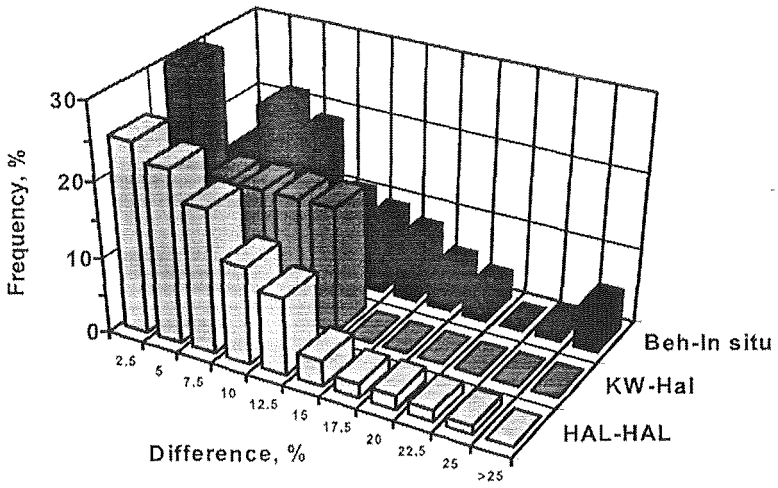


Figure 9. *Probability distribution for the difference between in-situ instruments and canister sampling for* propane *measurements made at Ny Alesund (Spitzbergen) in spring 1995 (B. Ramacher, private communication).*

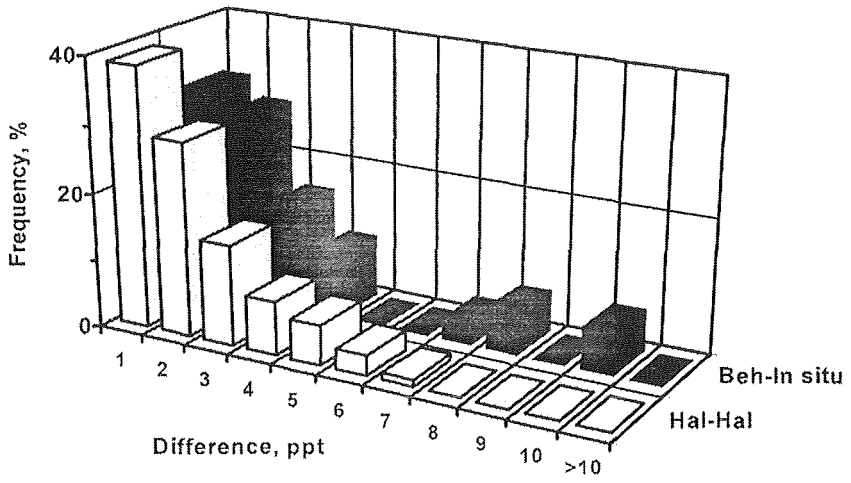


Figure 10. *Probability distribution for the difference between in-situ instruments and canister sampling for* toluene *measurements made at Ny Alesund (Spitzbergen) in spring 1995 (B. Ramacher, private communication).*

Table 1: *Stability of hydrocarbons in stainless steel canisters during storage for about 1000 h*.*

Compound	Average change (%)	Variability (%)
Acetylene	7.0	3.4
Ethene	2.8	12.7
Ethane	4.1	3.6
Propene	0.6	5.2
Propane	0.8	2.4
i-Butane	1.5	3.4
n-Butane	0.6	1.9
i-Pentane	1.2	3.0
n-Pentane	1.8	1.4
Isoprene	16.0	14.4
n-Hexane	–2.2	5.6
Benzene	–0.8	2.5
n-Heptane	–8.6	5.9
Toluene	–9.5	11.3

* Comparison of two series of measurements (total of 300 samples from semi rural areas), mixing ratios were in the range from 0.02 ppb to 24 ppb, negative changes indicate a decrease with time

Table 2. *Comparison of in-situ measurements with results from the analysis of samples collected in stainless steel canisters.*

Compound	Average difference (%)	Variability (%)
Acetylene	3.6	4.5
Ethene	0.9	2.8
Ethane	0.1	2.4
Propene	0.0	6.1
Propane	0.1	1.3
i-Butane	1.3	1.4
i-Pentane	1.4	3.5
n-Pentane	0.1	2.1
Isoprene	1.0	10.7
n-Hexane	2.2	2.0
Benzene	0.8	1.7
n-Heptane	0.7	8.9
Toluene	9.6	3.7

* Results from 4 pairs of measurements of semi rural air with mixing ratios between 0.03 ppb and 7 ppb

and usually ozone is reduced to insignificant levels already after several minutes. Also stainless steel inlet and transfer lines can cause a sufficient reduction of the ozone concentration to avoid sample degradation (Koppmann *et al.*, 1995).

However, for a substantial number of applications ozone has to be removed in an additional step. Different types of "ozone scrubbers" have been used (cf. Hoffmann, 1992; Helmig and Greenberg, 1994; Calogirou *et al.*, 1996, Wedel *et al.*, 1996), the most promising and generally applicable ozone removal procedure seems to be the addition of an excess of NO to the sample gas (Wedel *et al*, 1996). Ozone rapidly reacts with NO to form NO_2 which is considerably less reactive towards nearly all VOC than ozone.

4.6 Sampling

Rudolph *et al.* (1990) has given an overview of sampling methods for the analysis of organic compounds in air. Here only sampling in stainless steel cans will be discussed. Sample collection in stainless steel canisters with metal bellows valves is one of the most widely used method to sample air for the analysis of light and medium molecular weight hydrocarbons and a number of other trace gases (CO, H_2, N_2O, chlorofluoro carbons etc.).

The main advantage of this sampling technique is the easy sample collection in the field. Disadvantages are the risk of a loss of highly polar VOC and hydrocarbons of very low volatility on the walls of the sample container. Furthermore, there is artifact formation for light alkenes in stainless steel canisters. Although the artifact levels in thoroughly conditioned canisters are rather low, in the range of several ten ppt, these artifacts present a serious problem for measurements at remote locations. Examples of a comparison between results of in-situ measurements and canister sampling are shown in Figures 6–8. In many hydrocarbons the results agree within the estimated uncertainty of the measurements (cf. Figures 9 and 10). However, for propene there is a systematic difference of on average around 50 ppt with a broad scatter ranging from 20 ppt to roughly 100 ppt. It should be noted that the extent of alkene artifact formation in stainless steel cans depends in a very complex manner on pretreatment of the sampling cans, water content of the collected sample, and storage time.

Tables 1 and 2 compare the results of samples collected in a semi rural area simultaneously in stainless steel canisters and analyzed either directly after sampling or 40 days later. For these conditions sampling in stainless steel canisters is not only suitable for the analysis of alkanes, alkylbenzenes and isoprene, but also the results for light alkenes give no indication for systematic changes due to artifact formation in sampling canisters. Obviously, for mixing ratios of several hundred ppt and higher that are typical for semi-rural and urban areas, the highly variable alkene artifacts in the range of some ten ppt are no longer visible as systematic bias, but result in a higher variability of the measurements. It is important to recognize that tests of sampling or analytical procedures made under urban or semis rural conditions cannot be extrapolated to background conditions with very low mixing ratios.

5 Accuracy

The accuracy of measurements can only be determined by comparison of results obtained by independent methods. For analysis of hydrocarbons in the atmosphere this is only partly possible since for most VOC, gas chromatography in combination with a preconcentration step is the only suitable technique. Thus it is nearly impossible to use completely independent techniques for an assessment of the accuracy of VOC measurements. Therefore the following discussion will

concentrate on the comparison of the results from several different, but nevertheless more or less similar, instruments. The results of the measurements presented in this chapter are based on the same absolute calibration, but different reference gases were used. Uncertainties of absolute calibration will not be discussed in this paper.

Figure 11 compares the result of NMHC measurements with similar, although not completely identical instruments. Both instruments use cryogenic preconcentration and focusing steps, separation is done on an aluminum oxide PLOT column and the detectors are FIDs. In some details the instruments differ, e.g., the carrier gas flow rate and the temperature program. Thus the separations are not completely identical. The results shown are from two measurements of a semi remote air sample with the same instrument versus the results from the second instrument. The size of the symbols corresponds to a relative reproducibility of ±3%, correspond-

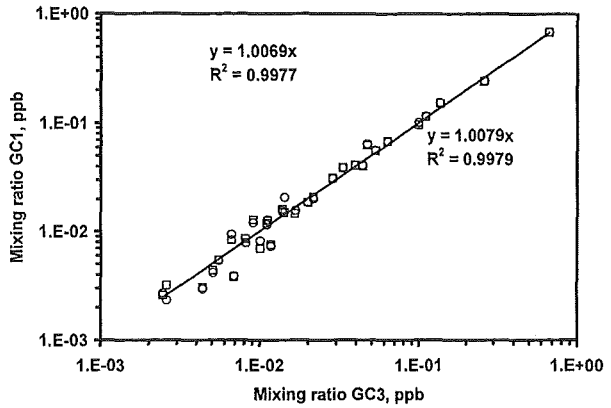


Figure 11. *Comparison of NMHC mixing ratios measured in the same sample with two different GC-systems. Both GCs use an aluminum oxide column for separation (B. Ramacher, private communication).*

ing roughly to the reproducibility of both instruments. Indeed, the symbols indicating the two measurements with the same instrument (squares and circles) nearly always overlap. Above 20 ppt there is only one result where the two instruments differ by more than 5%, in most cases the agreement is better than 3%. However, at mixing ratios below 20ppt, the results from the two different instruments differ often by more than 20%. Uncertainties in the range of several 10% can be expected for VOC measurements at mixing ratios below 20ppt. Nevertheless, it is worthwhile to notice that the reproducibility of the measurements is significantly better than the accuracy derived from the comparison of two similar instruments.

In Figure 12, results from an instrument (GC-5) with a different type of separation column (DB-1) are included in the comparison. For mixing ratios exceeding 300ppt, in general the results from the three instruments agree within the reproducibilities of a few percent. However, for lower mixing ratios the differences for some compounds are significantly higher than expected from the reproducibilities. In some cases, the reasons for the discrepancies could be identified, e.g., overlap and co-elution of different substances. However, a number of cases remain with no apparent explanation for the large deviations.

A comparison of the measurements of 10 samples (semi urban to urban air) with the three gas chromatographs is shown in Figures 13a–c. Plotted are the average relative differences

between the results obtained with the different instruments. For mixing ratios above 100ppt the differences are generally in the range of 10% or less. Significant exceptions are the xylenes and ethylbenzene. However, on aluminum oxide plot columns these peaks are rather broad and these substances, the average differences are compatible with the estimated accuracy (not including types of columns are not very suitable for the analysis of heavier alkylbenzenes. Apart form these

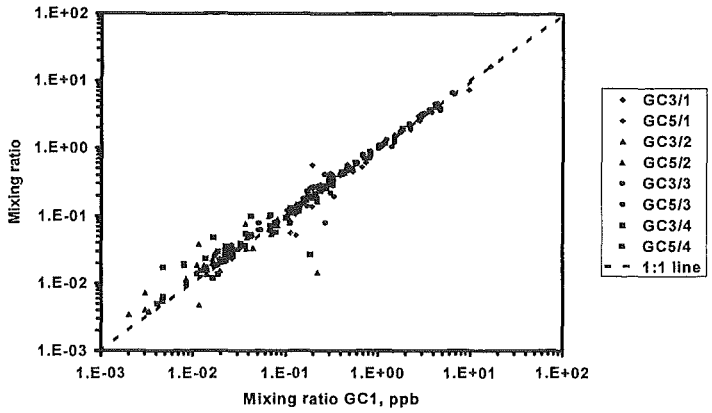
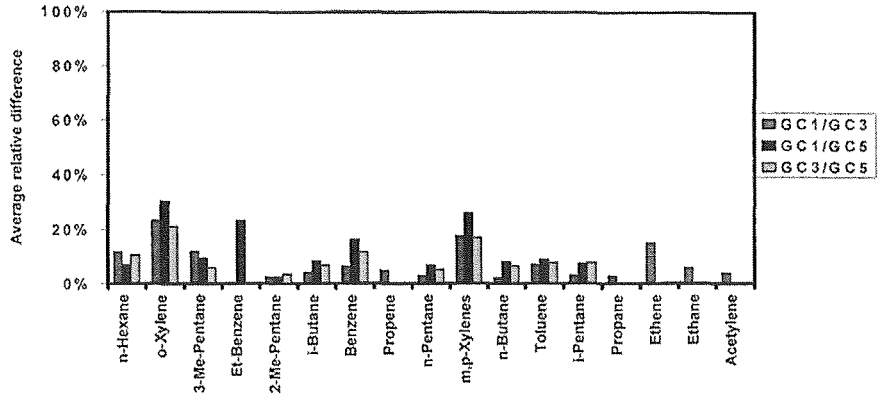


Figure 12. Comparison of NMHC mixing ratios measured in four samples sample with three different GC-systems. GC-1 and GC-3 are equipped with an aluminum oxide columns for separation, GC-5 with a DB-1 column.

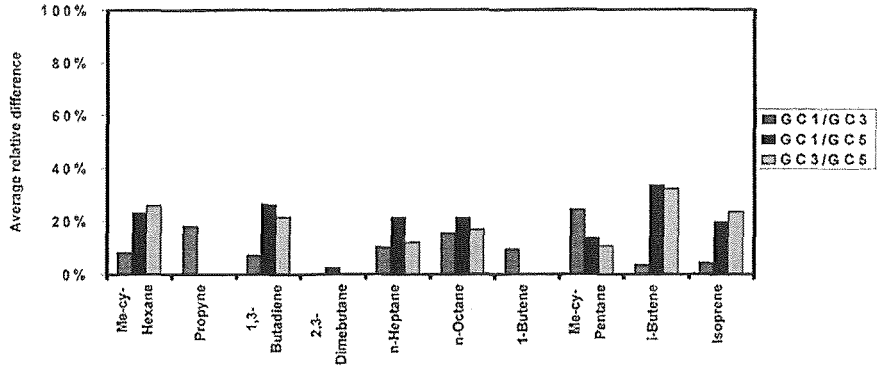
absolute calibration) of 5–10% for the instruments. It should be noted that, due to error propagation, an accuracy of 10% corresponds to an average difference of 14% (10%x$\sqrt{2}$). For compounds with mixing ratios in the range of 40ppt to 100ppt the results are similar, although one has to accept on average slightly less favorable accuracy, on average around 10–15 %. For substances with mixing ratios of less than 40ppt one can expect higher relative differences due to an increased uncertainty for measurements at low mixing ratios. Nevertheless, the average deviations are in several cases substantially larger than expected from the estimated accuracy of the individual measurements. The detection limits of the measurements are in the range of a few ppt and reproducibility of measurements at mixing ratios in the range of several ten ppt is on average about 10–20%. Clearly the occurrence of average differences in the range of 40–60% cannot be explained by a reduced reproducibility due to low mixing ratios alone. Most likely explanation of the reduced accuracy are unrecognized overlapping peaks, difficulties in the evaluation of small peaks overlapping with the tailing of major peaks and the impact of baseline drift on peak evaluation. Nevertheless, an average accuracy (not including absolute calibration) in the range of 30%, in several cases substantially better, seems reasonable for measurements of VOC mixing ratios of some ten ppt in a complex sample.

Figure 13. Average relative difference between NMHC measurements made with three different GC-systems (details see caption figure 12). The average is calculated from measurements of ten different samples. For averaging the absolute values (sign free) are used. Thus the differences include both systematic bias and random variations. (a) Compounds with mixing ratios above 100 ppt. (b) Compounds with mixing ratios between 40 ppt and 100 ppt. (c) Compounds with mixing ratios below 40 ppt.

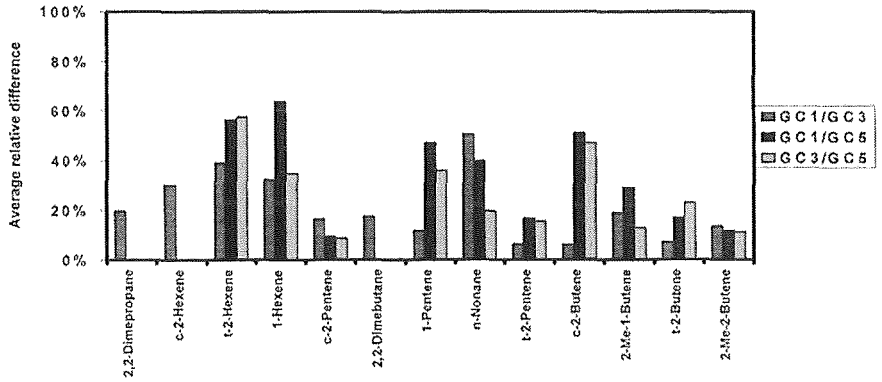
(a)


100%
80%
60%
40%
20%
0%
Average relative difference
GC1/GC3
GC1/GC5
GC3/GC5
n-Hexane
o-Xylene
3-Me-Pentane
Et-Benzene
2-Me-Pentane
i-Butane
Benzene
Propene
n-Pentane
m,p-Xylenes
n-Butane
Toluene
i-Pentane
Propane
Ethene
Ethane
Acetylene

(b)


100%
80%
60%
40%
20%
0%
Average relative difference
GC1/GC3
GC1/GC5
GC3/GC5
Me-cy-Hexane
Propyne
1,3-Butadiene
2,3-Dimebutane
n-Heptane
n-Octane
1-Butene
Me-cy-Pentane
i-Butene
Isoprene

(c)


100%
80%
60%
40%
20%
0%
Average relative difference
GC1/GC3
GC1/GC5
GC3/GC5
2,2-Dimepropane
c-2-Hexene
t-2-Hexene
1-Hexene
c-2-Pentene
2,2-Dimebutane
1-Pentene
n-Nonane
t-2-Pentene
c-2-Butene
2-Me-1-Butene
t-2-Butene
2-Me-2-Butene

6 Summary and conclusions

Presently, the most widely used and generally applicable method for VOC measurements is gas chromatography in combination with a preconcentration step. The detection limits are in the lowest ppt range, in some cases even well below one ppt. Gas chromatography allows the measurement of a rather broad range of compounds in one analysis. However, this generally requires rather long analysis times. The reproducibility and accuracy in the range of a few percent at sub ppb mixing ratios is adequate for most purposes. Nevertheless, several presently emerging new applications of VOC, e.g., as tracers for atmospheric processes, require improved methods with precession in the range of one percent at ppt levels. Up to now this has only been achieved for a few selected compounds. Methods to reliably analyze a broad range of VOC at ppt levels with high accuracy still need to be developed.

There are some other techniques which are suitable for VOC measurements, however many of them are specific for the analysis of highly polar compounds such as aldehydes and carboxylic acids, compounds that were not considered in this overview. However, there are a few other techniques, mainly based on optical spectroscopy, which can be applied for VOC measurements in the atmosphere, although none of them has the broad applicability of gas chromatography. Nevertheless, some of these methods definitely are of interest, e.g., for Intercomparison to assess the accuracy of VOC measurements. Several optical techniques are specifically suitable for spatially integrated measurements, an advantage for applications where average concentrations for larger areas are wanted. An example for such an application is column density measurements by high resolution FTIR-spectroscopy (cf. Zander *et al.*, 1991). Furthermore, some optical techniques potentially have higher time resolution than gas chromatography. E.g., it seems feasible to develop an acetylene measuring method based on tunable diode laser spectroscopy which would allow detection of acetylene at mixing ratios of 20 ppt with a time resolution of 5 seconds, a time resolution presently out of the reach of any gas chromatographic method for ambient NMHC measurements. Such a high time resolution would be of extreme value for all airplane-based measuring campaigns. In addition to optical methods, there are also some other methods that are potentially very useful, but not yet adequately developed for atmospheric VOC analysis. A potentially very powerful method is MS-MS coupling, possibly in combination with selective sample introduction techniques such as selective membranes.

But also for NMHC measurements by gas chromatography substantial progress can be expected in the near future. The use of narrow- and micro-bore capillary columns can improve the separation efficiency and detection limits, and also reduce analysis time. The problem of interfacing preconcentration and separation column has not yet been completely solved however there is already a number of promising and for some applications reasonably well working solutions.

However, the most significant advances can be expected due to improved and extended detection possibilities. Mass spectrometric detection facilitates identification and allows reliable, specific detection, even for very complex samples. The recent advances in this field make GC-MS not only affordable, but also suitable as routine method, even for field operation.

Another new development is the coupling of gas chromatography to isotope ratio mass spectrometry. Very recently, it has been demonstrated that this technique can successfully be applied to the measurement of the isotopic composition of atmospheric hydrocarbons (Rudolph *et al.*, 1997). This will give an additional level of information for atmospheric VOC. Considering the complexity of processes that determine atmospheric VOC concentrations, additional

information to constrain budgets, validate model calculations, and generally better understand atmospheric processes are urgently needed.

Finally, it should be realized that the usefulness of the enormous amount of complex information contained in atmospheric observations of VOC would depend on development of tools to extract this information. The advances in concepts, process understanding and numerical modeling in the past years are a very promising basis to systematically develop such tools. It should be remembered that very recently atmospheric VOC measurements have been successfully used to deduce important knowledge for atmospheric processes. Prominent examples are estimates of atmospheric OH-radical concentrations from NMHC measurements (Kramp *et al.*) and the discovery of Cl-atom chemistry in the troposphere (cf. Jobson *et al.*, 1994; Ramacher *et al.*, 1997).

7 References

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MEASUREMENT OF HALOCARBONS AND ALKYL NITRATES IN THE ATMOSPHERE

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1 Introduction

The analysis of volatile organic compounds in the atmosphere requires a variety of different approaches. Measurement of any single class of organic compound often presents unique problems associated with standardization, sampling, analysis, and detection. The problems are multiplied when the simultaneous measurement of different compound classes is desired. As an example of the different problems and solutions to measurement of atmospheric volatile organic compounds, this report will discuss the measurement of halocarbons and organic nitrates in the atmosphere.

A large range of halocarbons with different sources and chemical properties are emitted into the atmosphere, and there are significant changes in the abundance of many of these compounds (Montzka *et al.*, 1996). Perhaps the halocarbons best known to the general scientific community are the chlorofluorocarbons (CFC's). Because CFC's are very stable to loss processes in the troposphere, they are efficiently transferred to the stratosphere where chemical degradation occurs more rapidly. This degradation of CFC's leads to the release of active chlorine which can catalytically destroy stratospheric ozone, under certain conditions. Similarly, Halons (fire retardants) release active bromine to the stratosphere. Other halogen containing gases are released from industrial solvent usage or other processes. Many of these compounds are being regulated under an international agreement: the Montreal Protocol and its amendments. As CFC and solvent usage is curtailed, new compounds are being produced as replacements. These compounds are hydrofluorocarbons (HFC's) and hydrochlorofluorocarbons (HCFC's). A large number of other halocarbons are emitted from natural sources, such as the oceans, usually associated with biogenic production. The halocarbons to be discussed here are given in Table 1.

The term "organic nitrate" encompasses a rather large and varied range of compounds. Here we will consider the measurement of three broad classes of organic nitrate: alkyl nitrates, multifunctional nitrates, and peroxyacyl nitrates. All of these compounds can be formed during oxidation of hydrocarbons in the presence of NO or NO_2, and most provide a temporary reservoir for active nitrogen and radicals. In particular, peroxyacetyl nitrate (PAN) has been shown to be one of the major sources of odd-nitrogen in the remote troposphere (e.g., Singh and Hanst, 1981; Singh *et al.*, 1996; Ridley, 1991), while alkyl nitrates have been shown to be abundant in urban and rural areas (Flocke *et al.*,1991; Flocke *et al.*, 1998; Shepson *et al.*, 1993; Buhr *et al.*, 1990), Arctic regions (Bottenheim *et al.*,1992; Muthuramu *et al*, 1994; Beine *et al.*, 1996) and in certain marine areas (Atlas *et al.*, 1992, 1993; Walega *et al.*, 1992). Less is known about the variety of multifunctional organic nitrates (hydroxy nitrates, carbonyl nitrates, etc.), but these compounds may be most significant in sequestering and cycling reactive nitrogen in areas where biogenic hydrocarbons have a major impact on atmospheric chemistry (O'Brien *et al.*, 1995).

Some of the major concerns about measuring volatile organic compounds, and especially halocarbons and organic nitrates, are related to: 1) the chemistry of the individual compound

(stability and reactivity), 2) sample collection and storage, 3) techniques in compound separation and detection, and 4) standardization. In this report, we will draw primarily from the experience of the NCAR Stratospheric/Tropospheric Measurements group in the measurement of halocarbons and organic nitrates, but also rely on outside reports and publications when this experience is limited. It should be kept in mind, too, that the same issues, problems, and solutions presented here are applicable to other classes of volatile organic compounds in the atmosphere. One objective of this report is to provide for the analytical chemist a broad outline of the analytical chemical aspects of atmospheric halocarbons and organic nitrates. A second objective is to provide to those who routinely use trace gas measurements some appreciation of the measurement uncertainties inherent in the production of a final reported data set.

2 Sample collection/storage

It is often the case that in-situ instrumentation is unavailable or impractical to use in the field to measure the range of volatile organic compounds of interest. Thus, samples need to be collected and returned to the laboratory for detailed analysis. The sample containers used for sample storage should ideally be inert to the compounds of interest, but that is impossible for all the compounds considered here. Thus, by the very nature of the sample storage, only a limited subset of compounds may be measured. Only the more stable, non-reactive organic compounds are suitably analyzed from sample storage canisters.

Table 1. *List of selected halocarbons and organic nitrates measured in the atmosphere from canisters sampling at NCAR. Peroxyacyl nitrates and a variety of multifunctional organic nitrates are measured by other techniques described in the text.*

HYDROFLUOROCARBONS	HALONS	BROMO AND CHLOROCARBONS
HFC - 116	Halon 1301	Chlorodibromomethane
HFC - 23	Halon 1211	Bromodichloromethane
HFC - C318	Halon 2402	Bromochloromethane
HFC - 143a		Dibromomethane
HFC - 134a		Bromoform
CHLOROFLUOROCARBONS	**METHYL HALIDES**	**ALKYL NITRATES**
CFC - 11	Methyl chloride	Methyl nitrate
CFC - 12	Methyl bromide	Ethyl nitrate
CFC - 13	Methyl iodide	Isopropyl nitrate
CFC - 112		n-Propyl nitrate
CFC - 113		2-Butyl nitrate
CFC - 114		
CFC - 114a		
CFC - 115		
HYDROCHLORO-FLUOROCARBONS	**SOLVENTS**	
HCFC - 22	Dichloromethane	
HCFC - 142B	1,1,1-trichloroethane	
HCFC - 141B	Tetrachloromethane	
	Trichloromethane	
	Tetrachloroethylene	

The most common containers in use today are constructed from passivated stainless steel. Containers are usually filled with ambient air using a metal bellows (or similar non-contaminating) pump to an internal pressure between 30–50psia. The experience with stainless steel canisters in our laboratory at NCAR has, and continues to be, a continuing process of learning. For example, we find a dramatic difference in the behavior of stainless steel flasks toward specific compounds if an air sample is collected in the stratosphere (high ozone, low water vapor) versus the troposphere (lower ozone, higher water vapor). Furthermore, our experience, and those of other laboratories, has shown that details of the method used to clean stainless steel flasks can dramatically alter the behavior of the flask. Whether high or low temperatures are used in combination with high vacuum baking or wet/dry gas flushing can have a significant effect on the eventual stability of the sample collected in the flask. In most general terms, we have found that an oxidized and moist surface is most inert toward the compounds considered here. An example of the effect of water vapor on halocarbon stability in our canisters is shown in Figure 1. This figure demonstrates that not all compounds behave in the same way during storage, and, in fact, water vapor is critical to the stability of certain compounds in the stainless steel flasks used at NCAR. Furthermore, we find that continual monitoring of flask behavior is required to maintain quality control in our analysis.

Collection in stainless steel flasks is not the only method which has been used for storage of volatile organic compounds. Methods have been developed which utilize adsorbents to selectively retain organic compounds when ambient air is passed through the adsorbent material. For example, we have used a micro-charcoal cartridge to collect organic nitrates and some halocarbons from ambient air (Atlas and Schauffler, 1991). A solvent extract of the cartridge removes the compounds, and the extract is analyzed by conventional gas chromatography with electron capture or other detectors. This method has proven valuable, in particular, for the collection and measurement of polar organic compounds (e.g., hydroxy nitrates) which would be more difficult to process using strictly gas phase techniques. For more volatile and/or more non-polar compounds, adsorbents which release trapped compounds upon heating have been widely used (e.g., Simmonds *et al.*, 1995; Helmig *et al.*, 1996)

3 Sample analysis

The most common technique we have used at NCAR for the analysis of halocarbons and nitrates has been combined gas chromatography/mass spectrometry after cryogenic enrichment of organic compounds in the sample. Depending on the analysis to be performed, 100–500cm^3 of gas are passed through a glass-bead-packed trap submersed in liquid N_2. This technique traps organic compounds less volatile than ethane, and it allows permanent gases to flow through the trap. After evacuation of the sample loop, the cryogenic trap is heated to 80°C and the trapped gases are swept onto a chromatographic column for separation. We have used a non-polar capillary column (30m x 0.25mm x 1.0μ film) operated in a temperature programmed mode from –65°C to 175°C, though we have experimented with other columns, such as Al_2O_3 PLOT, for specialized analysis of volatile perfluorinated compounds. A schematic of the analytical system is shown in Figure 2.

The detector we have used on a routine basis is a quadrupole mass spectrometer. Both conventional electron impact ionization (EI) and negative-ion chemical ionization (NICI) techniques have been used. For analysis using the EI technique, we monitor selected ion fragments of the target compounds in specific retention time windows. With typical dwell times of 100–300msec on each ion, we achieve a sensitivity on the order of 0.05pptv or better for most compounds in a 500cm^3 sample. An example of a the sensitivity of the instrument in routine operation is shown

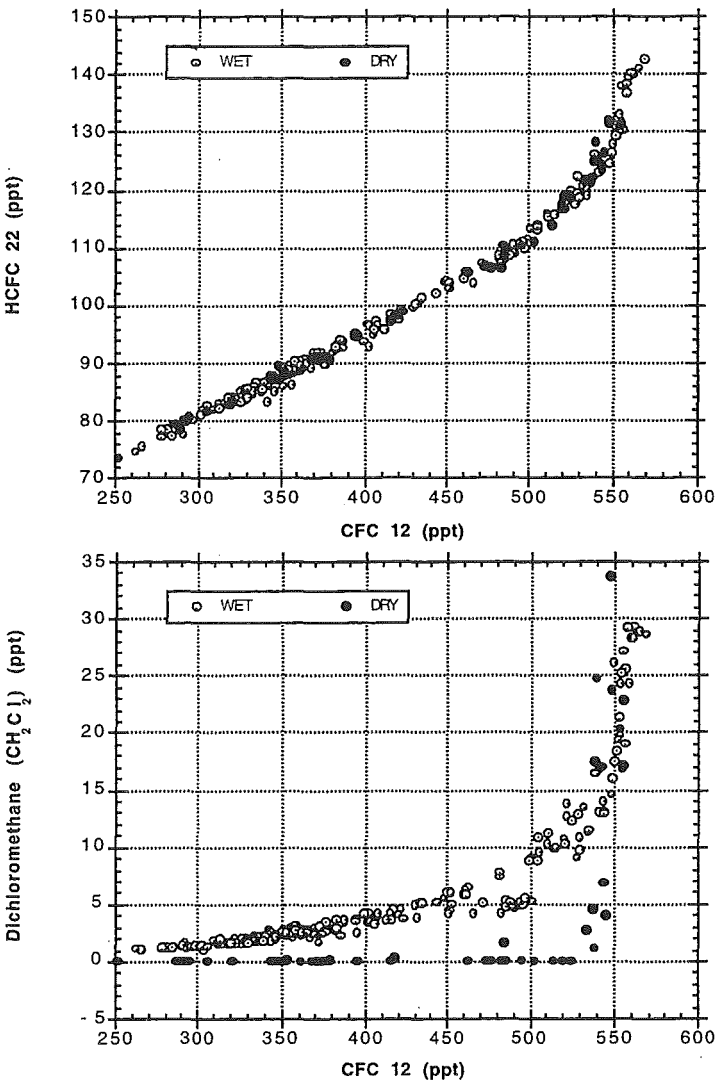

Figure 1. *Comparison of trace gas relationships observed in canisters collected in the stratosphere and upper troposphere during the NASA POLARIS campaign. Wet canisters had 3 torr of water vapor added to the evacuated canister prior to sample collection. Dry canisters were evacuated with no additional water added. CFC 12 and HCFC 22 are stable compounds in wet or dry canisters. Dichloromethane is lost in dry cans sampling stratospheric air, but normal moisture in the troposphere is sufficient to stabilize this compound.*

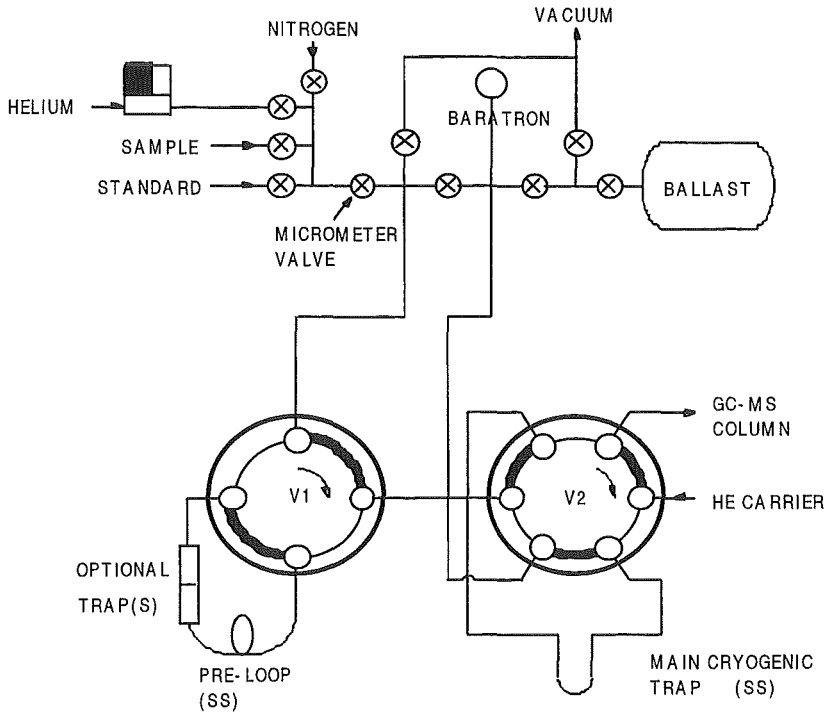

Figure 2. *Schematic diagram of cryogenic enrichment/sample introduction system used at NCAR. V1 is an optional valve used in some cases with chemical traps to remove water vapor and carbon dioxide. Exact configuration may be slightly different on different instruments.*

in Figure 3. Illustrated is the selected ion chromatogram for Halon 1211 at Å 3.8pptv in an ambient air sample.

The NICI technique produces a total ion signal that is similar to the response seen with an electron capture detector, and the sensitivity is also comparably high. Detection limits approach 0.01ppt or better for many compounds in a $100cm^3$ sample. In brief, for the compounds we measure, we find that halocarbons and organic nitrates undergo dissociative electron capture to produce stable negative ions of specific halogens or $NO_x^-(x=2$ or 3). Thus, chlorinated organic compounds yield ions (m/e) of 35^- and 37^-, which are the two main chlorine isotopes; brominated compounds yield m/e 79^- and 81^-; and iodine containing compounds produce m/e 127^-. This type of ionization provides a specific response for a range of halogenated species which would be difficult to characterize using other detection schemes, especially with an electron capture detector. An example of negative ion chromatograms of halogenated hydrocarbons in an ambient air sample is given in Figure 4.

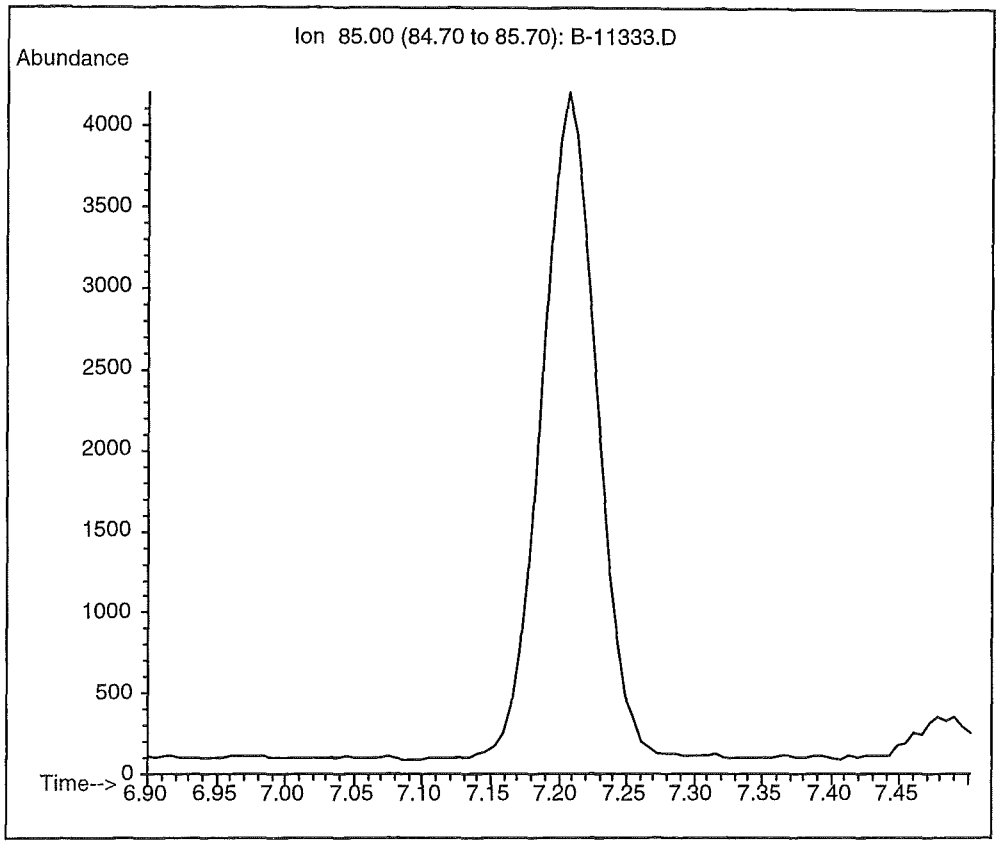

Figure 3. *Selected ion chromatogram (m/e=85) for quantification of Halon 1211. Trace was obtained from a Hewlett Packard Model 5971 MSD during routine operation. The air sample was approximately 550cm^3.*

The most abundant ion for organic nitrates is either 46 (NO_2^-) or 62 (NO_3^-). The remainder of the organic nitrate molecule may or may not produce a stable negative ion or fragment which could provide additional structural information. A negative ion mass spectrum of two organic nitrates (3-pentyl nitrate and 1-nitroxy-2-butanone) are shown in Figure 5. Based on a series of standards either synthesized in our laboratory or commercially available, we arrived at a systematic approach for identification of a variety of organic nitrates based on their fragmentation (Table 2). The information used in this Table has been applied to the complex mixture of nitrates observed in the ambient atmosphere. While alkyl nitrates are the main compounds identified in ambient air, there are a variety of multifunctional nitrates also observed. For example, Figures 6 and 7 show the selected ion chromatogram of an ambient sample showing the presence of alkyl nitrates as well as hydroxynitrates.

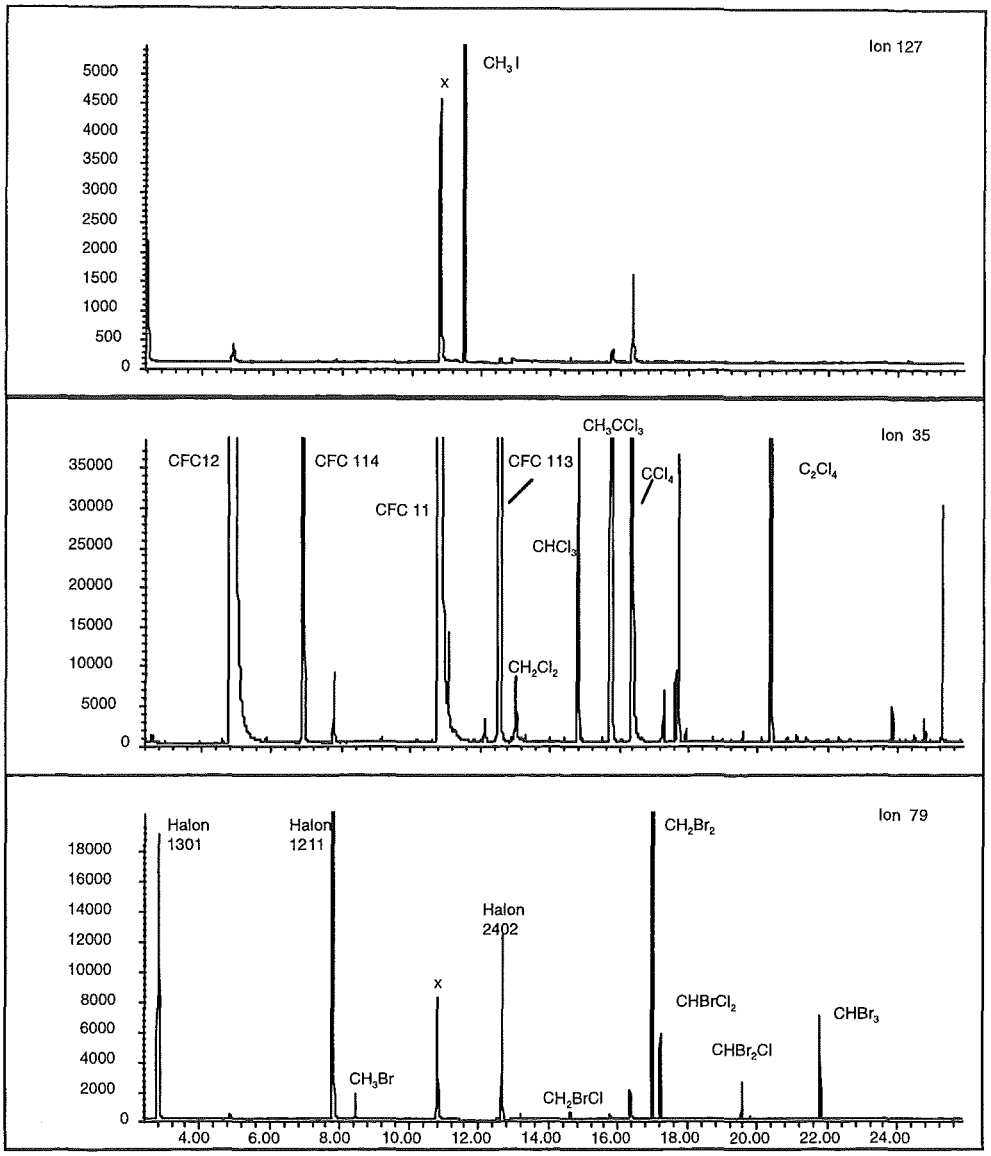

***Figure 4**. Selected ion chromatogram for halogenated hydrocarbons in a 100 cm^3 air sample collected at 2 km above San Francisco, California. Top = iodine (m/e=127), middle = chlorine (m/e=35) and lower = bromine (m/e=79). X indicates carryover from high concentration chlorinated hydrocarbon. To provide some indication of sensitivity, the following mixing ratios were calculated (in ppt): CH_3I = 0.16, C_2Cl_4=3.8, Halon 2402=0.43.*

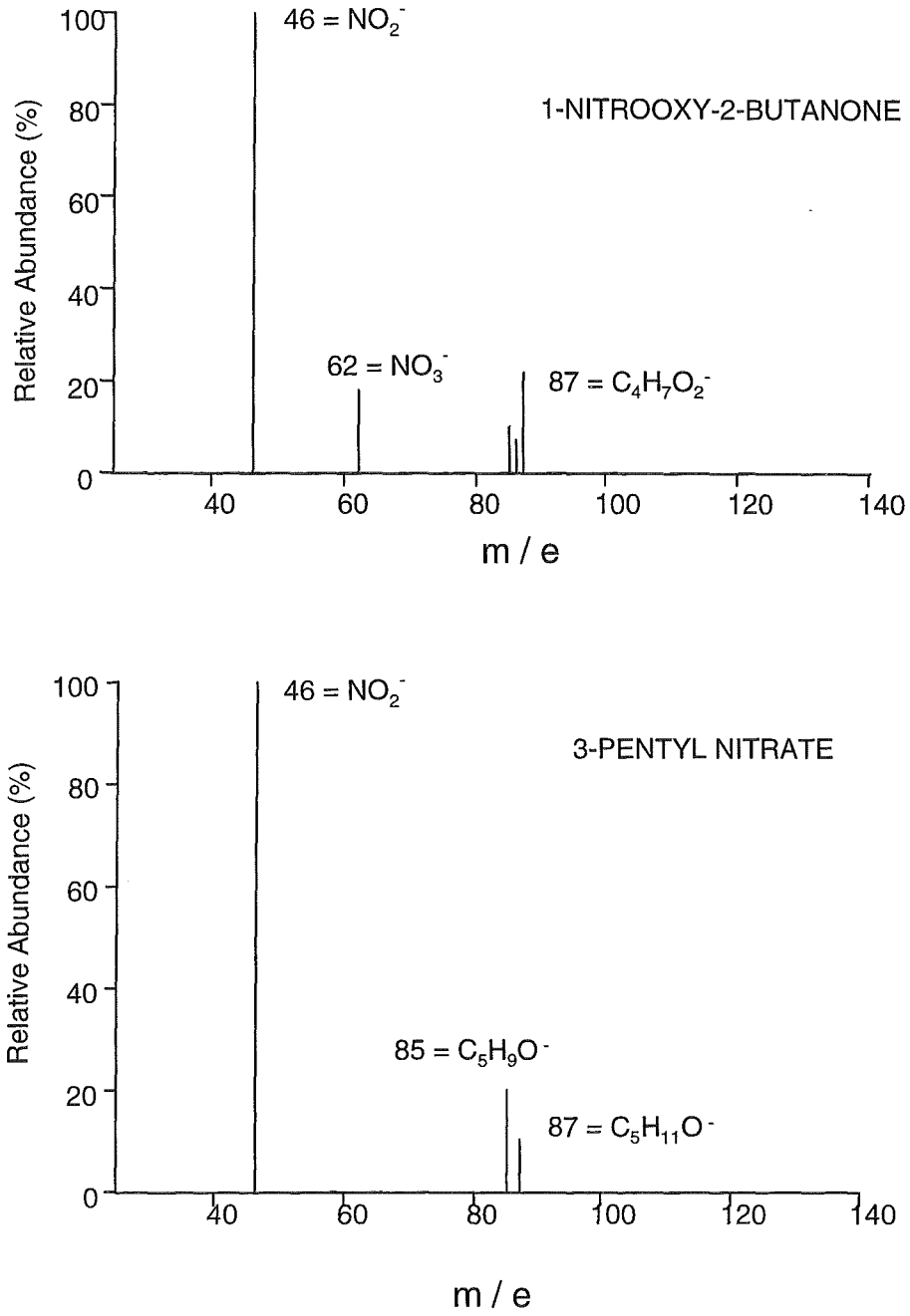

Figure 5. *Negative ion chemical ionization mass spectra of two organic nitrates. Top=1-Nitrooxy-2-butanone. Bottom=3-Pentyl nitrate.*

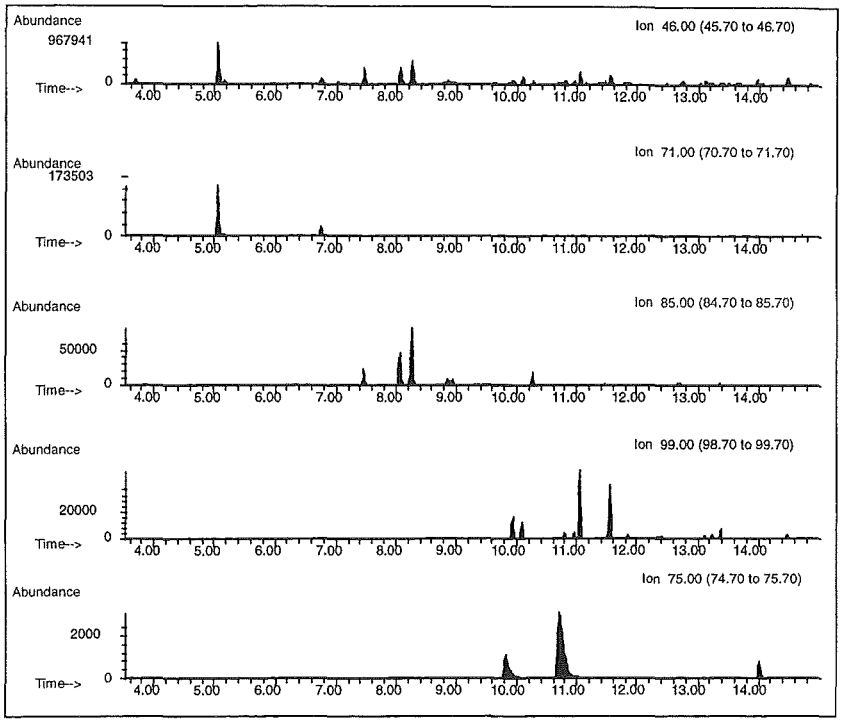

Figure 6. *Negative ion chromatograms from solvent extract of ambient air sample collected on charcoal. The 46 fragment (NO_2^-) is characteristic of most alkyl nitrates in this sample. Fragments of 71, 85 and 99 are characteristic of C_4, C_5, and C_6 alkyl nitrates, respectively. The fragment m/e = 75 is characteristic of hydroxypropyl nitrates.*

Table 2. *Negative ion mass fragments (m/e) which are characteristic of selected classes of organic nitrates are shown below. The characteristic fragmentation pattern combined with chromatographic retention behavior is used to interpret negative ion mass spectra of organic nitrates in ambient air.*

Carbon #	ALKYL	HYDROXY/ ALKYL	NITROOXY-CARBONYL	DI-NITROOXY	ARYL
ALL	46	46	46/62	62/46	46 (62)
C_1	29/31	-	-	-	-
C_2	43/45	59/61	57/59	59/61	-
C_3	57/59	73/75	71/73	73/75	-
C_4	71*/73	87/89	85/87	87/89	-
C_5	85*/87	101/103	99/101	-	-
C_6	99*/101	115/117	113/115	-	-
C_7	113*/115	-	-	-	77/105/107
C_8	127*/129	-	-	-	119/121

*Except for tertiary nitrates

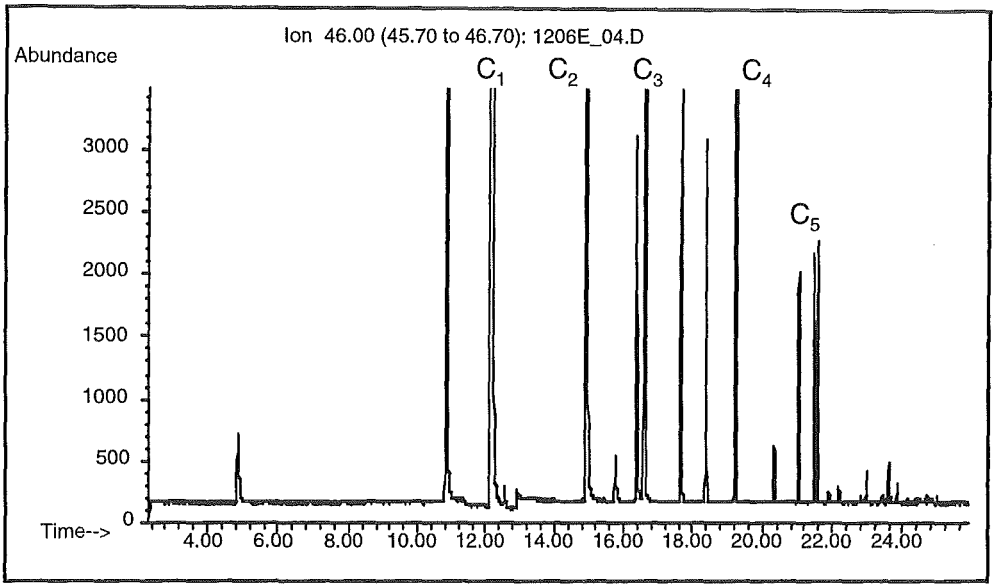

Figure 7. Selected ion, negative ion chromatogram of alkyl nitrates in whole air sample. (See Figure 4.)

One estimate of instrument performance can be obtained from the reproducibility of standard injections made throughout a day of analysis. For trace gases whose mixing ratios are greater than a few ppt, the coefficient of variation of the quadrupole instruments that we use is in the range of 2–4%, based on analysis during a recent campaign (Figure 8). This figure does not take into account drift in instrument response over the course of a day, so actually sample reproducibility is somewhat improved when drifts are considered.

Overall analytical performance can also be estimated from replicate analyses of duplicate samples collected under actual field conditions. One such test was done for samples collected aboard the NASA ER-2 aircraft during Spring, 1995. These samples showed that, for most compounds, the reproducibility was comparable for replicate analyses of the same canister or single analysis of replicate canisters. For some compounds with known canister losses at that time, such as carbon tetrachloride, inter-canister precision was much worse than precision obtained by replicate analyses from a single canister. An example of a vertical profile of methyl bromide taken during this test illustrates an overall excellent performance of sampling and analysis using the techniques described above (Figure 9).

4 Standardization

The quality of measurements is ultimately linked to accurate standardization. For halocarbons and organic nitrates, standardization is a difficult and time-consuming task. At NCAR, we have taken an approach to standardization which combines in-house preparation of primary standards, calibration of commercial mixtures, use of "certified" standard mixtures, and an informal comparison of standard scales between different laboratories. This last activity is an extremely valuable exercise to identify unseen problems and to assure that measurements obtained by different laboratories can be properly compared or combined.

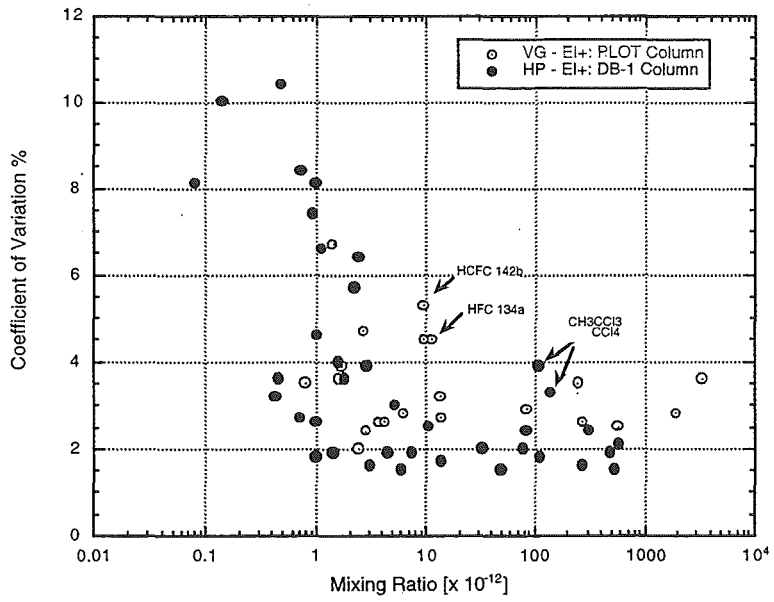

Figure 8. *Coefficient of variation of daily standards on two different GC/MS instruments. This plot shows typical variability of compounds tends to increase at low mixing ratios, and also helps identify "problem" compounds with higher than normal variability.*

Table 3. *Analysis of a certified NIST Reference Material SRM 1813 using an Atomic Emission Dector combined with gas chromatography. The carbon response of the AED is calibrated with a butane/ benzene mixture. Units are ppb compound.*

Analysis Date	Sept. 1995	January 1997		
Element used for calibration	C	C	Cl	NIST
Compound				
Vinyl Chloride	233	237	237*	241
Chloroform	236	239	238	247
Carbon Tetrachloride	237	239	244	245
Tetrachlorethylene	241	242	243	250

*Chlorine response was defined by carbon calibration for this compound. Other calibration based on chlorine are referenced to this value.

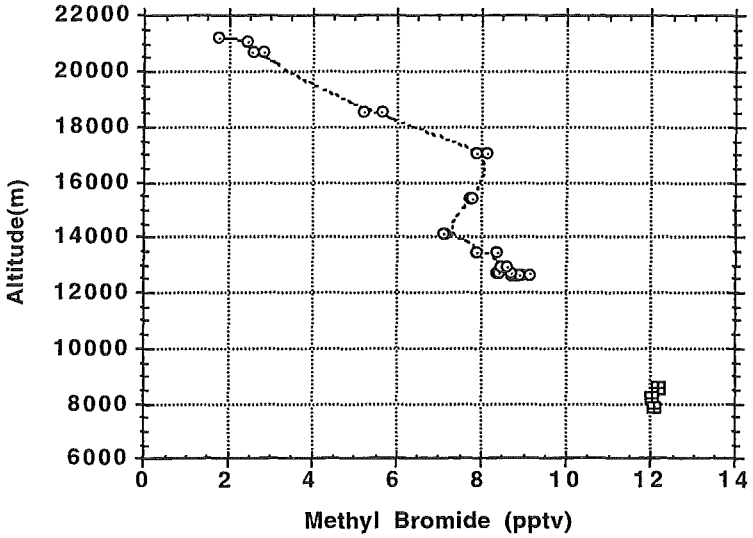

Figure 9. Altitude profile of methyl bromide in the upper troposphere/lower stratosphere over San Francisco, California during May 1995 test flights of the NASA ER-2 aircraft. Replicate samples were collected simultaneously at different altitudes and analyzed in random order in the laboratory. This test indicates excellent performance of the overall sampling and analytical protocol.

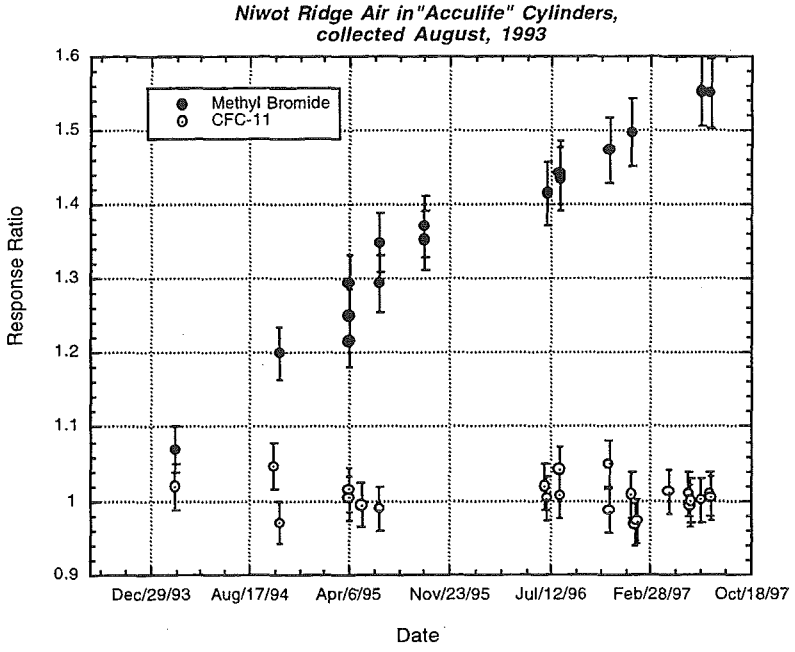

Figure 10. Temporal change in the ratio of methyl bromide and CFC 11 between two sample cylinders collected during 1993. CFC 11 showed excellent stability in both cylinders (these were also checked relative to other standard mixtures). Methyl bromide, however, decreased dramati-cally in one of the cylinders.

Among these different approaches, one unique method being tried at NCAR has been the use of an Atomic Emission Detector (AED) in combination with gas chromatography for absolute calibration of multicomponent mixtures of volatile organic species. The principle of the AED is that molecules eluting from the chromatographic column are excited to their constituent atomic species in a plasma, and the very specific atomic emission of the individual elements is detected with a diode array spectrometer. The unique aspect of this instrument is that the response to the atomic emission is independent of the molecular source of the constituent atom. This means that a certified hydrocarbon standard may be used to calibrate halocarbon mixtures, because the response to carbon is independent of whether the carbon comes from a hydrocarbon or halocarbon. This equivalence of response between different classes of compounds is not seen in any other detector. An example of a check of the system is shown in Table 3 where a certified NIST standard halocarbon mixture is calibrated using an independently prepared hydrocarbon standard. Ultimate calibration of working standards (we use large volume air samples collected at various sites near the laboratory) is based on flow dilution of the high concentration standard mixtures. Finally, one may intercompare actual samples between laboratories to verify and check standard scales which need to be accurate even at the ppt level. We have found agreement in such comparisons typically better than 5–10% for most of the compounds we measure in common with other laboratories.

An important issue in dealing with measurement of halocarbons at ppt levels in the atmosphere is the stability of standard mixtures. As noted we fill passivated aluminum high pressure cylinders or low pressure stainless steel containers with ambient air to serve as a working standard during routine analysis. Ideally, these samples can be used over several campaigns and last several years. However, it is important to verify that all analyses are stable in the working standard over the life of the cylinder. We have found, as have others, that there can be a significant drift in the concentration of individual trace gases over time. Thus, it is necessary to routinely compare working standards and primary standards. An example of the change in compound concentration over several years is illustrated in Figure 10. This figure highlights the fact that some sample components may be stable in cylinders while others may be quite variable over time.

5 In-situ instrumentation

We have discussed methods which utilize samples collected remotely, stored in canisters, and transferred to the laboratory for analysis. Use of in-situ instrumentation for measurement of halocarbons and other volatile organic compounds is often a desirable or necessary alternative to these methods. For halocarbons, in-situ instruments have been operated on a routine basis in remote locations as part of global scale monitoring efforts (e.g., ALE-GAGE-AGAGE; NOAA CMDL). These instruments are dedicated gas chromatographs with electron capture detectors, and they have provided a record of temporal trends in the major CFC's and chlorinated solvents. In-situ GC/MS instruments are now being added to the AGAGE network (Simmonds *et al.*, 1995), and these instruments can monitor an even wider range of trace gases. Details of the technique can be found in Simmonds *et al.* (1995), but in essence the method utilizes the same techniques described above: sample preconcentration (with thermal desorption), gas chromatography, and mass spectrometric detection (in this case with an ion trap instrument).

A very sophisticated version of an in-situ chromatograph for halocarbon analysis has been described by Elkins *et al.* (1996) for use aboard the ER-2 stratospheric aircraft (Figure 11). This is a multichannel instrument which is able to measure halocarbons, methane and hydrogen at

stratospheric and tropospheric mixing ratios using direct injection (no preconcentration) with a frequency of 3–6 minutes (Figure 12).

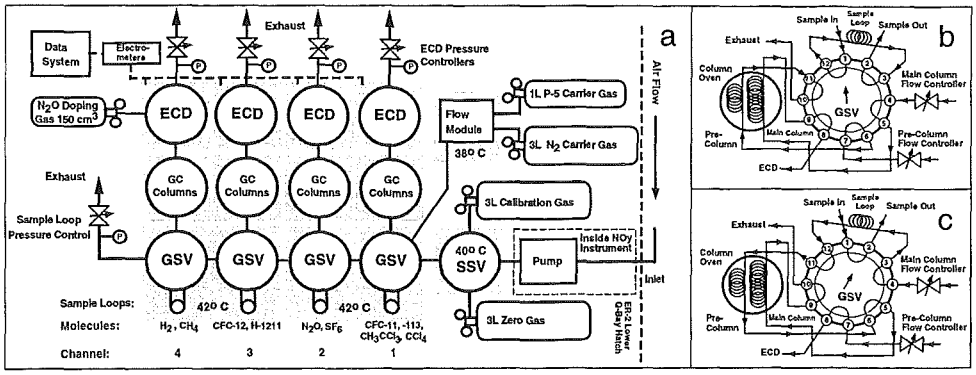

Figure 11. Schematic diagram of Airborne Chromatograph for Atmospheric Trace Species (ACATS-4) used aboard the NASA ER-2 aircraft and developed by J. Elkins and colleagues at NOAA CMDL. Figure from Elkins et al. (1996).

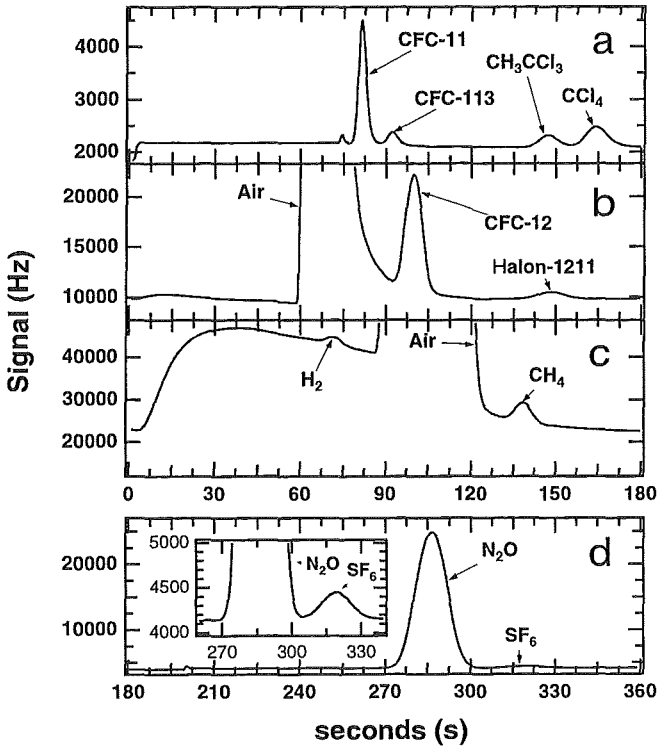

Figure 12. Examples of ECD chromatograms obtained from the ACATS instrument. Figure from Elkins et al. (1996).

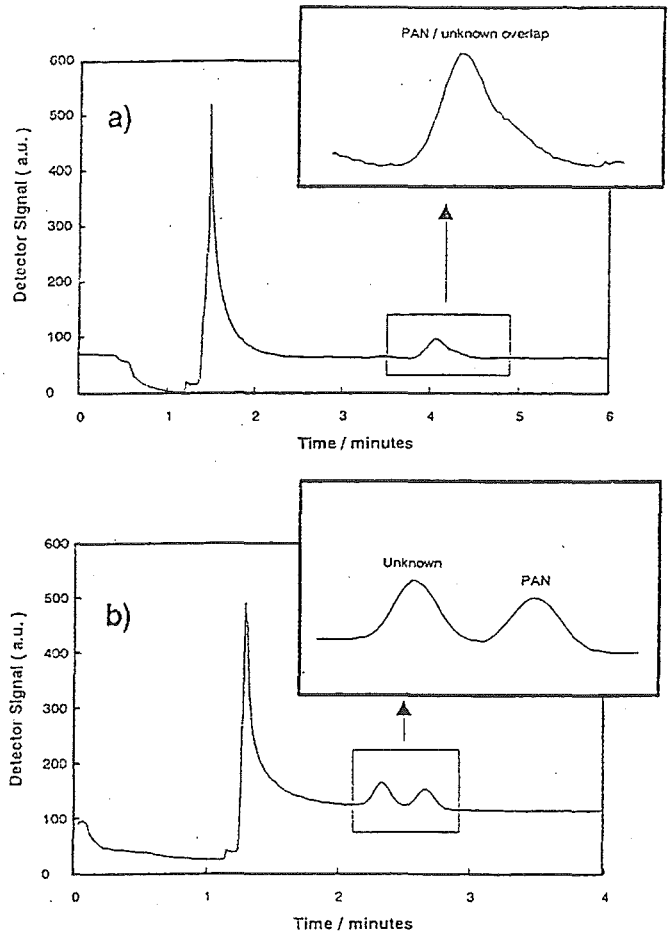

Figure 13. *Ambient air chromatograms. Top: separation on non-polar (Rtx-1) column does not provide separation of PAN from unknown artifact; Bottom: separation on serial non-polar and polar (Rtx-1701) columns separates PAN from unknown. From Schrimpf et al. (1995).*

While in-situ instruments for measurement of halocarbons provide useful alternatives to grab sampling, the use of in situ instrumentation is absolutely essential for the measurement of peroxyacyl nitrates. Because of its abundance and significance, peroxyacetyl nitrate (PAN) is the most commonly measured peroxyacyl nitrate in the atmosphere, and we will use PAN as the primary example in the discussion to follow. Currently, the most common methodology used for measurement of PAN and other peroxy nitrates is strikingly similar to that used for halocarbons, i.e., electron capture gas chromatography (with or without sample preconcentration). However, because peroxyacyl nitrates are thermally labile, temperatures in the chromatographic system must be kept to a minimum (low column and detector temperatures, isothermal analyses) and surfaces should be as inert as possible to avoid surface reactions and losses. Furthermore, standardization of instruments for peroxyacyl nitrates is much more complex than for stable

halocarbon gases. Typically, a continuous source of peroxynitrate is generated from a diffusion tube or from a photochemical source, and this stream is diluted for analysis by the electron capture instrument (Walega *et al.*, 1992)

One of the recognized problems in establishing a method for PAN utilizing electron capture detectors is the problem of co-eluting compounds. A wide variety of halocarbons and other trace gases (oxygenated hydrocarbons, alkyl nitrates) have an electron capture response, and, if the chromatographic separation is inadequate, artifacts may interfere with the accurate determination of PAN. The necessity of low temperatures and isothermal separations complicates the problem of potential interferences. Still, chromatographic conditions have been identified to suitably separate PAN from interfering compounds. An example is shown in Figure 13. In spite of all the "extra" difficulties associated with PAN measurement, the basic chromatographic technique has been employed successfully in long-term monitoring efforts (Bottenheim *et al.*, 1994), short-term intensive studies (e.g. Walega *et al.*, 1992), and a variety of airborne missions (e.g., Singh *et al.*, 1996).

6 Summary

This report has described some of the basic techniques, issues, and uncertainties associated with measurement of halocarbons and organic nitrates in the atmosphere. It is clear that there is no single universal technique applicable to all different trace gases, and each technique has its limitations. Ideally, these limitations and uncertainties are sufficiently well-described and understood to allow the trace gas measurements to be meaningfully applied to understanding atmospheric chemical processes.

7 Acknowledgments

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VOC LABORATORY INTERCOMPARISONS

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Anthropogenic and natural non-methane hydrocarbons (NMHCs) are important trace species that can influence the chemistry of the atmosphere in many ways. NMHCs are emitted into the atmosphere through a variety of sources and are present in the troposphere at mixing ratios ranging from ppbv to pptv. Transformation of NMHCs through chemical reactions leads to *in situ* formation of oxygen-containing volatile organic compounds (OVOCs) in the atmosphere (Killus and Whitten, 1984, Calvert and Madronich, 1987, Atkinson, 1990). A number of OVOCs are also emitted directly into the atmosphere from anthropogenic and natural sources. Key to understanding the complex chemical cycles involved in tropospheric chemistry are accurate and precise measurements of NMHCs and OVOCs.

Ambient hydrocarbon analyses are complicated by the large variety of hydrocarbon species that are present in the atmosphere. Typical chromatograms resulting from NMHC analysis in an urban area contain well over 100 compounds. The oxidation of each of these species creates a mixture containing many oxidation products as well. A number of hydrocarbons and their oxidation products have lifetimes of many days, and transport to relatively remote regions can occur. Other hydrocarbons are extremely reactive toward HO, NO_3, and ozone; their atmospheric lifetimes are only a few hours. The development of regional and global chemistry models require hydrocarbon data from scientists around the world. For example, the emerging North American Research Strategy on Tropospheric Ozone (NARSTO) will require measurements from a number of groups. Similar measurement programs are in place or planned in other parts of the world. It is imperative that measurements accurately reflect the true atmospheric composition. However, the analytical capability of individual measurement groups is difficult to assess because measurements are usually taken with a single instrument at a chosen location with its own unique and changing chemical and meteorological conditions. Hence, experiments cannot be repeated under identical conditions or, under the most common scenario, be compared directly with a co-located instrument or instruments. One way to gain confidence in the accuracy of data that is produced by independent research groups is to formerly intercompare their methodology.

It has been stated by a prominent group of atmospheric scientists (Albritton *et al.*, 1990) that "Intercomparisons are vital and indeed as much a part of doing atmospheric research as is gathering data to test a geophysical hypothesis." This same group of scientists made the following observation: "A reliable estimate of the uncertainty in a measurement is as important as the measurement itself." With such an estimate:

- observations and theory can be compared meaningfully
- results from separate campaigns can be merged reliably into a global data base
- spatial gradients from separate data sets can be characterized credibly
- time series from different networks can be used to establish long-term records

In the present context, the word Intercomparison means literally to examine in order to note the similarities or differences between or among groups. There are varying degrees of rigor in Intercomparisons ranging from informal, in which co-located simultaneous or near simultaneous measurements of the same species are compared during the course of an ongoing field experiment to formal in which the Intercomparison is designed as a stand-alone experiment carried out with a strict protocol. The features of the most successful Intercomparisons tend to be the following:

- design of the experiment led by referee but with input from each of the participants
- involve several different techniques for measuring the same species
- measure at the same time and same place
- measure under typical operating conditions to the extent possible
- state the accuracy and precision estimates in advance
- spike the atmospheric samples with known (to the referee) amounts of species that are potential artifacts
- each investigator's results prepared independently and separately (blind) from the others and in a publication ready status
- referee compiles jointly the separate results and assesses the state of agreement or disagreement
- publish the results in a refereed journal.

The most common approach for ambient hydrocarbon analysis is based upon cryotrapping or adsorbent-based sample concentration followed by gas chromatographic separation of the individual hydrocarbons followed by flame ionization detection (FID). More recently, gas chromatographic separation followed by mass spectrometric detection (GC-MS) has become popular as a technique for ambient hydrocarbon analysis both in the laboratory and in the field. A new technique that may become more popular in the future is GC coupled with atomic emission detection. This technique is currently being used at the National Center for Atmospheric Chemistry (NCAR) and at the US Environmental Protection Agency, Research Triangle Park, NC (EPA-RTP). With any GC technique, separation of the compounds of interest is accomplished through the proper choice of a column stationary phase and the temperature program of the oven in which the column resides. Many column materials have been used successfully in recent years and the column chosen by an investigator is dependent upon the analysis required. For example, a different column would be chosen by an investigator who is interested in only low molecular weight hydrocarbons (e.g., C_2 to C_6) as compared to an investigator who is interested in a whole range of hydrocarbons (e.g., C_2 to C_{10}). Sometimes an investigator may choose to employ two or more different columns in order to cover the full range of desired compounds.

Various hydrocarbon standards are used by investigators to calibrate their instruments in order to quantify the mixing ratio of hydrocarbons in an ambient air sample. Some investigators prepare their own standards. Others use secondary standards from a commercial source, while still others purchase gravimetric standards from a National Laboratory. Some laboratories rely on the near-proportional response to carbon in an FID detector for most NMHCs and reference results to a single NMHC standard. Other laboratories use a standard for each compound that they wish to analyze, and calibrate their instruments accordingly. A summary of the analysis procedures for a large number of participants in the NOn-Methane Hydrocarbon InterComparison Experiment (NOMHICE, discussed below) is shown in Table 1.

Table 1.

lab	*analytical column*	*preconcentraton trap*	*detector*	*standard*
A	DB-1	Glass bead cryo	FID	in-house
B1	PLOT AL_2O_3	Glass bead cryo	FID	in-house
B2	DB-1	Glass bead cryo	FID	in-house
C	DB-5	Glass bead cryo	ECD/FID	not specified
D1	PLOT AL_2O_3	Fused Silica capillary cryo	FID	Scott Spec. 54 Mix/in house
D2	DB-5	Fused Silica capillary cryo	FID	Scott Spec. 54 Mix/in house
E	PLOT AL_2O_3	Glass bead cryo	FID	Scott Spec. neohexane
F	PLOT AL_2O_3	Glass bead cryo	FID	NPL propane
G1	DB-1	Glass bead cryo	FID/MS	NIST propane/n-butane
G2	Phenyl isocyanate	Glass bead cryo	FID	NIST propane
H	DB-1	Cryo	FID/MS	in-house
I	DB-1	Cryo	FID	not specified
J	PLOT AL_2O_3	1/8" AL_2O_3 precol. @ - 100C	FID	NIST n-butane/benzene
K	PLOT GS-Q	Glass bead cryo	ECD/FID	Calibrated high pressure air
L	DB-Wax	Cryo	FID	Scott Spec. 54 Mix/Perm. tube
M1	DB-1	Glass bead cryo	FID	Scott Spec. n-butane/benzene
M2	PLOT AL_2O_3	Glass bead cryo	FID	Scott Spec. n-butane/benzene
M3	Cyclodex	Glass bead cryo	FID	Scott Spec. n-butane/benzene
N	PLOT AL_2O_3	Tenax/Carbotrap	FID	Alphagaz - cmpd(s) not specified
O	DB-1	Treated glass bead cryo	FID	Scott Spec. propane/NIST propane
P	PLOT AL_2O_3	Carbosieve S3/ Carbotrap C	FID	Perm. Tube - cmpd(s) not specified
Q	3 m Porasil Q/OPN	Glass bead cryo	FID	Scott Spec. propane/hexane
R1	PLOT GS-Q	Cryo	FID	in-house gravimetric
R2	DB-1	Cryo	FID	in-house gravimetric
S1	PLOT AL_2O_3	Cryo on Carbosieve S3/ Carbotrap/Carbotrap C	FID	NIST n-butane/benzene
S2	PLOT AL_2O_3	Tenax TA/Carbosphere	FID	NIST n-butane/benzene
S3	DB-1701	Tenax TA	FID	NIST n-butane/benzene
T	OV-1	Carbotrap B/Carbosieve S3	FID/MS	NIST benzene
U	DB-1	Glass bead cryo	FID	Scott Spec. neohex/NIST prop.
V	PLOT AL_2O_3	Glass bead cryo	FID	NIST n-butane/benzene
W	Poraplot Q	Carbosieve S3/Carbotrap	FID	Certified spiked Tenax cartridge
X	DB-1	Glass bead cryo	FID	Diluted NIST propane
Y1	PLOT AL_2O_3	Glass bead cryo	FID	Octane (source not specified)
Y2	DB-1	Tenax TA	FID	Octane (source not specified)
Z	DB-1	Glass bead cryo	FID	NIST propane
AA1	PLOT AL_2O_3	Glass bead cryo	FID	NIST propane
AA2	DB-1	Glass bead cryo	FID	NIST propane
AB	DB-5	Teflon Capillary Cryo	FID	in-house gravimetric

Several potential problems exist in sampling reactive hydrocarbons. Reactions between alkenes and any residual ozone remaining after the collection procedures may occur as a result of storage in bulbs or during the preconcentration step. A variety of ozone scrubbers have been used to circumvent this problem. However, results from investigators using different ozone scrubbers have never been fully evaluated by way of an intercomparison. When using cryogenic preconcentration to sample hydrocarbons present in low concentrations, a large amount of sample must be collected and, consequently, a relatively large amount of water may also be collected in humid environments

during the process. This can lead to freeze-up and solubility problems in the analytical systems if some type of water management is not used. There have been several solutions to this problem including a multistage trapping sequence in which water is left behind in one of the traps, chromatographic separation of the water from the sample (Riemer *et al.*, 1997) and Nafion tubing (as a dryer) among others. However, all of these methods have the potential for either compound losses or artifact formation.

GC-FID peak identifications are typically accomplished by running known standard mixtures (qualitative) and noting the retention time of each particular compound of interest. Retention times for each hydrocarbon on a given column can be very reproducible if the system is operated under nearly identical flow and temperature conditions for each run. Small differences in retention times between runs can be compensated for by referencing to a retention-index library based upon the standard known mixture (Hoekman, 1992) or to added internal standard which bracket time regions of the chromatogram. Inevitably, in complex mixtures, some components are difficult to resolve satisfactorily for accurate peak identification and quantification. Peak identification is more facile for GC-MS systems as one can use the mass spectrometer for specific detection (assuming unique fragmentation patterns) even if there is co-elution.

There have been few VOC intercomparisons reported in the literature. However, a great deal of progress has been made through the international NOMHICE program, an activity of the International Global Atmospheric Project (IGAC). NOMHICE was designed to evaluate current methods being used to determine the ambient levels of various atmospheric NMHCs, to identify existing problems in these analyses, to correct these problems, and to help ensure quality control of hydrocarbon analyses made by atmospheric scientists throughout the world. Forty research groups worldwide have participated in the NOMHICE program to date. The primary objective of the NOMHICE program has been to assess how accurately a large range of hydrocarbons (from C_2 to C_{10}) can be measured by individual scientists and laboratories and to provide discreet guidance where necessary to improve measurement capabilities of the participating laboratories. The NOMHICE approach has been to conduct a series of planned experiments which involve all of the common classes of the atmospheric hydrocarbons: alkanes, alkenes, aromatic hydrocarbons, and the terpenes. The various tasks of the study have been arranged in increasing order of complexity so that problems may be addressed as they arise during the course of the Intercomparison. The ongoing research of the NOMHICE program has allowed close examination of the various methods of analysis now in use and to test their efficacy in identification and quantification of the various hydrocarbon species that are present in the ambient air. A total of 5 planned experiments (or Tasks) have been conducted to date. Task 1 of NOMHICE involved the circulation of a 2-component (n-butane and benzene), gravimetrically prepared (by the National Institute for Standards and Technology (NIST)) hydrocarbon mixture of known com-position (concentration unknown to participants) to 37 participating scientific groups from laboratories throughout the world. This experiment was planned to check on the reliability of the standards employed by each of the participating groups. Task 2 involved the circulation of a more complex, gravimetrically prepared, 16-component hydrocarbon mixture (composition and concentration unknown to participants) to determine whether suitable separation, identification, and quantification could be made of the individual hydrocarbons present in the mixture. For a discussion of Task 1 and 2 results see Apel *et al.* (1994). Task 3 involved the circulation and analysis of a synthetic air mixture (60 major components, composition and concentration unknown to participants). For Task 4, participants analyzed a whole air sample (urban air, cryogenically collected). In Task 5, participants analyzed samples of clean continental air containing NMHCs at much lower mixing ratios than in any of the previous tasks. In all experiments NCAR-NOMHICE analyzed the canisters before they were shipped to participants and after the canisters were returned. Results were referenced to NIST for Tasks 1 and 2 and to NCAR-NOMHICE for Tasks 3 through 5.

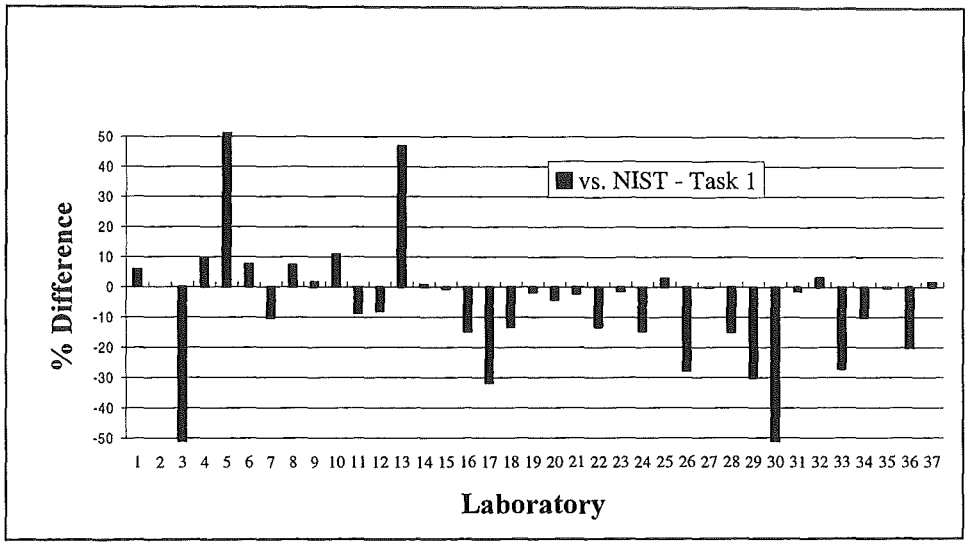

Figure 1. *Task 1 results for n-butane.*

Results for the Task 1 standard (nominally 10 ppbv) are given in Figure 1 for n-butane. The numbers along the x-axis represent identifiers for individual laboratories in a random order. There were 37 participants in this task. Examination of the figure reveals that some laboratories demonstrated good quantitative results whereas others showed significant deviations from expected results. In most cases discrepancies could be linked to inadequate standards or lack of precision in the methodology.

Figure 2 shows the results for the Task 2 NIST-prepared gravimetric sample. This sample contained sixteen hydrocarbons (from C_2 through C_{10}) in the 10–100 ppbv range. Participant's results are given in terms of the absolute value of the percent difference (from NIST gravimetric values) averaged over all compounds that were quantified in the sample. The number of compounds quantified are shown on top of each bar in the figure for each individual laboratory. Eight laboratories were within 10% of the NIST gravimetric values for the compounds which they analyzed. Other laboratories experienced significant problems. In these cases NOMHICE personnel consulted with the individual laboratories making the measurements and made every effort to help identify and resolve discrepancies.

Tasks 3, 4, and 5 involved the circulation of complex challenge mixtures. The NMHC compound mixing ratios are shown in Figure 3 for selected compounds in each sample. Task 4 mixing ratios are representative of a fairly typical urban air sample whereas Task 5 mixing ratios are representative of clean continental air. Task 3 mixing ratios are higher than typically found in an urban area.

Task 3 involved the analysis of some 60 NMHCs in a test sample prepared by Scott-Marrin, Inc. and certified by NCAR-NOMHICE and Dr. William Lonneman at EPA-RTP. Figure 4 shows some of the results (Apel *et al.*, 1997a) for Task 3 presented in an analogous fashion to results presented in Figure 2. In Task 3, however, the results are compared to NCAR-NOMHICE values obtained both before the canister was sent to participants and after its return. In this task, one of the biggest challenges was to be able to chromatographically resolve a large number of compounds. These results indicated that some laboratories continued to do well and progress was being made by others.

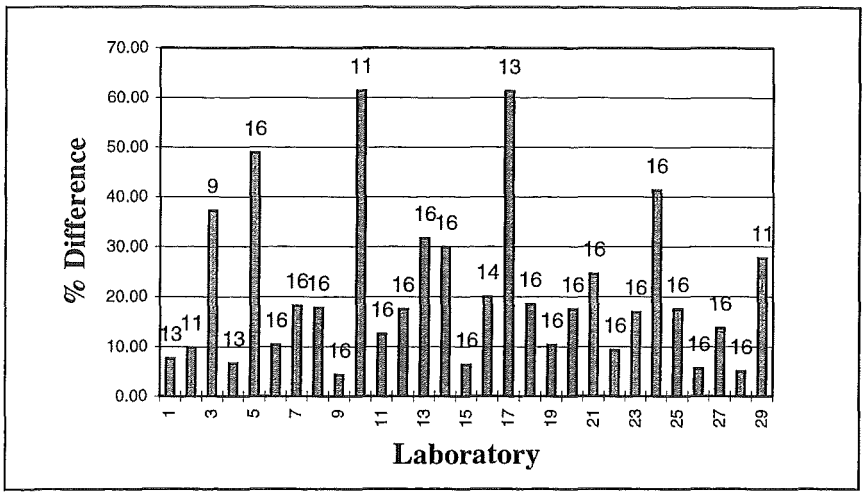

Figure 2. Task 2 results for 16 component standard.

Figure 5 shows the results (% differences) obtained by NCAR-NOMHICE in the before and after analysis of the canisters that were sent to the Task 4 participants (Apel *et al.*, 1997a). Close inspection of the figure reveals that, for most compounds, the NCAR-NOMHICE before and after analyses agreed quite well and that the NCAR-NOMHICE results have a high precision even for low concentration compounds. Some of the largest discrepancies occur for alkenes (increase in concentration with time) and for some of the higher molecular weight compounds (decrease in concentration with time). Participant results for Task 4 were in reasonable agreement with NCAR-NOMHICE for many of the compounds. The analysis for some compounds were more problematic than for others. For example, some of the largest discrepancies occurred for the alkenes and also for some of the higher molecular weight compounds. These differences were real and not a result of canister artifacts. Differences were explored with each individual group.

There are relatively few research groups that are interested in measuring very low NMHC mixing ratios such as were found in the Task 5 air sample. However, the measurement of low mixing ratios of NMHCs is highly relevant for atmospheric chemistry studies. Despite the low concentrations, the majority of compounds were stable in the canisters over the course of the experiment (approximately 3 months). Some compounds were problematic and the low concentrations of compounds in the sample most likely exacerbates the problem. Propylene again showed an increase in concentration versus time but, unlike Task 4 results, the butenes did not. Isobutene decreased with time in the canisters as did isoprene and some of the higher molecular weight compounds.

Preliminary results indicate that the participant laboratories results tended toward higher concentrations than the NCAR-NOMHICE results for many of the compounds and that clear discrepancies were observed for many of the alkenes. The causes for the discrepancies are being investigated.

In addition to the NOMHICE intercomparisons, a good deal of recent effort has focused on the quantitative analysis of oxygen-containing OVOCs (Apel *et al.*, 1997b,c, Riemer *et al.*, 1997, Starn *et al.*, 1997). OVOC standards were prepared and calibrated. Side-by-side comparisons of CG-MS systems and cartridge systems were conducted during the Southern Oxidants Study (SOS) Nashville Intensive. The results showed that OVOCs such as methanol, formaldehyde, acetaldehyde, and acetone were present at significant levels at the semi-rural site. Figure 6 shows the result of a side-by-side comparison of GS-MS systems for acetone (Apel *et al.*, 1997b). The systems tracked each other fairly well but there was an offset that could be fully accounted for only during part of the measurement period when the results were adjusted to a common standard.

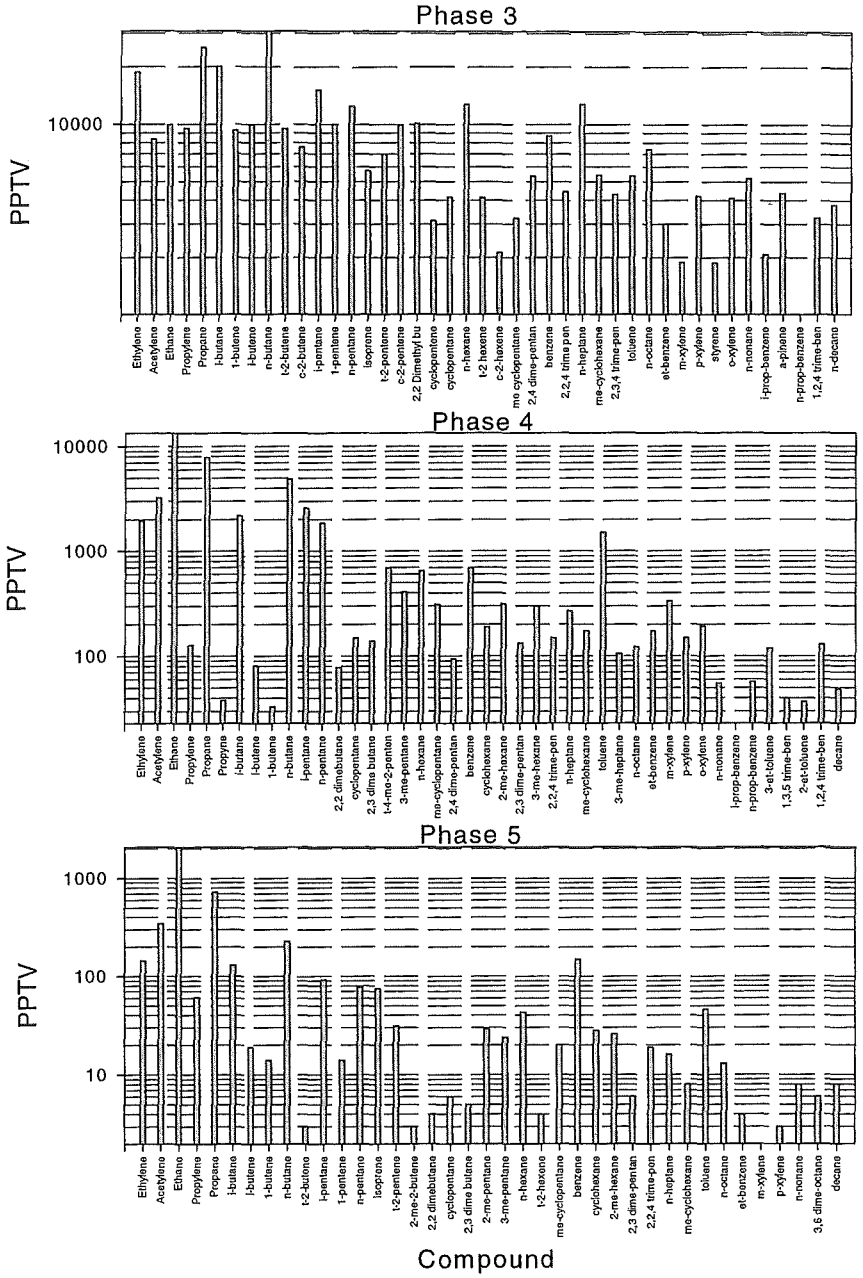

Figure 3. *Mixing ratios of Task 3, 4, and 5 samples.*

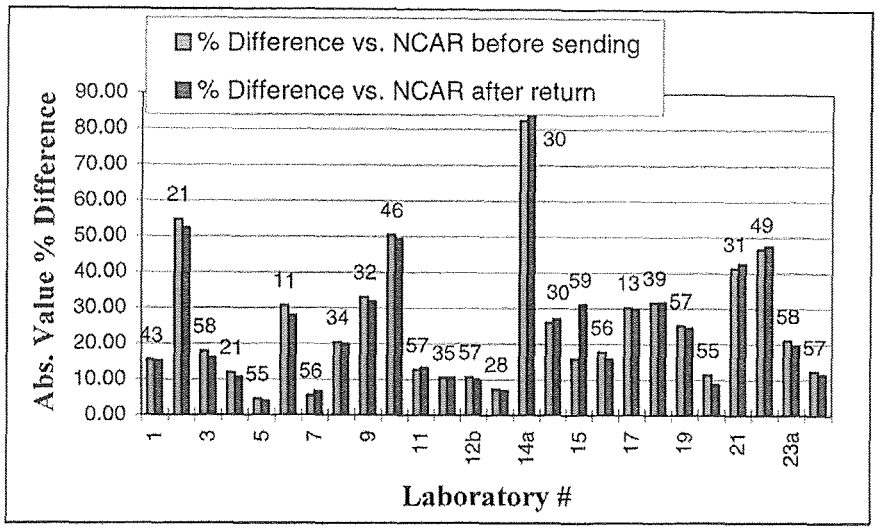

Figure 4. Task 3 results.

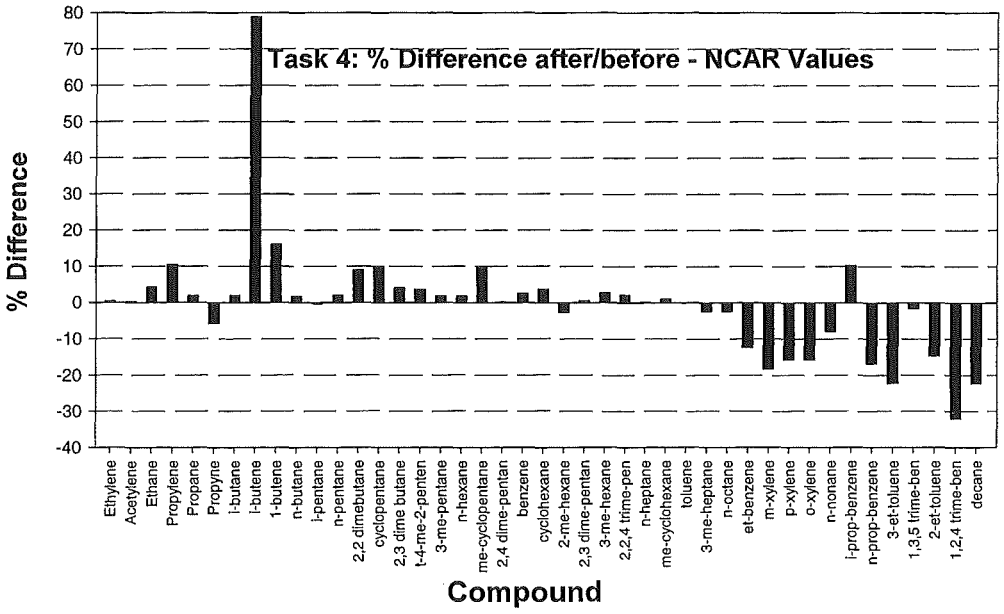

Figure 5. NCAR-NOMHICE before and after results for Task 4 canister samples.

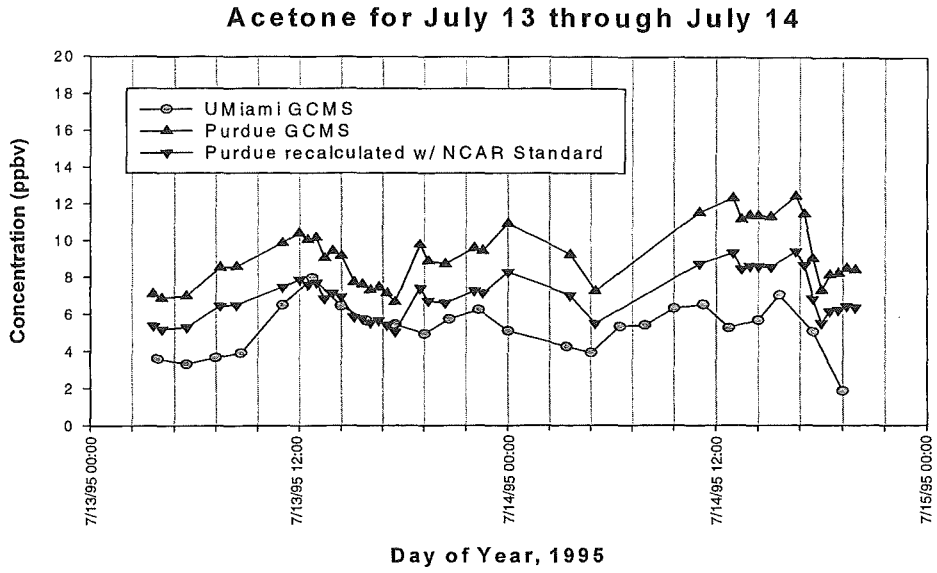

Figure 6. Comparison of GC-MS results for acetone during SOS field experiment.

A conclusion from the study was that a number of OVOCs should be routinely measured and that improvements in the accuracy and comparability of techniques is a must. The NCAR group also recently completed an intercomparison of continuous and cartridge-based formaldehyde measurement techniques (Gilpin *et al.*, 1997). A conclusion from this study was that gas-phase standards should be used by all investigators regardless of the instrument being used to measure formaldehyde.

A majority of the problems encountered with the analysis of NMHCs in common standard mixtures and in common ambient samples have been addressed through NOMHICE. It is clear that some compounds tend to be more problematic than others. Some problems are traceable to storage problems in canisters. Precision and accuracy suffer when very low mixing ratios are encountered. To date the NOMHICE program has focused on the analyses of canisters and has not addressed a number of *in situ* measurement issues which could be addressed by: 1) the side-by-side instrument comparison under controlled laboratory conditions of known VOC concentrations in which various potential interferants such as ozone, water vapor, aerosols or trace gases are added to the flowing gas stream and 2) side-by-side instrument intercomparison of identically sampled ambient air under a variety of chemical and meteorological conditions.

Because instrumentation for measurements of VOCs continually changes (sometimes in subtle ways and sometimes in less subtle ways), VOC intercomparisons will continue to be an integral part of the research in VOC measurements. Investigators should build well-thought-out intercomparisons into any field experiment requiring VOC measurements.

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HYDROCARBONS FROM MAN-MADE SOURCES: INTERPRETATION OF AIR QUALITY DATA

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1 Introduction

The role and importance in atmospheric chemistry of hydrocarbons from human activities was established about fifty years ago by Haagen-Smit in his pioneering studies of Los Angeles smog. He identified the key importance of hydrocarbon oxidation, in the presence of sunlight and oxides of nitrogen, as a photochemical source of ozone and other oxidants. Detailed understanding of the mechanism of photochemical smog formation has developed since then through the combination of smog chamber, laboratory chemical kinetics, field experiment, air quality monitoring, and computer modelling studies.

Since these early pioneering studies, photochemical smog has subsequently been detected in almost all of the world's major urban and industrial centres, at levels which exceed internationally agreed criteria values, set to protect human health. Chlorinated hydrocarbons from human activities now reach the stratosphere, where processing by solar radiation yields active odd-chlorine species which are potent depleting agents of the stratospheric ozone layer.

Volatile organic compounds, or VOCs, are an important class of air pollutants, commonly found in the atmosphere at ground level in all urban and industrial centres. There are many hundreds of compounds which come within the category of VOCs and the situation is yet further complicated by different definitions and nomenclature. Strictly speaking, the term volatile organic compounds refers to those organic compounds which are present in the atmosphere as gaseous compounds derived from pure compounds which under normal conditions of temperature and pressure would be liquids or solids. A volatile organic compound is by definition an organic compound whose vapour pressure at say 20°C is less than 760 torr (101.3kPa) and greater than 1 torr (0.13kPa). Many common and important organic compounds would be ruled out of consideration in this review if the upper and lower limits were adhered too rigidly. Other terms used to represent VOCs are hydrocarbons (HCs), reactive organic gases (ROGs) and non-methane volatile organic compounds (NMVOCs).

Man-made hydrocarbons arise mainly from motor vehicle exhausts, evaporation of petrol vapours from motor cars, solvent usage, industrial processes, oil refining, petrol storage and distribution, land-filled wastes, food manufacture, and agriculture. Because of the very large number of individual air pollutants that come within the definition of man-made hydrocarbons, their importance as a class of ambient air pollutants has only recently become recognised. Progress has been slow because intensive air monitoring to confirm their occurrence in the ambient atmosphere has only recently been started and because of the lack of basic information with which to target research activities. The situation has improved dramatically over the last few years and the important role played by organic compounds in a range of environmental problems of concern can now be identified.

These important roles are in stratospheric ozone depletion, ground level photochemical ozone formation, toxic or carcinogenic human health effects, enhancing the global greenhouse effect, accumulation and persistence in the environment.

1.1 Stratospheric Ozone Depletion

Many man-made hydrocarbons are stable enough to persist in the atmosphere and to survive tropospheric removal processes and to reach the stratosphere. If they contain chlorine or bromine substituents, the processes of stratospheric photolysis and hydroxyl radical destruction may lead to the release of active ozone-destruction chain carriers and to further stimulation of stratospheric ozone layer depletion and Antarctic "ozone hole" formation. Many chlorinated solvents and refrigerants and bromine-containing fire retardants and fire extinguishers have been identified as belonging to the category of organic compounds which may lead to stratospheric ozone layer depletion. Such compounds come within the scope and control of the Montreal Protocol.

1.2 Ground Level Ozone Formation

Hydrocarbons play a crucial role in ground level photochemical oxidant formation since they control the rate of oxidant production in those areas where NO_x levels are sufficient to maintain ozone production. The contribution that man-made hydrocarbons make to the exceedence of environmental criteria for ozone across Europe is now widely recognised. Long-range trans-boundary transport of ozone and action to control its precursors is an important feature of the problem. All man-made hydrocarbons produce photochemical ozone in the troposphere, come within the scope of the Geneva Protocol to the UN ECE International Convention on Long Range Transboundary Air Pollution.

Ground level ozone is of concern not only with respect to human health but also because of its effects on crops, plants, and trees. Elevated ozone concentrations during summertime photo-chemical pollution episodes may exceed environmental criteria set to protect both human health and natural ecosystems. It is these concerns which led to the formulation of the Geneva Protocol and which underpin the reductions in emissions and control actions which it stipulates.

1.3 Toxic and Carcinogenic Health Effects

Man-made hydrocarbons may have important impacts on human health through direct mechanisms in addition to their indirect impacts through photochemical ozone formation. Some hydrocarbons affect the human senses through their odour, some others exert a narcotic effect, and certain species are toxic. Concern is particularly expressed about those organic compounds which could induce cancer in the human population: the human genotoxic carcinogens. The term "air toxics" is usually given to those man-made hydrocarbons that are present in the ambient atmosphere and have or are suspected to have the potential to induce cancer in the human population.

The control of air toxics is currently both a national and an international activity, involving a wide range of international fora. A wide range of chemicals are also coming under scruting in this context. The most important hydrocarbons which belong to the air toxic category, and are widely distributed in the ambient atmosphere, include:

- benzene and 1,3-butadiene (buta-1,3-diene), as potential leukaemia-inducing agents,
- formaldehyde (methanal), as a potential nasal carcinogen,
- polynuclear aromatic hydrocarbons, as potential lung cancer inducing agents,
- polychlorinated biphenyl compounds PCBs and polychlorinated terphenyl compounds PCTs,
- dioxins and furans.

1.4 Global Greenhouse Effect

Almost all of the hydrocarbons emitted as a result of human activities are discharged into the atmospheric boundary layer, the shallow region of the troposphere next to the earth's surface whose depth is typically a few hundred metres in winter to perhaps 2 km in mid-summer. Many of the reactive hydrocarbons are quickly oxidized in the atmospheric boundary layer. However, some survive and are transported into the free troposphere above the boundary layer during particular meteorological events such as the passage of fronts, convection, and in the passage of air masses over mountains.

Some of the longer-lived organic compounds are accumulating in the troposphere, or may have the potential to do so. If any of these compounds can absorb solar or terrestrial infrared radiation, then they may contribute to the enhanced greenhouse effect. Many organic compounds are, however, not themselves radiatively active gases, but they do have the property of potentially being able to perturb the global distributions of other radiatively active gases. Organic compounds can behave as secondary greenhouse gases by reacting to produce ozone in the troposphere and by increasing or decreasing the tropospheric OH distribution and hence perturbing the distribution of methane.

Once in the free troposphere, long-lived organic compounds can stimulate ozone production there. Ozone levels in this region are believed to be rising steadily and this is of some concern because ozone is an important global greenhouse gas. However, the importance of the emissions of organic compounds from human activities in the build-up of global tropospheric ozone is still under evaluation.

1.5 Accumulation and Persistence

Some of the higher molecular mass organic compounds are persistent enough to survive oxidation and removal processes in the boundary layer and may be transported over large distances before being removed in rain. There is an important class of organic compounds, the semi-volatile VOCs which, because of their molecular size and complexity, tend to become adsorbed onto the surface of suspended particulate matter. In this form they undergo long-range transport and may be removed in rain remote from their point of original emission. Once deposited in rain, they may re-evaporate back into the atmosphere and begin the cycle all over again. Ultimately this material may be recycled through the atmosphere before reaching its more permanent sink in the colder aquatic environments in polar regions. Biological accumulation in these sensitive environments can lead to toxic levels in human foodstuffs in areas exceedingly remote from the point of original emission.

The identification of those man-made organic compounds which are likely to persist in the environment, to bio-accumulate, and hence to find a pathway back to man, is still in its early days. Already some classes of organic compounds can be identified including the PCBs, PCTs, and phthalic acid and its derivatives. International action through the UN ECE international convention on Long Range Transboundary Air Pollution and its protocol on Persistent Organic Pollu-

tants has begun to tackle the problems of the long-range transboundary transport of compounds which may persist and accumulate in polar environments.

2 Sources of VOCs

Emission inventories are now becoming available for the low molecular mass hydrocarbons compounds for most European countries and the countries with the largest emissions appear to be USSR, Italy, and the Federal Republic of Germany. The major source categories identified include mobile sources through all modes of transport, stationary sources including evaporation, solvent usage, the industrial processes of oil refining and chemicals manufacture, oil and gas production, and agriculture. Altogether, European emissions of low molecular mass volatile organic compounds from human activities amounted to about 23.8 million tonnes/yr in 1989. This total is comparable with that of sulphur dioxide (as S) and of nitrogen oxides (as NO_2), with each of the order of 20 million tonnes/yr for Europe as a whole.

European emissions of methane amounted to about 46 million tonnes/yr in 1990 but are subject to large uncertainties. They are thought to arise from coal mines, natural gas leakage, landfill gas, offshore oil and gas operations and from agriculture, with the largest contribution being from cattle.

By combining figures for the total man-made hydrocarbon emissions by source category with the profile of the mass emissions of individual organic compounds, it is possible to derive emission estimates for individual organic compounds. On this basis, the speciated emissions of over 90 individual organic compounds have been identified in UK source categories. Toluene appears to account for the greatest percentage, about 7% of the total. Of all the classes of VOC species, the alkanes appear to account for the greatest percentage of UK national emissions.

3 Ambient concentrations of organic compounds

A summary is provided in Figure 1 of the measured concentrations of man-made hydrocarbons in cities throughout the world and in Figure 2 in a range of sites across Europe. Concentrations steadily decrease through three orders of magnitude, from the urban kerbside where concentrations are typically 10's ppb, to urban background, to rural and to remote maritime background sites (10s–100s ppt). Since the concentration ratios do not stay constant, particularly for reactive hydrocarbons, air at remote sites is not merely diluted urban air. Many different sources, as well as depletion by chemical conversion, contribute to the observed spatial patterns and the differences between the mean concentrations at the different sites.

The species distribution of the organic compounds at the remote maritime sites are dominated by the alkanes, ethane and propane, presumably reflecting the importance of natural, marine sources. By comparison, the species distribution observed at the urban kerbside site is heavily dominated by ethylene, n-butane and acetylene, the major components of motor vehicle exhaust and evaporated motor spirit.

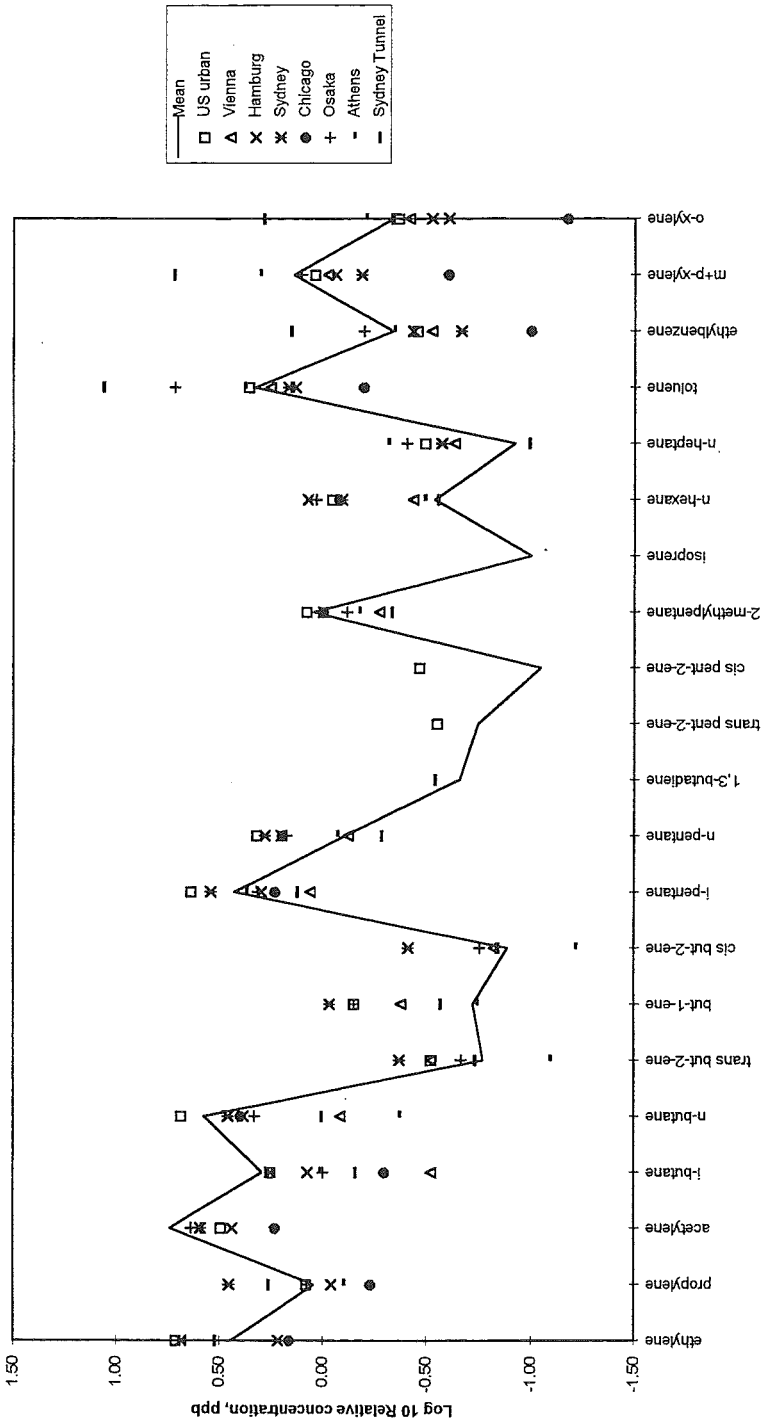

Figure 1. Hydrocarbon concentrations relative to benzene in UK urban background air compared with those reported in other cities throughout the world.

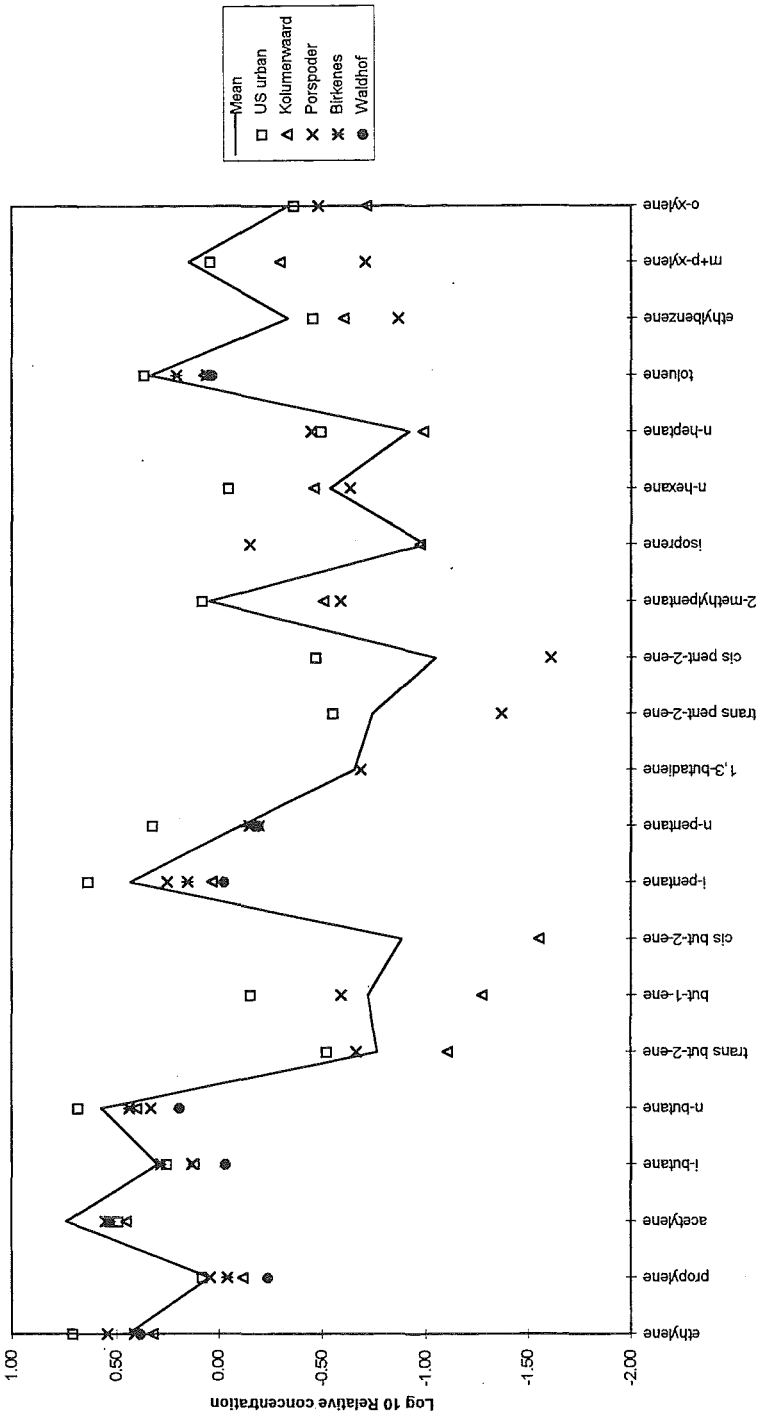

Figure 2. Hydrocarbon concentrations relative to benzene in UK background air compared with those reported for remote rural sites in Europe.

4 Fates of man-made hydrocarbons

As a class, man-made hydrocarbons all share the same major atmospheric removal mechanisms, which include photochemical oxidation by hydroxyl (OH) radicals in the troposphere, photolysis in the troposphere and stratosphere, deposition and uptake at the earth's surface, and reaction with other reactive species such as chlorine atoms, nitrate radicals at night, and ozone.

4.1 Photochemical Oxidation by OH Radicals in the Troposphere

The reactive free radical species, hydroxyl or OH, plays a central role in tropospheric chemistry by cleansing the atmosphere of most of the trace gases emitted by human activities, particularly the hydrocarbons which are the subject of this review. This steady state of hydroxyl radicals is maintained by a set of rapid free radical reactions which comprise the fast photochemical balance of the troposphere and so define the oxidation capacity of the troposphere.

The hydroxyl radical oxidation sink for organic compounds is operating throughout the troposphere and is not limited in its spatial regime merely to the atmospheric boundary layer. This oxidation sink determines the atmospheric lifetimes for the vast majority of this class of atmospheric species. Lifetimes, together with emission rates, determine the global concentrations which would eventually build up if emissions continued indefinitely.

It is difficult to generalise about the atmospheric lifetimes for a wide range of organic compounds which result from oxidation by tropospheric hydroxyl radicals. The alkanes generally have lifetimes of about 2–30 days, with lifetime decreasing along the homologous series. The first two members of the alkane series have significantly longer lifetimes than the above range, with methane about 10 years and ethane about 120 days. Alkenes generally have the shortest lifetimes of the major classes of organic compounds found in the atmosphere. Their lifetimes range from about 0.4–4 days, with lifetimes decreasing along the homologous series. Aromatic hydrocarbons show lifetimes in the range 0.4–5 days, with the first member of that series, benzene, showing an uncharacteristically long lifetime of 25 days.

4.2 Photolysis in the Troposphere and the Stratosphere

Photolysis is an important removal process for only the limited range of organic compounds which show strong absorption features in the ultraviolet and visible regions of the spectrum. The extent of the overlap between these absorption features, the quantum yields for the various pathways, and the solar actinic flux determines the lifetime of the photochemically labile species. The solar actinic fluxes vary considerably with time-of-day, latitude, and season and quite importantly with height in the atmosphere. The solar spectrum seen by photochemically labile organic compounds is characteristically different in the troposphere and stratosphere. In the latter, the wavelengths extend down to 180 nm, whereas in the former they do not extend much below 295 nm.

Photolysis is an important loss process for the aldehydes and ketones in the troposphere where it also acts as an important source of free radical species. Photolysis lifetimes of aldehydes and ketones in the sunlit troposphere may be of the order of several days. In the stratosphere, vacuum ultraviolet photolysis of chlorine-containing organic compounds is an important removal mechanism for the chlorocarbons. This latter process, however, acts as a source of active chlor-

ine carriers which can catalyse the destruction of the ozone layer in the presence of polar stratospheric clouds. Lifetimes due to stratospheric photolysis for organic compounds released at the earth's surface are generally of the order of 40 years or more.

4.3 Deposition and Uptake at the Earth's Surface

Deposition to water surfaces, plants, vegetation, and soil surfaces is generally termed dry deposition, and requires both the transport of the trace gas species to the surface within the atmospheric boundary layer and its subsequent reaction or adsorption at the surface or on surface elements. For the majority of the man-made hydrocarbons, little information is available concerning the importance of dry deposition. The general impression is that this process is not important. For example, soil uptake of methane accounts for a removal lifetime of 160 years.

The removal of trace gases by precipitation, referred to as wet deposition, results from the incorporation of material into falling precipitation (wash-out) and by incorporation into cloud droplets (rain-out). These removal processes are necessarily only significant for those species which are readily soluble. The vast majority of low molecular mass hydrocarbons are not in this category and so are generally not removed significantly by wet deposition. The highly polar carboxylic acids and alkyl hydrogen peroxides are probably the only classes of organic compounds which undergo wet removal.

As the molecular mass of an organic compound increases, its volatility tends to decrease and increasingly it becomes adsorbed onto the atmospheric aerosol. Semi-volatile organic compounds tend to behave more like aerosol particles than the parent organic compounds from which they are formed. Deposition by dry and wet deposition rather than oxidation by hydroxyl radicals are the major removal mechanisms for semi-volatile organic compounds.

4.4 Reactions with chlorine atoms, nitrate radicals and ozone

Of all the reactive atoms and radical species, the hydroxyl radical is relatively unusual in its high reactivity with most inorganic and organic substances found in the atmosphere. Fluorine atoms share this wide spectrum of reactivity with the hydroxyl radical but lack significant atmospheric sources. Chlorine atoms react rapidly with most organic compounds but, like fluorine, lack significant atmospheric sources. Except in rather special circumstances, chlorine atom reactions can generally be neglected in the determination of atmospheric lifetimes of organic compounds.

During nighttime in the unpolluted troposphere, a steady state of nitrate radicals builds up through the reactions of nitrogen dioxide with ozone. Nitrate radicals may react with the highly reactive alkenes and dialkenes to form nitrato-carbonyl compounds by addition reactions. The atmospheric fates of the various bifunctional addition compounds have yet to be identified. For the large number of man-made hydrocarbons, however, nitrate radicals are not reactive enough to contribute significant atmospheric removal. Ozone reactions appear to be significant compared with hydroxyl radical reactions for this same class of alkenes and dialkenes as for nitrate radicals.

4.5 Fates

The overall impact of these removal processes on the fates and behaviour of man-made hydrocarbons is markedly dependent upon the physical and chemical properties of the individual organic compound. For the bulk of the organic compounds emitted by human activities in the northern

mid-latitudes, atmospheric lifetimes are generally one hundred days or less. They are likely to spread vertically up to the tropopause and through much of the northern hemisphere, at least over the continental regions. For those with lifetimes of five days or less, they are likely to be found to any significant extent only in the atmospheric boundary layer and within a thousand kilometres or so of major source regions.

Highly unreactive organic compounds may exhibit atmospheric lifetimes measured in years or tens of years. An important class is that of the ozone-depleting substances where lifetimes span 5 years for methyl chloroform (1,1,1-trichloroethane) to about 130 years for CFC-12. Some organic compounds with long atmospheric lifetimes are also important radiatively-active gases. This class includes methane with its 10 year lifetime and the replacement CFCs such as HFC 134a and 143a with lifetimes of 16 and 41 years, respectively.

For those low volatility high-molecular mass organic compounds, their fate is largely determined by the extent of their attachment by adsorption to the atmospheric aerosol. Semi-volatile organic compounds attached to aerosol particles behave quite differently from gaseous organic compounds. The former are removed from the atmosphere largely by wet and dry deposition and the latter by hydroxyl radical oxidation. Lifetimes for semi-volatile organic compounds adsorbed onto aerosol particles are similar to those of aerosol particles themselves, generally about 5–10 days, close to the Earth's surface. Lifetimes for gaseous organic compounds are highly variable from days to years.

Fates are different also for the gaseous organic compounds compared with the organic compounds adsorbed onto particles. Atmospheric oxidation involves the complete destruction of the organic compound, ultimately to carbon dioxide and water, whereas deposition of the semi-volatile organic compounds leads to the ecosystem contamination and the transfer of the organic compound into different environmental media.

Acknowledgments

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NATURAL EMISSIONS OF VOLATILE ORGANIC COMPOUNDS

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1 Sources and compounds

What are natural and biogenic sources?

Some emission sources have little or no human influence, including ice, oceans, and wilderness areas. Many other sources that we might think of as natural can be significantly influenced by human activities, including soils, vegetation, animals and biomass burning. Biogenic emissions are generally considered to be the biological production and release solely due to biological activity. Thus fossil fuel combustion, which results from the abiotic processing of organic compounds that were originally produced by biological activity, is not considered a biogenic emission source.

Biogenic VOC include the following:

1) Hydrocarbons

- a) Alkanes
  - i) Methane
  - ii) Ethane
  - iii) Up to C_{17}
- b) Alkenes
  - i) Terpenoids
    - (1) Hemiterpenes (C_5): isoprene
    - (2) Monoterpenes (C_{10}): α-pinene
    - (3) Sesquiterpenes (C_{15}): β-carophyllene
  - ii) Other
    - (1) Ethene (C_2)
    - (2) Propene (C_3)
    - (3) Up to C_{10}
- c) Arenes (Aromatic): ρ-cymene (a monoterpene)

2) Oxygen containing

- a) Aldehyde
- b) Ketone

c) Alcohol

d) Carboxylic acid

e) Ester

f) Ether

3) Sulfur containing

4) Nitrogen containing

5) Halogen containing

Of the above VOC, some of the most important include

1. Isoprene and methylbutenol (C_5) which dominate emissions from many forested areas.

2. Monoterpenes (C_{10}) including α-Pinene, β-Pinene, Δ^3-Carene, δ-Limonene, Myrcene, Sabinene, Camphene, α-Thujene, β-Phellandrene, Terpinolene, α-Terpinene, γ-Terpinene, ρ-Cymene, Ocimene, 1,8-Cineole, Camphor, Bornyl acetate, Piperitone.

3. Hexenal family (C_6 oxygenated) including hexenal, hexenylacetate, hexenol, hexanal compounds. Emissions of these compounds are strongly influenced by wounding.

4. Reactive C_1–C_3 VOC including formaldehyde, formic acid, acetaldehyde, acetic acid, ethene, butene, propene.

5. Less reactive C_1–C_3 VOC including methanol, ethanol, acetone, ethane, and propane.

2 Flux measurements

Figure 1 illustrates some of the techniques used to investigate biogenic VOC emissions. A variety of flux measurement techniques are described in detail by Guenther *et al.* (1996). Flux measurement systems that operate on small scales, such as enclosures, are used to investigate how biological and environmental conditions control emission rates. Individual leaves, branches, or entire trees can be enclosed and their environment carefully characterized. Micrometeorological flux systems measure above canopy fluxes and are used to evaluate the net flux predicted by emission models. These systems can be deployed on towers, tethered balloons and aircraft. The horizontal canopy area characterized by these flux techniques, which is dependent on factors that include the height of the flux system and the meteorological conditions, is typically about 0.01 to 3 km^2 for tower based systems and 3 to 100 km^2 for tethered balloon or aircraft systems. Tower flux systems are particularly useful for investigating how emissions vary with time on diurnal, seasonal and year-to-year time scales. The tethered balloon and aircraft systems are used to characterize large areas.

Flux measurement methods include eddy flux, gradient flux, tracer, and mass balance. Each method is described briefly below:

Eddy Flux

Flux = *Mean*[(vertical wind deviation) x (concentration deviation)]

Relate flux to the movement of the gas across a horizontal plane in a turbulent boundary layer. Direct method requires measuring wind speed and concentration very fast (2–20 times per second). Techniques are available (intermittent sampling, cospectral similarity, eddy accumulation, relaxed eddy accumulation) that allow us to use slower sensors or collect samples that can be analyzed later.

Tracer

Flux = (flux of tracer) x (concentration / conc. of tracer)

Relate flux to another (better known) flux. Use for emission sources (e.g. biomass burning) that produce several trace gases via the same process or devise an artificial release of a trace gas (e.g. SF_6) that can simulate the source.

Gradient

Flux = (eddy diffusivity coefficient) x (vertical concentration difference)/(vertical distance)

Relate flux to a concentration gradient. Gradient can be within the surface or mixed atmospheric boundary layer or between the ocean and atmosphere.

Mass balance within a box

Flux = (concentration difference in time and/or space) + (sinks)

Relate flux to chemistry and transport within a domain. Chambers can be used to physically enclose a source or draw an imaginary 'box' within the boundary layer.

3 Emission modeling

Hydrocarbon emission models are a necessary component of the chemistry and transport models that synthesize our understanding of atmospheric chemistry and are an important tool for investigating the processes that control the composition of the atmosphere. Global models are used to predict how human perturbations might result in changes in climate and the chemical composition of the atmosphere. Emissions of biogenic hydrocarbons are sensitive to global changes in climate and landcover. While both biogenic and anthropogenic emissions are important for global atmospheric chemistry, the total annual emission of reactive VOC to the global atmosphere is dominated by biogenic sources. For example, Guenther *et al.* (1995) estimate that the total global emission of biogenic VOC of about 1150Tg per year is more than seven times greater than the total global emission of anthropogenic VOC.

Numerical studies have shown that an effective ozone control strategy for many regions requires an understanding of both anthropogenic and biogenic emissions of its precursor compounds (Chameides *et al.*, 1988) even though only anthropogenic emissions are considered for emission reduction. A good example is the Atlanta, GA urban area. Chameides *et al.* (1988) estimated that biogenic VOC emissions in excess of 50 kg km^{-2} d^{-1}, in the presence of anthropogenic NO_x, could result in harmful ozone levels, above 120ppb, even if there were no anthropogenic VOC emissions. Geron *et al.* (1995) estimated that biogenic VOC emissions in the Atlanta urban area are about 56 kg km^{-2} d^{-1} indicating that it is not possible to reduce ozone to below 120ppb by reducing anthropogenic VOC emissions and that instead reductions in anthropogenic NO_x emissions are required.

How can we estimate biogenic emissions for the highly variable, and in many cases little understood, sources? The first step in the emission estimation process is to calculate the order of magnitude of a source. Rasmussen (1972) based the first U.S. estimate of isoprene and monoterpene emissions on an emission rate that was determined by placing a mix of oak and pine foliage in a one liter flask. This rate was multiplied by 1800 hours (180 ten hour days) and a canopy depth that was assumed to range from 10 to 200cm. The resulting estimated range of 2.3–46.4 Tg per year demonstrated that natural emissions could be a significant component of the total U.S. VOC flux. The next step in the emissions estimation process is to compile a database of emission estimates, which is known as an emission inventory. Estimates generated for the U.S. and Europe, although very uncertain, have been incorporated into regulatory oxidant models and demonstrated that, in some cases, model ozone predictions were sensitive to estimates of biogenic VOC emissions.

Emission inventories can be used as inputs to photochemical models, but a more useful tool is a dynamic emission model that responds to changes in environment, land use and other factors. This enables the photochemical modeler to predict emissions for the specific scenario under investigation. Emission models also benefit from biochemical and ecological studies of the processes controlling biogenic emissions. These studies can identify the factors controlling emissions and suggest a framework for numerical algorithms. Models predict emission rates, E, as the product of 1) an emission factor that represents the emission rate at a given activity level, 2) activity factors that represents the activity level, and 3) a source density factor that represents quantity within an area. The same general approach can be used for both anthropogenic and natural emissions.

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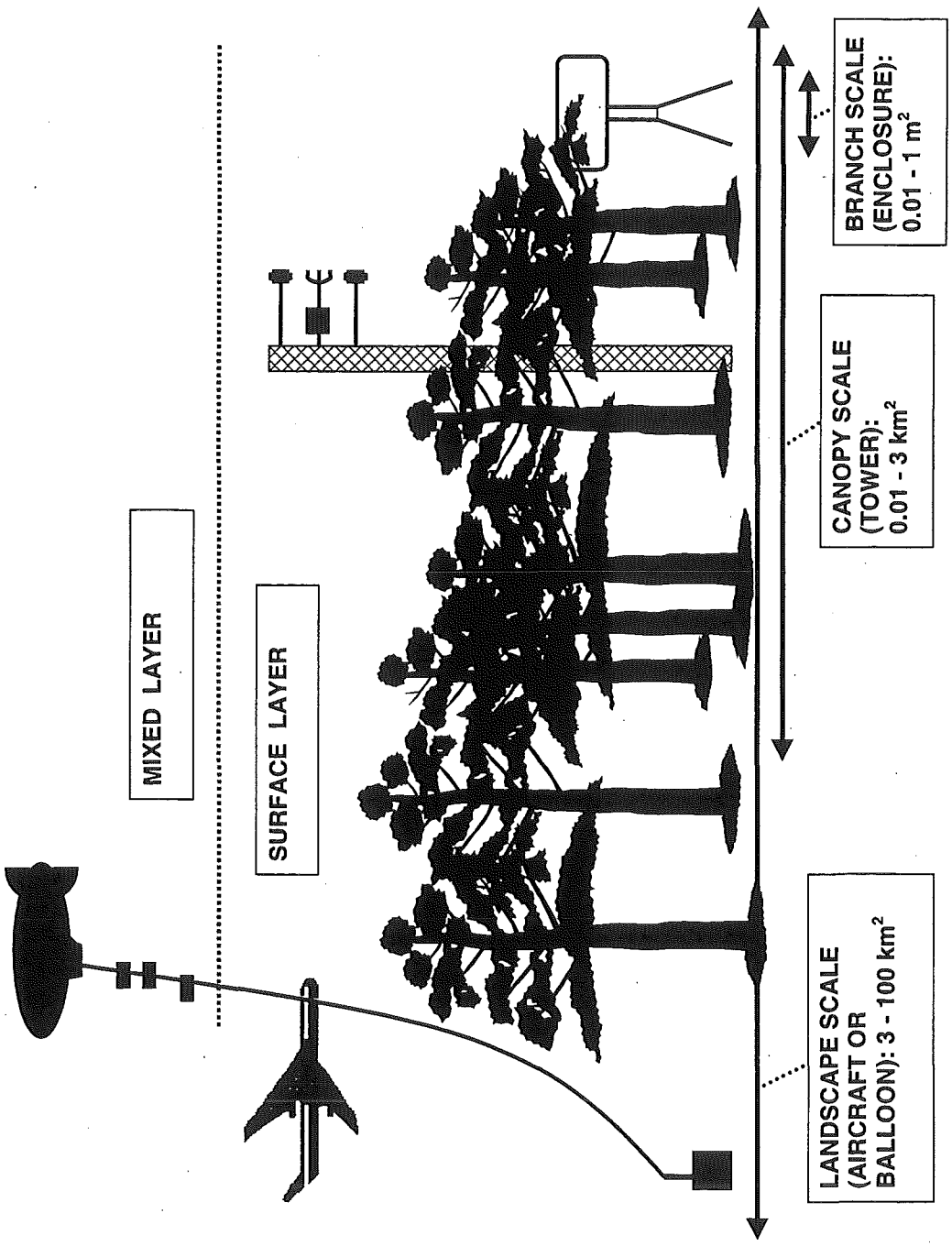

Figure 1. *Measurement techniques used to investigate biogenic emissions at branch, canopy and landscape scales.*

LATITUDINAL AND SEASONAL VARIATION OF TROPOSPHERIC NMHCS

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Because nonmethane hydrocarbons (NMHCs) have diverse anthropogenic and natural emission sources and moderately short atmospheric lifetimes (ranging from hours to months), significant latitudinal, seasonal, and vertical gradients are found. Their chemical reactivity makes NMHCs highly effective ozone precursor species which thus play a critical role in determining the oxidative capacity of different regions of the troposphere (Davis *et al.*, 1996a; Crawford *et al.*, 1997; Jaffe *et al.*, 1997). NMHC gases are useful markers for distinguishing marine boundary layer (MBL) air (Davis *et al.*, 1996b; Wingenter *et al.*, 1996) and, when combined with trajectory analysis, provide a means of estimating the degree of anthropogenic influence in remote marine air masses (Gregory *et al.*, 1996; Talbot *et al.*, 1996, 1997a; Blake, D.R., *et al.*, 1996a, b; Blake, N.J., *et al*, 1997). In addition, because of their differing atmospheric lifetimes, the ratios of the concentrations of selected NMHC species within an air mass offer a useful tool for establishing the relative time since exposure to outside sources (e.g., Smyth *et al.*, 1996; McKeen *et al.*, 1996).

The main sink for NMHCs and halocarbons with an extractable hydrogen atom is through reaction with hydroxyl radicals (HO). The same is true for organic gases with an unsaturated bond, such as C_2Cl_4. Because the photochemical production of HO is favored by sunlight and higher humidity, its formation rate varies diurnally and seasonally. Minimum HO levels are found at high latitudes during winter in association with significantly reduced removal rates for many trace gases. Consequently, those gases with substantial emissions maintained throughout the year exhibit maximum background levels in late winter, with minimum levels occurring during late summer. This seasonal variation in boundary layer (BL) concentrations has been reported for many NMHCs (e.g., Singh *and* Salas, 1982; Hov *et al.*, 1984; Blake *and* Rowland, 1986; Hov *et al.*, 1991; Penkett *et al.*, 1993; Jobson *et al.*, 1994b; Goldstein *et al.*, 1995). Few seasonal airborne, or nonboundary layer, measurements have been made (Lightman *et al.*, 1990; Penkett *et al.*, 1993), and all were confined to the lower free troposphere (<3km). The upper tropospheric seasonal variation of ethane over Europe has been observed by remote laser measurements (Ehhalt *et al.*, 1991).

Few NMHC measurements have been made in the troposphere over the Pacific region. The PEM-West A and B data (Blake, D.R.. *et al.*, 1996a; Blake, N.J. *et al.*, 1996) are the most comprehensive available and highlighted the large scale concentration distribution up to the maximum flight altitude of 12.7km in both the northern hemisphere summer and winter seasons. Most other available measurements in the Pacific region were collected during shipboard studies. Donahue *and* Prinn (1993) measured C_2-C_5 NMHCs and Atlas *et al.* (1993) measured NMHCs and halocarbons in the mid Pacific.

Latitudinal data can be employed to provide baseline reference conditions for each latitude band upon which to assess the local, regional, and global significance of specific emission sources, such as the release of NMHC gases during the smoldering phase of biomass burning. Measurements collected on the NASA DC-8 aircraft over the South Atlantic, Africa and Brazil during the NASA TRACE-A experiment in September and October 1992 are a good example (Blake, N.J., *et al.*, 1996). Large perturbations in the concentrations of potential tropospheric

ozone precursor NMHC compounds as the consequence of regional biomass burning were found over the whole South Atlantic region. However, because of the large and far reaching effects of this seasonal source, the perturbation was most dramatic when compared to the complementary ground-based measurements in the South Pacific region for the same season. Only very sparse and episodic measurements of this wide range of hydrocarbons now exist in the scientific literature, particularly for the southern hemisphere. Hydrocarbon data have also been employed to determine background or baseline levels with which to compare various trends and individual observations made over the Canadian wetlands in summer 1990 during the NASA ABLE-3B project (Smith, 1993; Blake, D.R., *et al.*, 1994), the PEM-WEST A and B projects in the Western Pacific in summer and winter, respectively (Blake, N.J., *et al.*, 1997), and in the southern hemisphere during ACE-1 (Blake, D.R., *et al,* 1996c).

Aircraft data are also very useful in interpreting surface results. The vertical NMHC distributions up to 12.3km obtained during several different aircraft missions have been employed to estimate the regional and global burdens and emissions of these gases. Table 1 shows the average background mixing ratios $\pm 1\sigma$ at the surface for different latitude bands in the northern and southern hemisphere from March 1994 through March 1995 for selected hydrocarbon gases (ethane, ethyne, propane). Figure 1 displays these averages versus the month with sine curve fits to each hydrocarbon. The figure clearly illustrates the different phases and amplitudes of the seasonal cycles in the two hemispheres. For example, the high northern hemisphere average of ethane varies as a function of season between about 2200pptv in February and 700pptv in August in the northern hemisphere above 30°N. The same phase cycle but with a much lower amplitude (from about 1000pptv to 500pptv) is found for the low latitude northern hemisphere. At high latitudes in the southern hemisphere, the amplitude for ethane is even lower but a clear seasonal cycle, with a maximum of about 400pptv in September and a minimum of about 200pptv in March, is still observed. These maxima and minima are in austral late winter/spring and late summer/fall, respectively, in both hemispheres, consistent with OH removal.

Figure 1 also shows that ethyne, propane, *i*- and *n*-butane, *i*- and *n*-pentane, have lower mixing ratios compared to longer-lived ethane but similar phase and relative amplitude trends in both the high and low latitude regions of the northern hemisphere, with the shorter-lived gases tending to peak somewhat earlier in the winter and decay faster in the summer. In each case, the concentrations of these gases are significantly higher in the northern hemisphere than in the south, indicating substantially larger emissions in the north. The interhemispheric ratio is at a minimum in the northern hemisphere summer. Such observations for a variety of gases are potentially very useful in constraining regional source strengths and HO fields for model calculations.

Figure 1 shows that ethyne has a similar seasonal variation to ethane, but with a southern hemisphere winter maximum value of about 70pptv in August and a summer minimum of about 20pptv in February/March. By contrast, high latitude southern hemisphere propane levels show very little seasonal change, with mixing ratios between 60 and 80pptv. In addition, low latitude southern hemispheric levels show a late summer maximum in February/March and a distinct late winter minimum in August/September. This is in phase with its the northern hemisphere variation and so is not consistent with seasonal OH levels in the southern hemisphere. Transport from the northern hemisphere would have the largest effect in the winter months when the interhemispheric ratio is largest but would have effected the levels of other gases including ethyne. In addition, the interhemispheric ratio for ethyne is higher and its summer southern hemisphere background levels lower compared to propane, even though the two gases have similar atmospheric lifetimes (about 20 days for ethyne and 15 days for propane), making interhemispheric transport an extremely unlikely explanation. Thus, it is unclear what may have caused

this low latitude cycle but a larger summer compared to winter southern hemisphere source of propane may be involved.

Southern hemispheric variations of *i*- and *n*-butane have maxima in early winter (May/ June), minima in early summer (November/December), and an amplitude of about 10pptv. This is consistent with their relatively short lifetimes with respect to OH removal. By contrast, both *i*- and *n*-pentane have similar seasonal variations to that of propane, with peak mixing ratios in late summer (February/March) and lowest levels in late winter (August/September). However, their concentrations in the southern hemisphere are very low (2–10 pptv for *n*-pentane and 4–20 pptv for *i*-pentane) and the amplitude of their average seasonal cycles are only 5 to 10pptv.

The short-lived gas ethene also exhibits pronounced southern hemispheric maxima in late summer (January–March) and minima in late winter (July–August). The even shorter-lived gas propene has a smaller seasonal cycle but is in phase with ethene. These alkenes are too short-lived (2 days or less) to be transported from southern hemisphere continental sources, particularly at low latitudes and in summer, making summer continental emissions an extremely unlikely cause of the summer maxima. However, these gases have been reported to have oceanic sources. Thus, summer production in surface sea water that is high enough to overcome the increased rate of destruction in the summer is the most likely explanation of this observed seasonal alkene trend.

Table 1 shows the average surface NMHC mixing ratios for each season on a high and low hemispheric, as well as a global basis, and also their average atmospheric burden calculated employing the vertical distribution information obtained from various NASA and NSF airborne experiments (Blake, D.R ., *et al.*, 1992, 1994, 1996a, 1996b, 1996c; Anderson *et al.*, 1993; Blake, N.J., *et al.*,, 1996, 1997). These annual average global burden values (±1 standard deviation) for the period March 1994 through March 1995 have been calculated to be 638±59pptv for ethane; 115±28pptv for ethyne; and 153±40pptv for propane. The sigma values presented here are the consequence of a global average dominated by the real atmospheric seasonal and hemispheric variability, and not to measurement errors.

Experimental

The combined NMHC/halocarbon analytical apparatus is a six column system utilizing DB-1, DB5-MS, DB-1701, Cyclodex-B, and PLOT Al_2O_3/KCl columns. Each cryogenically-trapped air sample is warmed and injected and then split into six streams, with each stream feeding a separate GC column. The Cyclodex-B column, which is coupled to an FID, is used for separating C_6–C_{11} NMHCs, and provides excellent resolution for benzene, toluene, and the xylenes. This column also separates terpenes when present, and can resolve some chiral compounds. The DB-1 column separates many C_3–C_{10} NMHCs detected by an FID. The PLOT column, also coupled to an FID, is used for determining C_2–C_5 NMHCs, many of which are not resolved adequately by the DB-1 column. The DB-5MS column is plumbed to an ECD and is used primarily for CH_3Br and CH_3I quantification. The DB-1701 column is connected to an ECD and separates organic nitrates. Most remote samples contain relatively few hydrocarbons at levels above their detection limit of 3pptv. The measurement precision for the alkanes and alkynes is generally 1% or 2pptv (1σ), whichever is larger, and 3% or 3pptv (1s) for the alkenes.

Calibration of the NMHC compounds has been achieved by employing standards from Scott Specialty Gas together with standards prepared from pure liquids. A 0.99ppmv gravimetrically prepared propane standard purchased from NBS was also used to verify the Scott mixing ratios. Sets of standards for NMHCs ranging from C_2–C_7 were prepared from the Scott

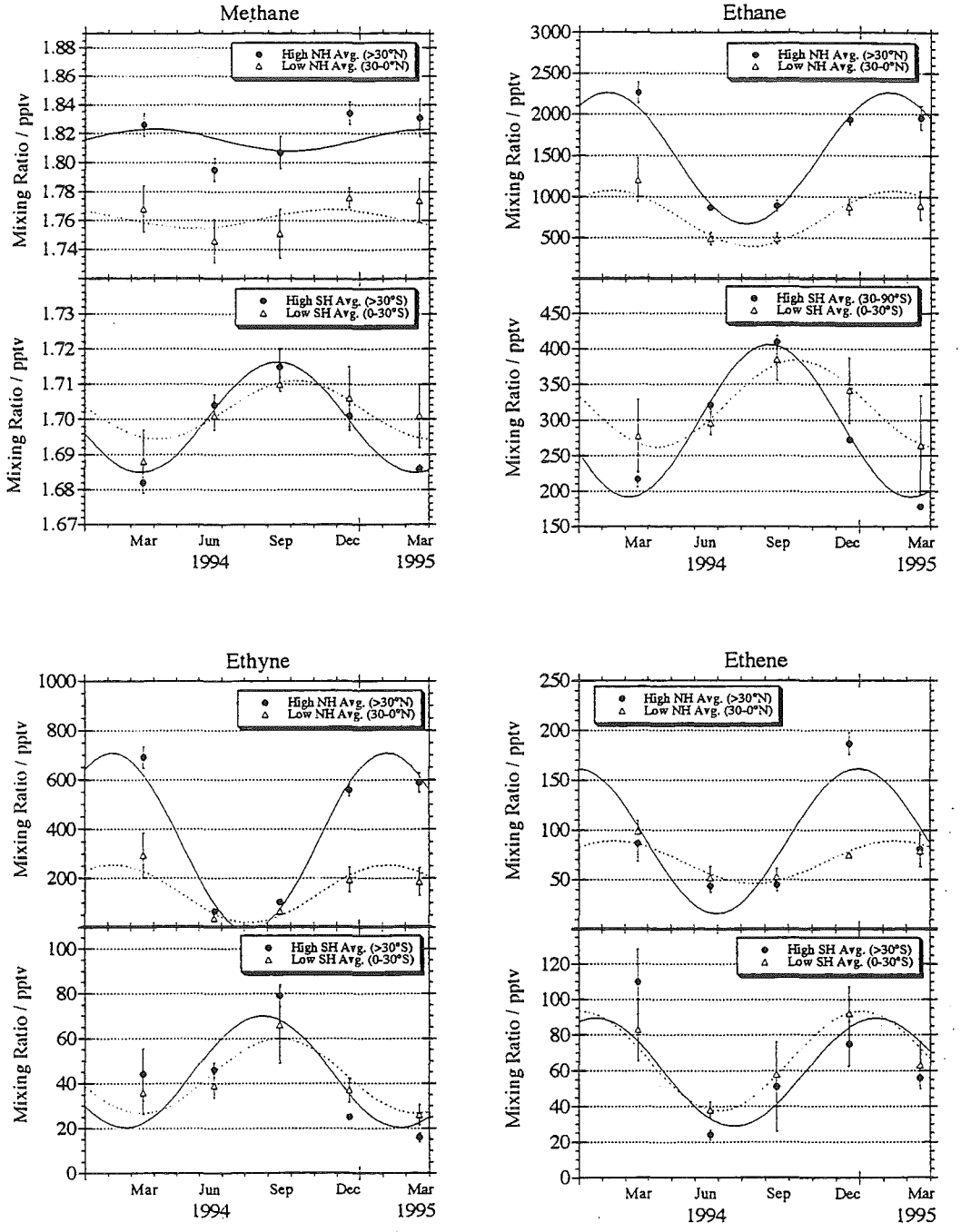

Figure 1. Average background mixing ratios $\pm 1\sigma$ at the surface for high and low latitude bands of the northern and southern hemisphere, March 1994 through March 1995.

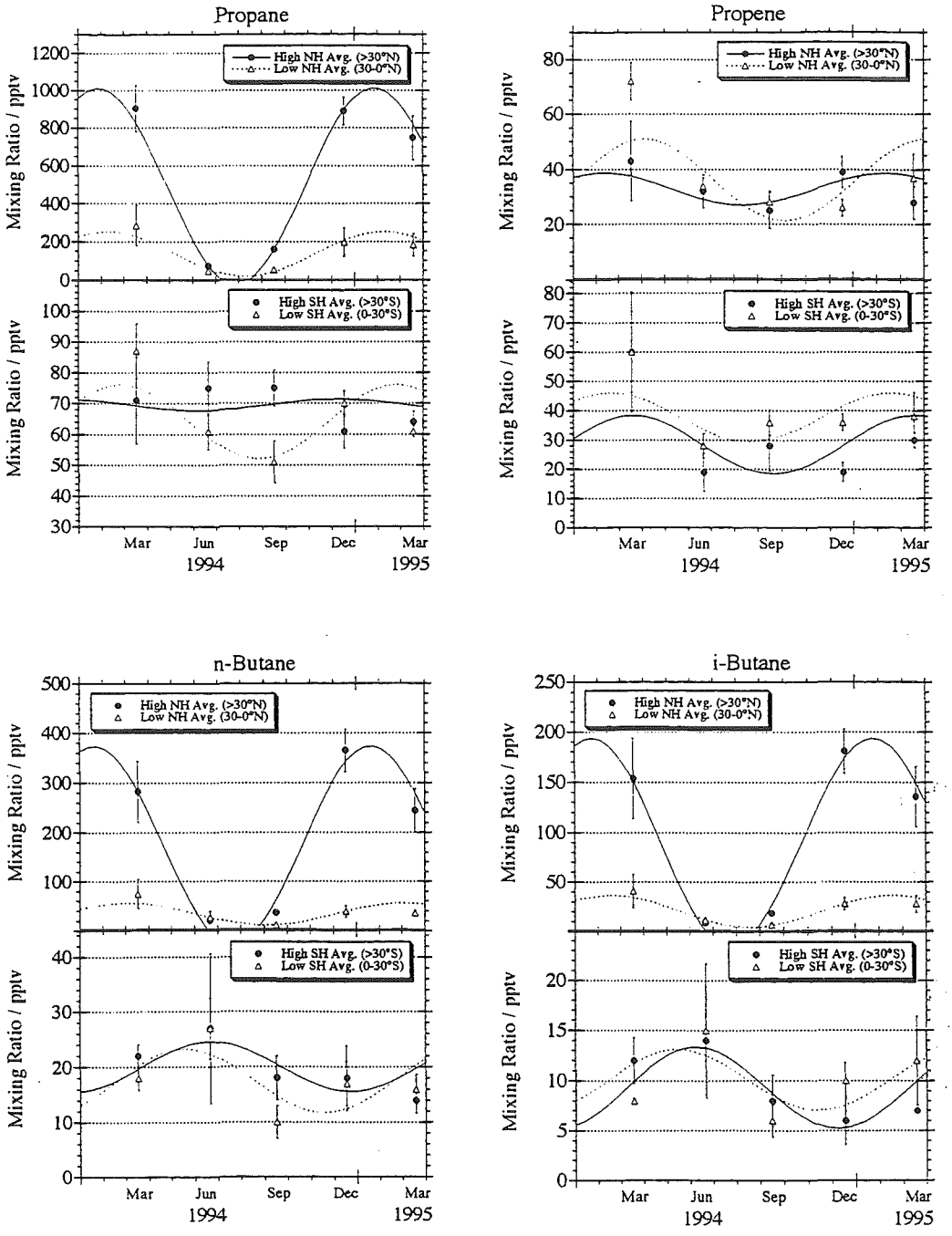

Figure 1 (continued). *Average background mixing ratios $\pm 1\sigma$ at the surface for high and low latitude bands of northern and southern hemispheres, March 1994 through March 1995.*

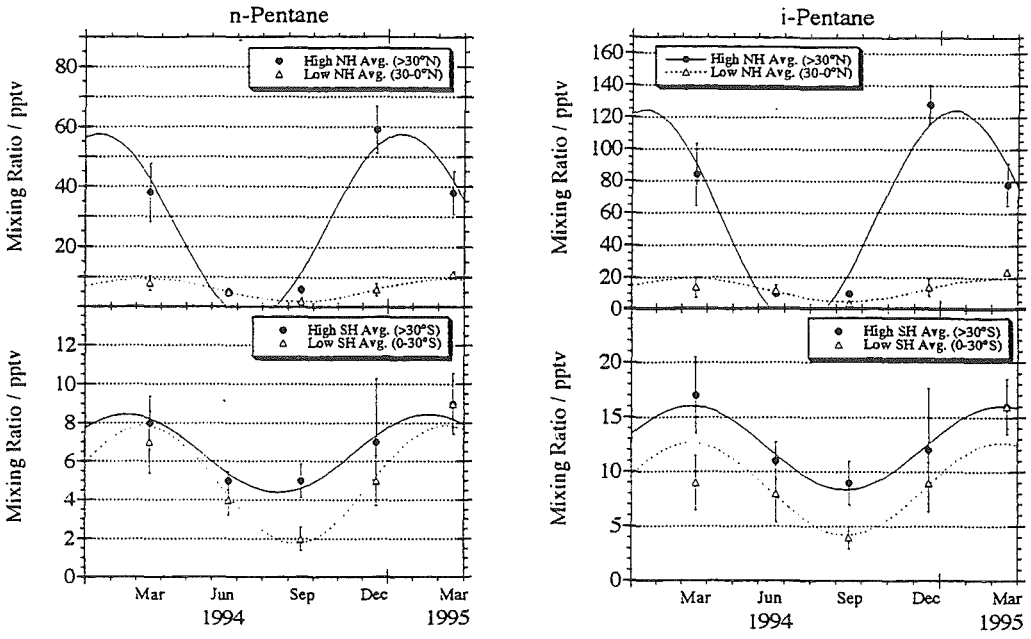

Figure 1 (continued). *Average background mixing ratios $\pm 1\sigma$ at the surface for high and low latitude bands of northern and southern hemispheres, March 1994 through March 1995.*

standards by diluting them with helium down to the 10^{-9} mixing ratio range in multiple step dilutions. The absolute accuracy of the diluted gases is ±5%.

In this manner, NMHC standards have been prepared over a wide range of concentrations which are then used as primary standards for calibrating the 7500 liter (high pressure) whole air „working" standards collected at Niwot Ridge, Colorado, Scripps Institute of Oceanography, La Jolla, California, or San Simeon, California. These Aculife and SpectraSeal treated Luxfer cylinders are periodically calibrated against each other and newly prepared calibration standards, and have been shown to be capable of maintaining the integrity of their contents over long periods.

Linearity studies in the range 0.1ppbv C_1 to 20ppbv for C_2–C_7 hydrocarbons were carried out using two different methods. One method employed serial dilution of the synthetic standards using the same parent standard. For the other, a single standard was analyzed, but the sample amount was varied to correspond to the full range of mixing ratios. These tests confirmed the linearity of the detector over the range and the accuracy of the sample dilution procedure. However, when response factors were determined, they were found to be not quite proportional with increasing carbon number. This artifact was observed to be column dependent. When a large number of NMHCs ranging from C_2–C_{10} were used to evaluate this slight nonlinearity it was observed that the per carbon response was linear up to i-pentane on the PLOT column, the C_6 range for the DB-1 column, and through C_7 for the Cyclodex-B column. Beyond each of these ranges, the per carbon response systematically decreased by approximately 2–3% for each additional carbon, except for the PLOT column. On the PLOT column, it was not possible to quanti-

tatively evaluate any peaks beyond the *i*-pentane peak as subsequently eluting gases tended to be lost to varying degrees by adsorption on the solid support of the column.

Identification of the different NMHCs was accomplished by running qualitative standards doped into „clean" tropospheric air collected during aircraft campaigns. Whole air was chosen over the blank matrix gas because slight shifts in retention times stemming from the minor differences between the matrix gas and whole air can make qualitative identification more difficult, especially if dealing with a large number of compounds.

Table 1: *Background seasonal variations of nonmethane hydrocarbons. Average burdens calculated using vertical profiles*

Average Surface Mixing Ratios and Atmopsheric Burdens in pptv

	High NH (90°-30°N)			Low NH (30°-0°N)			Low SH (30°-0°S)			High SH (90°-30°S)			Global Seasonal		
Avg	Surface		Burden	Surface		Burden	Surface		Burden	Surface		Burden	Surface		Burden
Date	Avg	±1σ	Avg	Avg	±1σ	Avg	Avg	±1σ	Avg	Avg	±1σ	Avg	Avg	±1σ	Avg
Ethane															
3/18/94	2263	128	1630	1207	266	1026	278	51	362	217	11	239	991	224	814
6/21/94	869	38	913	488	74	488	296	16	296	321	6	321	494	62	505
9/16/94	891	66	802	492	64	590	385	29	385	410	9	410	521	54	547
12/17/94	1931	63	1545	881	97	793	342	46	376	273	4	300	856	173	753
3/19/95	1955	145	1408	896	177	761	265	70	344	178	1	196	823	190	677
Ethyne															
3/18/94	691	44	456	294	92	235	36	10	44	44	5	53	266	72	197
6/21/94	67	4	77	38	5	38	39	5	39	46	1	46	48	4	50
9/16/94	103	6	83	67	4	80	66	17	56	79	2	71	77	6	72
12/17/94	558	24	391	194	50	194	37	5	49	25	1	27	204	57	165
3/19/95	589	39	388	187	57	150	26	5	32	16	1	17	205	62	147
Propane															
3/18/94	903	123	596	284	107	227	87	9	104	71	8	85	336	94	253
6/21/94	76	6	87	47	5	47	61	6	61	75	4	75	67	4	68
9/16/94	160	10	128	55	6	66	51	7	43	75	2	68	80	11	76
12/17/94	889	75	622	197	74	197	70	4	91	61	3	67	304	91	244
3/19/95	749	116	494	183	60	147	61	2	73	64	3	71	264	79	196

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EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM BIOMASS BURNING

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1 Introduction

Biomass burning is the burning of living and dead vegetation. 90 % of all biomass burning events are thought to be human initiated. Human induced fires are used for land management, such as shifting cultivation, agricultural expansion, deforestation, bush control, weed and residue burning, and harvesting practices. Other 'applications' are forest and grassland management. A considerable amount of biomass is burnt world wide in household fires for cooking and heating purposes. Furthermore, accidental fires which are related to population density, political situation and poor management practices contribute to global biomass burning. Natural fires are grassland and forest fires mainly induced by lightning.

Figure 1 shows the types of biomass burned based on an estimate of 8700 Tg dry matter/year. 66 % of the biomass burns in savanna and agricultural fires, while biofuel and tropical forests contribute about 15 % to the total biomass burnt globally. The contribution of boreal forests is low compared to other areas, however the biomass burned in boreal forests increased by a factor of 10 during the last 20 years. The geographical distribution of all fire events is given in Figure 2. Africa is dominating with 42 % of all fires, 26 % occur in South America and 32 % are distributed over the rest of the world.

Emissions from biomass burning are known to be a considerable source of atmospheric hydrocarbons, especially in tropical and subtropical regions (Greenberg et al. 1984; Greenberg and Zimmerman, 1984; Crutzen et al., 1985; Zimmerman et al., 1988, Bonsang et al., 1991, Rudolph et al., 1992; Rudolph et al., 1995). Due to transport these emissions also have a significant impact on the budget of organic trace gases in the tropical marine atmosphere (Koppmann et al., 1992; Swap et al. 1996). Moreover, owing to their impact on the photochemical ozone formation, organic trace gases influence the budget of tropospheric ozone (Fishman et al., 1990, Helas et al., 1995, Thompson et al., 1996).

Between 1982 and 1989 growing number of studies were published that deal with field measurements of emissions from biomass burning in South America and especially in Africa, which contains about two thirds of the world's savanna regions (Delmas, 1982, Bonsang et al., 1991, Rudolph et al., 1995, Lacaux et al. 1995).

The impact of biomass burning on the atmosphere and biosphere is investigated within BIBEX (Biomass Burning Experiment) under the IGBP core project IGAC (International Global Atmospheric Chemistry). This program organizes and coordinates field experiments in South America, Africa and Russia.

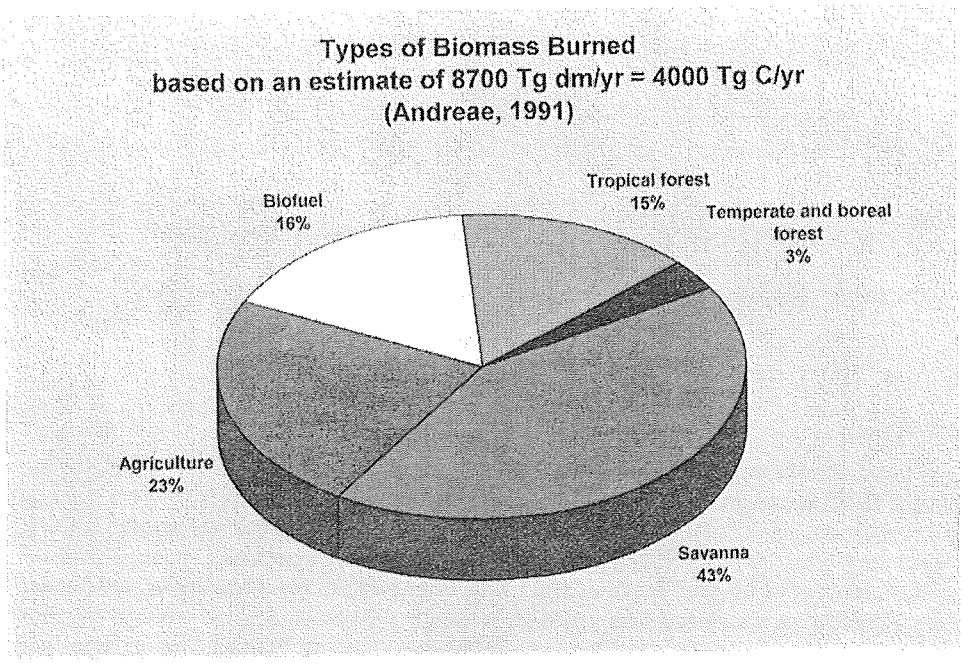

Figure 1. Types of biomass burned (after Andreae, 1991).

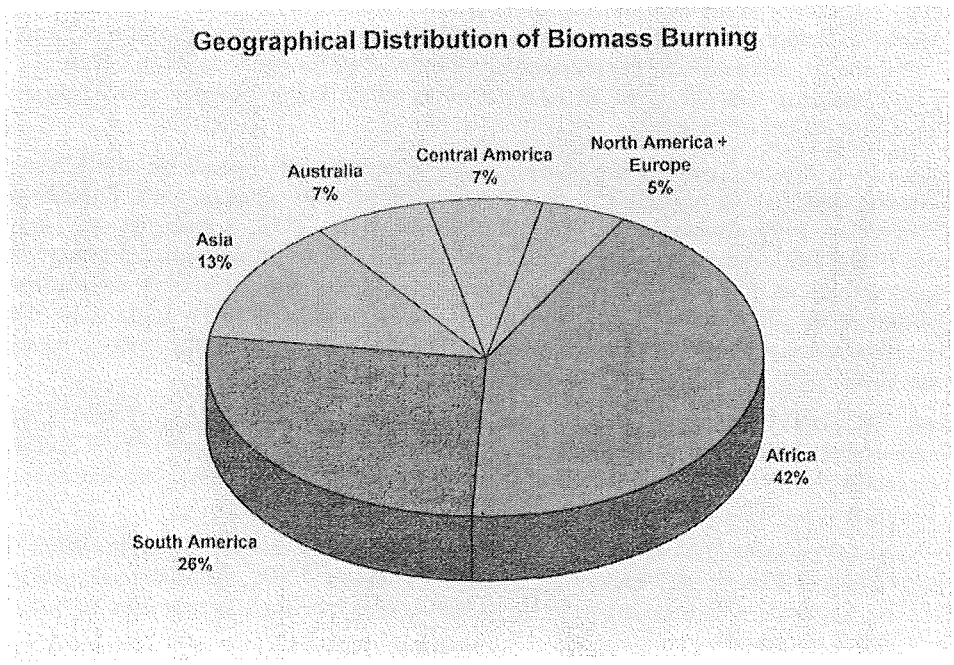

Figure 2. Geographical distribution of biomass burning.

Within this program a number of large projects were conducted:

SAFARI (Southern African Fire Atmosphere Research Initiative)

TRACE-A (Transport and Atmospheric Chemistry near the Equator - Atlantic)

FIRESCAN (Fire Research Campaign Asia North)

SCAR (Smoke, Clouds and Radiation)

The results showed that during the biomass burning season the concentrations of CO and organic trace gases in the planetary boundary layer were considerably enhanced over those in the wet season (Rudolph et al., 1992). Meanwhile, laboratory experiments have supplied more information about the parameters that determine the emission factors such as different burning stages, meteorological conditions and fuel types (Lobert et al., 1991, Manø, 1997, Czapiewski, 1995). It has been shown that the burning of organic material in oxygen-deficient fires leads to the emission of methane, nonmethane hydrocarbons and a variety of partially oxidized organic compounds. In some cases the emissions of medium and higher molecular weight organic compounds exceed those of light nonmethane hydrocarbons. Thus, these emissions contribute significantly to the local budgets of organic trace gases in the regions of biomass burning and may have a considerable impact on the formation of ozone in these areas. Very recent studies showed the significant abundance of higher molecular weight VOC in biomass burning plumes.

Table 1: *Buest guess estimates of gaseous and particulate emissions from global biomass burning and all anthropogenic sources.*

Species	Biomass burning contribution*)	All anthropogenic sources*)	% due to biomass burning
CO_2	13500	33700	40.1
CO	680	1600	42.5
CH_4	43	275	15.6
VOC	42	100	42.0
H_2	16	40	40.0
NO	21	70	30.0
N_2O	1.3	5.5	23.6
NH_3	6.7	57	11.8
SO_2	4.8	160	3.0
COS	0.21	0.38	55.3
CH_3Cl	1.1	1.1	100.0
CH_3Br	0.019	0.11	17.3
Total particulate matter	90	390	23.1
Carbon	60	90	66.7

*) data given in Tg of species per year (Levine, 1996)

2 Organic composition of biomass burning emissions

Vegetation material is made up of cellulose, hemicelluloses, lignin, proteins, nucleic acids, amino acids and volatile substances (Franke, 1989). During the first phase of a fire the volatile compounds such as aldehydes, alcohols and terpenes are released. In the following phase thermal cracking of the fuel molecules occurs. Higher molecular weight compounds are decomposed into a variety of volatile organic compounds (Lobert and Warnatz, 1993). In previous field studies only the light hydrocarbons were investigated. However, also a variety of higher molecular weight organic trace gases are emitted from biomass burning. They include alcohols, aldehydes, ketones, carboxylic acids, esters, ethers, furanes etc. These partly oxidized compounds are predominantly emitted during the smoldering phase of fires (Czapiewski, 1995). Table 1 compares the emissions from biomass burning with all other anthropogenic emissions.

Figure 3 shows a capillary column chromatogram of $\geq C_5$ VOC of an air sample collected inside the plume of an uncontrolled fire at Drakensberg. The mixing ratios of CO_2 and CO in this sample were 399.5 ppm and 4420 ppb, respectively. The average $\Delta(CO)/\Delta(CO_2)$ ratio (calculated from samples collected during all passages through the plume) was 9.36 $\pm$ 1.30 %. This indicates a mix of flaming and smoldering combustion at the time of the plume passages. The sum over the mixing ratios of C_2 and C_3 hydrocarbons was 364 ppbC. More than 140 major peaks are found in this chromatogram, about 70 of which could be identified.

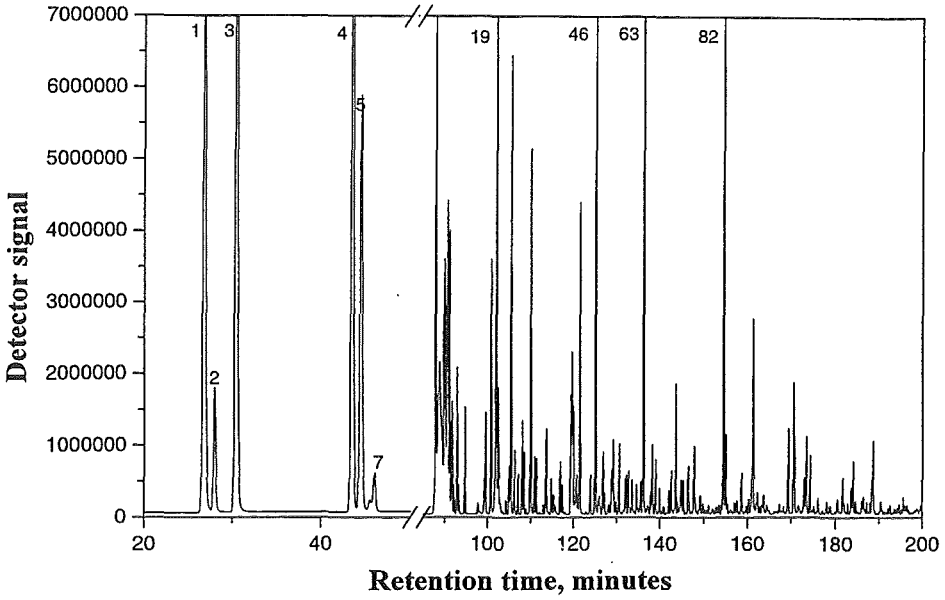

Figure 3. Chromatogram of an air sample collected inside the plume of a savanna fire. Selected compounds are: 1 Ethene, 2 Ethyne, 3 Ethane, 4 Propene, 5 Propane, 7 Propyne, 19 Acetone, 46 2-Methylfuran, 63 Benzene, 82 Toluene.

Table 2 gives an overview of the most important higher molecular weight VOC and their emission ratios relative to CO_2 for the different types of fires. A description of the identification procedure and list of the identified compounds are given in (Koppmann et al., 1997). In general, the mixing ratios of the different members of the various compound groups decrease with increasing number of carbon atoms. This is in good agreement with laboratory studies carried out with tropical wood which showed very similar emission patterns (v. Czapiewski, 1995). From these data emission ratios are calculated on a ppb carbon basis and the contribution of these compounds to the total emission of organic trace gases and relative to CO and CO_2 can be derived.

CO_2 is the dominant carbon species emitted from fires followed by CO. The emission ratio of CO relative to CO_2, $\Delta CO/\Delta CO_2$, are used to characterize the different burning stages. During the flaming phase this ratio is relatively low, in general 5-10 %. During the smoldering phase of a fire due to low oxygen supply more CO is emitted and the ratio of $\Delta CO/\Delta CO_2$ increases. Typical values observed during this phase vary between 10 and 15 %. Also, the emissions of organic compounds vary as a function of the burning stage. The correlation of an organic trace gas with CO_2 allows to estimate the emission ratios of that trace gas as function of type of fire and the different burning processes and the burning stages.

Table 3 summarizes the emission ratios of the two sugar cane fires, the Kruger National Park fire and the Drakensberg fire for CO, CH_4, the sum of C_2-C_4 hydrocarbons as well as the sum of organic trace gases with 5 or more carbon atoms. The total amount of organic trace gases with 5 or more carbon atoms is based on all FID-responsive compounds found in the chromatograms. As mentioned above, the emission ratio of CO relative to CO_2 allows to characterize the burning conditions of the different fires. For the fire at Drakensberg smouldering is likely to be the dominant burning process, while the sugar cane fires were largely flaming fires. The fire of Block 55 in the Kruger National Park seemed to be a mixture of both. The flaming phase of the fire was followed by a brief smouldering phase. Since this fire covered a large savanna area, emissions from both phases of the fire converge in the smoke plumes leading to the observed emission ratios. It can be seen that the emissions of the sum of the light NMHC are comparable or even larger than the emission ratio of methane.

This has already been observed during previous field studies of large savanna fires with similar $\Delta CO/\Delta CO_2$ ratios in Africa and Australia (Bonsang et al., 1991; Rudolph et al., 1992; Hurst et al., 1994). Our results show further that the emission ratio of organic compounds with a carbon numbers of 5 or more add up to at least half of the contribution of light NMHC.

The emission ratios of the total measured organic compounds relative to CO_2 were $(13.7 \pm 0.9)*10^{-3}$ ($ppbC/ppbCO_2$) for the Drakensberg fire, $(7.4 \pm 1.6)*10^{-3}$ ($ppbC/ppbCO_2$) for the Kruger National Park fire and $(3.9 \pm 2.9)*10^{-3}$ and $(1.7 \pm 0.7)*10^{-3}$ ($ppbC/ppbCO_2$) for the sugar cane fires #1 and #2, respectively. These values are in agreement with measurements of fires under laboratory conditions as reported by Manø (1997) and v. Czapiewski (1995), who give an average emission ratio of the sum of organic compounds for their experiments of $8.4*10^{-3}$ and $3*10^{-3}$, respectively. Lobert et al. (1991) report an average of $11.9*10^{-3}$ based on 10 different experiments. The ratio found for the Kruger National Park fire is in good agreement with the laboratory measurements while the ratio found for the Drakensberg fire exceeds the laboratory values. The emission ratios of the predominantly flaming sugar cane fires are considerably lower than the results of the laboratory studies. This may be due to the fact that large flaming combustion can not be simulated realistically in confined fires which are controlled by their artificial boundaries. Especially the response of fires to wind and the access to oxygen for combustion, which affects mainly the flaming phases differs significantly between free and confined fires (Albini, 1993).

Table 2: *Emission ratios relative to CO_2 for the most abundant higher molecular weight VOC for different types of fire.*

Compound	Drakensberg fire	Kruger National Park fire #2	Sugar cane fires
1-Pentene	$(1.1 \pm 0.3) * 10^{-4}$	$(5.8 \pm 1.3) * 10^{-5}$	$(1.7 \pm 2.5) * 10^{-5}$
2-Methyl-1-Butene	$(5.9 \pm 1.9) * 10^{-5}$	$(0.5 \pm 1.0) * 10^{-5}$	$(0.7 \pm 1.2) * 10^{-5}$
2-Methyl-2-Butene	$(8.7 \pm 2.0) * 10^{-5}$	$(1.8 \pm 1.2) * 10^{-5}$	$(5.7 \pm 9.2) * 10^{-6}$
4-Methyl-1-Pentene	$(7.9 \pm 3.5) * 10^{-5}$	$(7.8 \pm 5.2) * 10^{-5}$	$(2.7 \pm 3.5) * 10^{-5}$
1-Hexene	$(1.3 \pm 0.3) * 10^{-4}$	$(8.4 \pm 1.1) * 10^{-5}$	$(2.6 \pm 4.0) * 10^{-5}$
1-Octene	$(2.2 \pm 0.8) * 10^{-5}$	$(1.6 \pm 0.8) * 10^{-5}$	$(0.7 \pm 1.2) * 10^{-5}$
2-Octene	$(2.0 \pm 1.8) * 10^{-6}$	-	$(2.8 \pm 3.1) * 10^{-7}$
2-Methyl-2-Propanol	$(6.7 \pm 6.9) * 10^{-6}$	$(6.1 \pm 7.0) * 10^{-6}$	$(1.4 \pm 1.0) * 10^{-5}$
1-Butanol	$(6.0 \pm 1.8) * 10^{-6}$	$(5.9 \pm 4.6) * 10^{-6}$	$(3.8 \pm 5.7) * 10^{-6}$
Cyclopentanol	$(5.0 \pm 2.5) * 10^{-5}$	$(5.1 \pm 3.8) * 10^{-5}$	$(2.8 \pm 3.0) * 10^{-5}$
2-Methyl-Propanal	$(1.8 \pm 0.8) * 10^{-5}$	$(1.3 \pm 0.9) * 10^{-5}$	$(3.1 \pm 2.3) * 10^{-6}$
Butanal	$(8.4 \pm 1.9) * 10^{-5}$	$(6.7 \pm 6.1) * 10^{-5}$	$(2.9 \pm 3.5) * 10^{-5}$
3-Methylbutanal	$(2.4 \pm 0.7) * 10^{-5}$	$(1.6 \pm 1.5) * 10^{-5}$	$(7.4 \pm 9.3) * 10^{-6}$
2,2-Dimethylpetanal	$(5.7 \pm 4.5) * 10^{-6}$	$(1.2 \pm 2.5) * 10^{-6}$	$(1.4 \pm 2.1) * 10^{-6}$
Hexanal	$(4.9 \pm 2.8) * 10^{-5}$	$(3.9 \pm 2.2) * 10^{-5}$	$(1.9 \pm 1.3) * 10^{-5}$
Benzaldehyde	$(4.2 \pm 1.9) * 10^{-5}$	$(4.5 \pm 3.0) * 10^{-5}$	$(1.4 \pm 1.3) * 10^{-5}$
Acetic acid-2-methylpropylester	$(1.5 \pm 0.5) * 10^{-5}$	$(8.2 \pm 0.5) * 10^{-5}$	$(1.7 \pm 2.4) * 10^{-6}$
3-Methylbutanon	$(8.2 \pm 1.2) * 10^{-6}$	$(7.5 \pm 5.2) * 10^{-6}$	$(2.5 \pm 3.1) * 10^{-6}$
1-Penten-3-on	$(6.6 \pm 2.7) * 10^{-6}$	$(4.4 \pm 2.5) * 10^{-6}$	$(2.1 \pm 3.0) * 10^{-6}$
2-Pentanon	$(3.7 \pm 1.8) * 10^{-5}$	$(2.5 \pm 1.8) * 10^{-5}$	$(0.9 \pm 1.1) * 10^{-5}$
2-Heptanon	$(2.9 \pm 1.9) * 10^{-6}$	$(9.5 \pm 7.6) * 10^{-6}$	$(3.9 \pm 2.2) * 10^{-6}$
6-Methyl-2-heptanon	$(3.3 \pm 1.6) * 10^{-5}$	$(2.5 \pm 1.8) * 10^{-5}$	$(1.3 \pm 0.6) * 10^{-7}$
2-Methylfuran	$(2.9 \pm 0.8) * 10^{-4}$	$(8.0 \pm 3.4) * 10^{-5}$	$(2.0 \pm 3.3) * 10^{-5}$
3-Methylfuran	$(5.0 \pm 1.0) * 10^{-5}$	$(1.8 \pm 0.2) * 10^{-5}$	$(5.2 \pm 8.0) * 10^{-6}$
Tetrahydrofuran	$(2.5 \pm 0.6) * 10^{-5}$	$(2.4 \pm 1.7) * 10^{-5}$	$(0.9 \pm 1.1) * 10^{-5}$
2,3-Dihydrofuran	$(2.1 \pm 0.7) * 10^{-5}$	$(1.9 \pm 1.1) * 10^{-5}$	$(0.8 \pm 1.0) * 10^{-5}$
2-Ethylfuran	$(6.0 \pm 3.5) * 10^{-6}$	$(2.1 \pm 2.5) * 10^{-6}$	$(0.9 \pm 1.3) * 10^{-6}$
2,4-Dimethylfuran	$(4.1 \pm 1.1) * 10^{-5}$	$(1.4 \pm 0.3) * 10^{-5}$	$(4.2 \pm 6.5) * 10^{-6}$
Benzofuran	$(2.9 \pm 1.2) * 10^{-5}$	$(2.5 \pm 1.5) * 10^{-5}$	$(7.8 \pm 9.2) * 10^{-6}$
1-Ethyl-2-Methylbenzene	$(5.2 \pm 2.5) * 10^{-6}$	$(3.8 \pm 2.9) * 10^{-6}$	$(1.3 \pm 1.2) * 10^{-6}$
1,2,4-Trimethylbenzene	$(3.2 \pm 2.7) * 10^{-6}$	$(0.9 \pm 1.3) * 10^{-6}$	$(1.3 \pm 1.5) * 10^{-6}$
1-Ethyl-3-Methylbenzene	$(7.8 \pm 1.1) * 10^{-6}$	$(4.9 \pm 2.0) * 10^{-6}$	$(2.6 \pm 3.7) * 10^{-7}$
Propylbenzene	$(3.2 \pm 2.7) * 10^{-6}$	$(2.1 \pm 2.1) * 10^{-6}$	$(7.0 \pm 6.7) * 10^{-7}$
o-Xylene	$(2.9 \pm 0.8) * 10^{-5}$	$(1.7 \pm 1.0) * 10^{-5}$	$(6.8 \pm 9.4) * 10^{-6}$
Ethylbenzene	$(2.8 \pm 1.1) * 10^{-5}$	$(1.8 \pm 1.0) * 10^{-5}$	$(6.6 \pm 1.1) * 10^{-5}$
Toluene	$(4.6 \pm 2.3) * 10^{-4}$	$(2.2 \pm 0.6) * 10^{-4}$	$(5.7 \pm 8.7) * 10^{-5}$
Benzene	$(8.8 \pm 1.3) * 10^{-4}$	$(4.9 \pm 0.7) * 10^{-4}$	$(3.1 \pm 1.8) * 10^{-4}$
Phenol	$(1.0 \pm 0.6) * 10^{-5}$	$(5.2 \pm 2.4) * 10^{-6}$	$(1.8 \pm 2.8) * 10^{-6}$

Table 3: Emission ratios of CO, CH_4, light VOC and higher molecular weight VOC relative to CO_2 obtained for different types of fire during SAFARI.

Fire	$\Delta(CO)/\Delta(CO_2)$ %	$\Delta(CH_4)/\Delta(CO_2)$ %	$\Delta(\Sigma\ C_2\text{-}C_4)/\Delta(CO_2)$ %	$\Delta(\Sigma\ C_5\text{-}C_9)/\Delta(CO_2)$ %
Sugar cane	4.38 ± 2.09	0.26 ± 0.22	0.26 ± 0.20	0.13 ± 0.09
KNP	5.29 ± 0.71	0.28 ± 0.07	0.46 ± 0.06	0.28 ± 0.10
Drakensberg	9.36 ± 1.30	1.03 ± 0.17	0.93 ± 0.40	0.44 ± 0.05

3 Impact of VOC on the formation of ozone

In order to estimate the impact of VOC on the formation of ozone in biomass burning plumes we conducted a simple model calculation using the Regional Acid Deposition Model (RADM2) published by Stockwell et al. (1990). We are aware of the fact that RADM2 was not originally designed for a VOC mix as it is observed in biomass burning plumes and not all measured organic compounds are accounted for individually. They are lumped according to their reactivity towards OH radicals. The substantial contributions from the light hydrocarbons are taken explicitly into account. Nevertheless, this model is used as a simplified approximation to simulate the formation of ozone in the plumes and get information about the contribution of VOC to this process.

The calculations were initialized with measured mixing ratios from the sugar cane fires which showed the lowest VOC emission ratios and the Drakensberg fire with the highest observed VOC emission ratios. The NO_2 mixing ratio was derived from the NO_2/CO_2 ratio given by Andreae et al. (1997) and our CO_2 measurements. The initial mixing ratios for short lived trace gases that were not measured (for example OH, HO_2, NO, etc.) were derived from a steady-state approximation. The solar zenith angle was fixed to 24 degrees.

Under realistic conditions the ozone formation is substantially influenced by transport processes causing a dilution of the trace gases within the plume (see for example Lelieveld et al. (1996)). In order to account for this we included dilution with surrounding air in our simulation. Initially the plume is enclosed in a volume V(0) which increases with time to the volume V(t) thereby mixing in background air with fixed mixing ratios of $(CO)^0 = 100$ ppb, $(CH_4)^0 = 1.7$ ppm, $(O_3)^0 = 50$ ppb, and $(VOC)^0 = 5$ ppbC. The time dependence of V(t) was parameterized by

$$V(t) = V(t_e) + (1 - V(t_e)) \exp(-t/\tau)$$

where τ is the time constant for dilution and $V(t_e)$ is the final size of the plume at the end of the integration at time t_e, assuming ($\tau << t_e$). The dilution factor is given by $D = V(t_e)/V(0)$.

Measurements of air samples collected outside the plumes gave CO_2 mixing ratios which were on average 10 ppm above the global background. The dilution was treated in a way that the CO_2 mixing ratios measured in the plumes was finally reduced to the CO_2 mixing ratio observed in the air outside of the plumes.

In the case of the Drakenberg fire the final dilution was D = 2, the dilution time constant was assumed to be τ = 2 h. Ozone mixing ratios (initialized with a background value of 50 ppb) in the plume are shown in Figure 4. If only CH_4 and CO as oxidizable carbon compounds are taken into account, ozone reaches a maximum mixing ratio of 134 ppb after 30 sunlit hours. The VOC were included in two steps, first the light hydrocarbons up to C_4 (figures in parentheses) and then all VOC. Taking into account the measured VOC the ozone mixing ratio increases steeper and earlier, because the ozone formation is now driven by the degradation of the hydrocarbons that react faster with OH than CO and CH_4. Ozone mixing ratios increase rapidly to values around 90 ppb within the first two hours after the emissions, followed by a further slower increase to about (175 ppb) 195 ppb. Thus, the mixing ratio of ozone in the plume is about (30 %) 45 % larger if the impact of VOC is included with the peak mixing ratio reached about 30 h after the emission. The initial NO_2 mixing ratio of 30 ppb was taken from the average of the measured data that varied between 6 ppb and 60 ppb for different plume passages. The amount of ozone produced depends strongly on the NO_2 mixing ratio. Clearly, better temporally and spatially resolved NO_x data are necessary to further assess the impact of biomass burning to the global ozone budget.

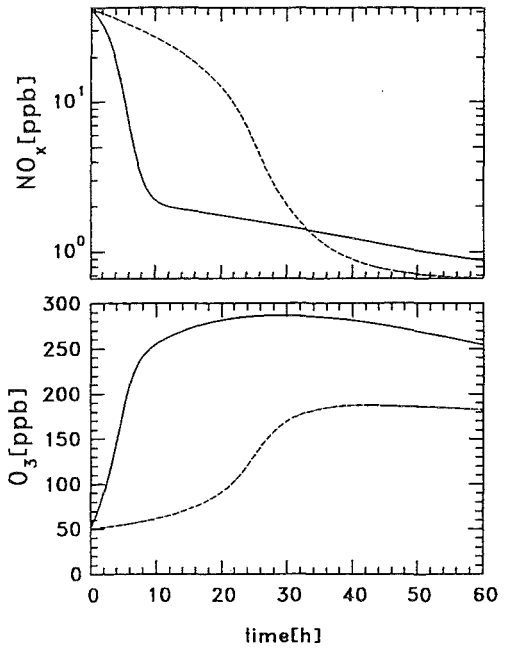

Figure 4: Time dependence of the ozone and NO_x mixing ratios. Initial conditions were taken from the Drakensberg record. Solid (dashed) curve includes (excludes) the VOC. The gas-phase chemistry RADM2 was used. No dilution was applied.

4 Impact on global VOC emissions

The analysis of NOAA-AVHRR data indicate that in 1992 the burning season in southern Africa occurred between July and September with the SAFARI campaign covering the end of the burning season. Furthermore, in 1992 there was about 50 % less burning than in 1989 (Justice et al., 1996). It should be added, that the samples are not likely to be representative for biomass burning on a global scale, since they represent only a very limited fraction of the areas burnt globally each year. Therefore, any extrapolations of our emission ratios to global scales are highly uncertain. In order to get an idea about the impact of biomass burning emissions to atmospheric chemistry it is nevertheless worthwhile to compare the emissions of organic trace gases with global budgets. Table 5 summarizes the emission of total carbon species and CO from the various types of biomass burning based on compilation of literature data (Andreae, 1991, 1993; Hao and Liu, 1994; Andreae et al., 1997; and references therein). Since the emissions of VOC are better correlated with CO than with CO_2, we base our extrapolation on VOC/CO emission ratios. Table 4 gives an estimate of the CO emission from various biomass burning sources. If we use the emission ratios from the sugar cane fire #2 as a lower limit (mean $\Delta(VOC)/\Delta(CO) = 0.08$ %) and those from the Drakensberg fire as an upper limit (mean $\Delta(VOC)/\Delta(CO) = 0.15$ %) the estimated total carbon released in form of VOC (CH_4 not included) ranges between $25*10^{12}$ g C/yr and $48*10^{12}$ gC/yr.

Table 4 : *Estimate of the CO emissions from various biomass burning sources*

Source	Biomass burned Tg (dry matter)/yr	Carbon released Tg/yr	CO emission ratio, %	CO emission Tg C/yr
Tropical forest	1260	567	10.9	62
Extratropical forest	1150	518	11.2	58
Savanna	3690	1661	6.2	103
Biomass fuel	1940	873	8.3	73
Charcoal	20	42	20.0	8
Agricultural waste in fields	850	383	7.2	28
Total	8910	4043	8.2	331

The higher molecular VOC contribute up to 50 % to that value. This coarse estimate of the source strength of organic compounds based on our measurements is a factor of two higher than the results of previous estimates by Bonsang et al. (1991), who give $12*10^{12}$ g/yr derived from measurements over large savanna fires during the DECAFE project in the Ivory Coast. This number is below the lower limit of the emission range based on our estimates, because Bonsang et al. (1991) based their estimates on measurements of light nonmethane hydrocarbons only. From laboratory studies Lobert et al. (1991) calculate $42*10^{12}$ g/yr, a value at the upper end of our estimation range. These results indicate that the emissions of biomass burning contributes significantly to the local and regional budget of organic compounds in the troposphere.

5 Laboratory studies

Biomass burning experiments were conducted under defined conditions in the laboratory at the burning apparatus of the Max-Planck-Institute für Chemie in Mainz, Germany. For details of the apparatus see Lobert (1991). In these experiments different types of fuel wood typically used in tropical and subtropical region were investigated. The mass loss of the fuel, exhaust temperature and exhaust flow rate were monitored continuously. VOC were analysed from grab samples in stainless steel canisters taken over the course of the fire. The samples were analysed for CO, CO_2, CH_4 and VOC in the laboratory by GC/FID and GC/MS.

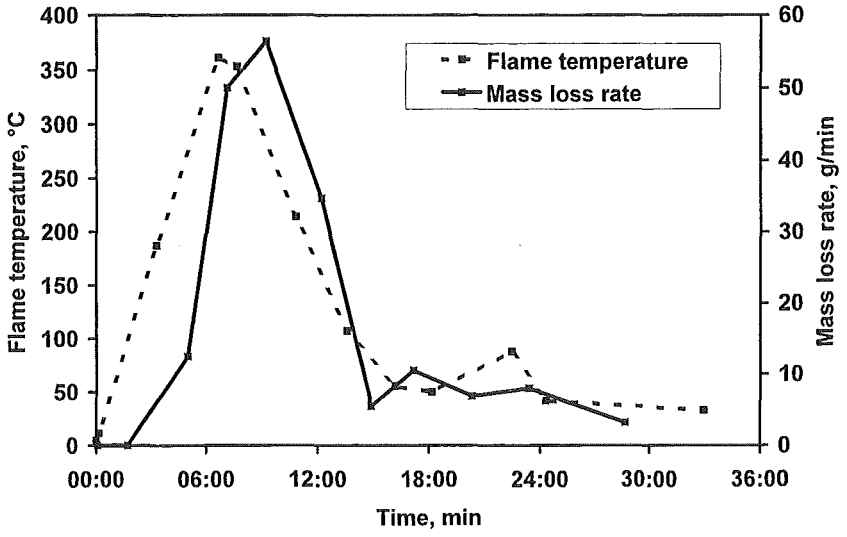

Figure 5. Flame temperature and mass loss rate during a laboratory fire.

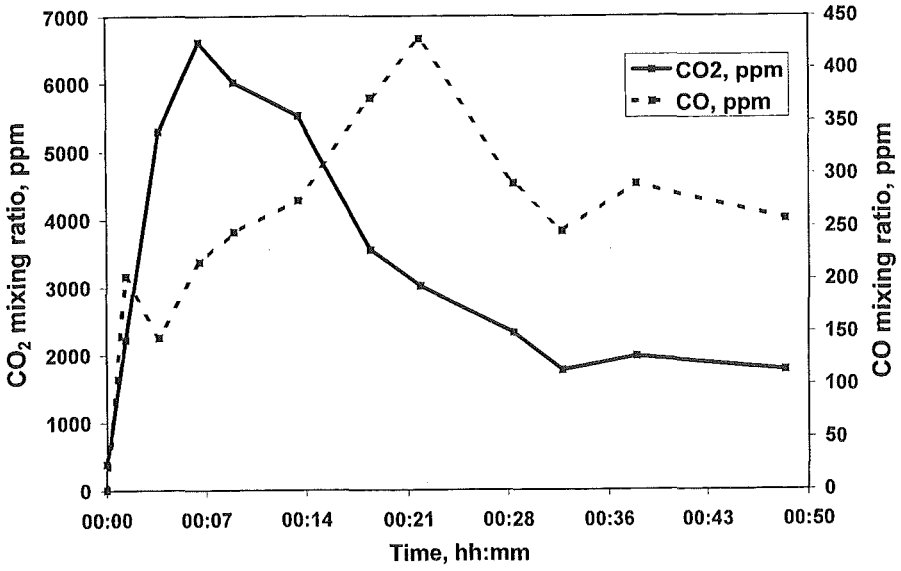

Figure 6. Course of CO_2 and CO mixing ratios in the exhaust gas of a typical laboratory fire.

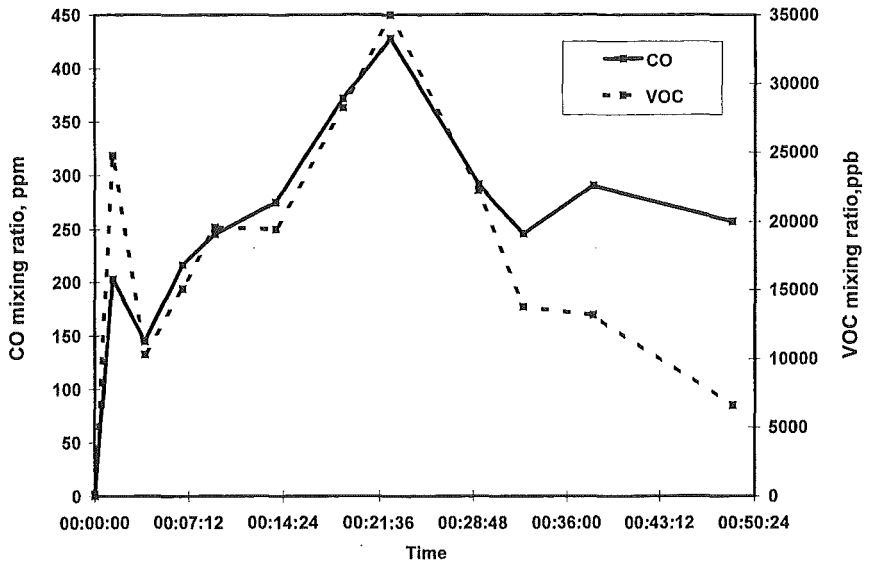

Figure 7. Course of CO and total VOC mixing ratios in the exhaust gas of a typical laboratory fire .

Figure 5 shows the flame temperature and the mass loss rate, Figure 6 the course of CO_2 and CO for a typical fire. The maximum of CO_2 emissions represents the flaming phase, the maximum of CO emissions represent the smouldering phase of the fire. Both phases can be clearly distinguished. Figure 7 compares the course of the CO emissions with that of the sum of all measured VOC indicating that VOC are emitted predominantly during the smouldering phase of a fire. This behaviour was also observed for fires investigated in field studies. As an example, in Figure 8 the mixing ratios of the sum of alkanes and alkenes measured in the exhaust gas are plotted versus those of CO showing a significant correlation.

***Table 5:** Emission factors of CO2, CO, CH4 and VOC for different types of fuel wood.*

	Musasa	Chingunguru	Muhacha
Combustion Efficiency	0.92	0.90	0.89
Water Content (%)	13.7	11.0	13.2
Emission Factor (g/kg)			
CO_2	1580.0	1868.0	1788.0
CO	74.0	119.0	125.0
CH_4	4.1	9.1	6.9
VOC	3.2	4.2	6.1

In a number of experiments the influence of different parameters on the emissions of VOC was investigated. Different fuel woods were burnt under similar conditions (amount of fuel, water content and burning efficiency). Table 5 summarizes the results. While the emission factors of CO_2 vary by about 20 %, the emission factors of CO, CH_4 and VOC show variations of a factor of two. Table 6 shows the results of different burning experiments with the same fuel wood.

In this case the water content of the fuel wood was varied. In one experiment the water content was reduced to 3.4 % by drying the wood, in another experiment the wood was moistened to a water content of 16 %. The results show that the emission factors increase dramatically with increasing water content of the fuel. For CO the emission factor increase by about a factor of two, when the water content is increased by a factor of 4, the emission factor of VOC increased by a factor of 8.

Table 6: *Emission factors of CO_2, CO, CH_4 and VOC for one type of fuel wood with different water contents.*

	Musasa	Musasa	Musasa, dried	Musasa, moist
Combustion Efficiency	0.92	0.86	0.89	0.83
Water Content (%)	13.7	8.5	3.4	16.0
Fuel Load (kg)	0.6	1.9	2.0	2.1
Emission Factor (g/kg)				
CO_2	1580.0	1389.0	1405.0	1209.0
CO	74.0	110.0	79.0	126.0
CH_4	4.1	11.0	6.0	15.0
VOC	3.2	19.5	9.8	25.5

Figure 9 shows the contribution of the different classes of VOC to the total VOC emissions averaged over four different burning experiments. Surprisingly, the pattern of VOC does not change significantly, even if different fuel woods are burnt or burning conditions are changed.

Table 7: *Comparison of emission ratios (given in ppbC/ppb) obtained in laboratory and field measurements.*

	Field study		Laboratory study	
	Zimbabwe[1]	Nigeria[2]	Chingunguru,dried	Chingunguru
$\Delta CO/\Delta CO_2$, %	8.05	10.47	8.71	12.44
$\Delta VOC/\Delta CO_2$ %	1.53	2.19	0.25	1.03
Water Content, %	dry[3]	moist[3]	4.00	11.00
Combustion Efficiency	0.94	0.89	0.95	0.90

[1]fuel was collected during the dry season, [2]fuel was collected during the raining season, [3]only estimated moisture data available

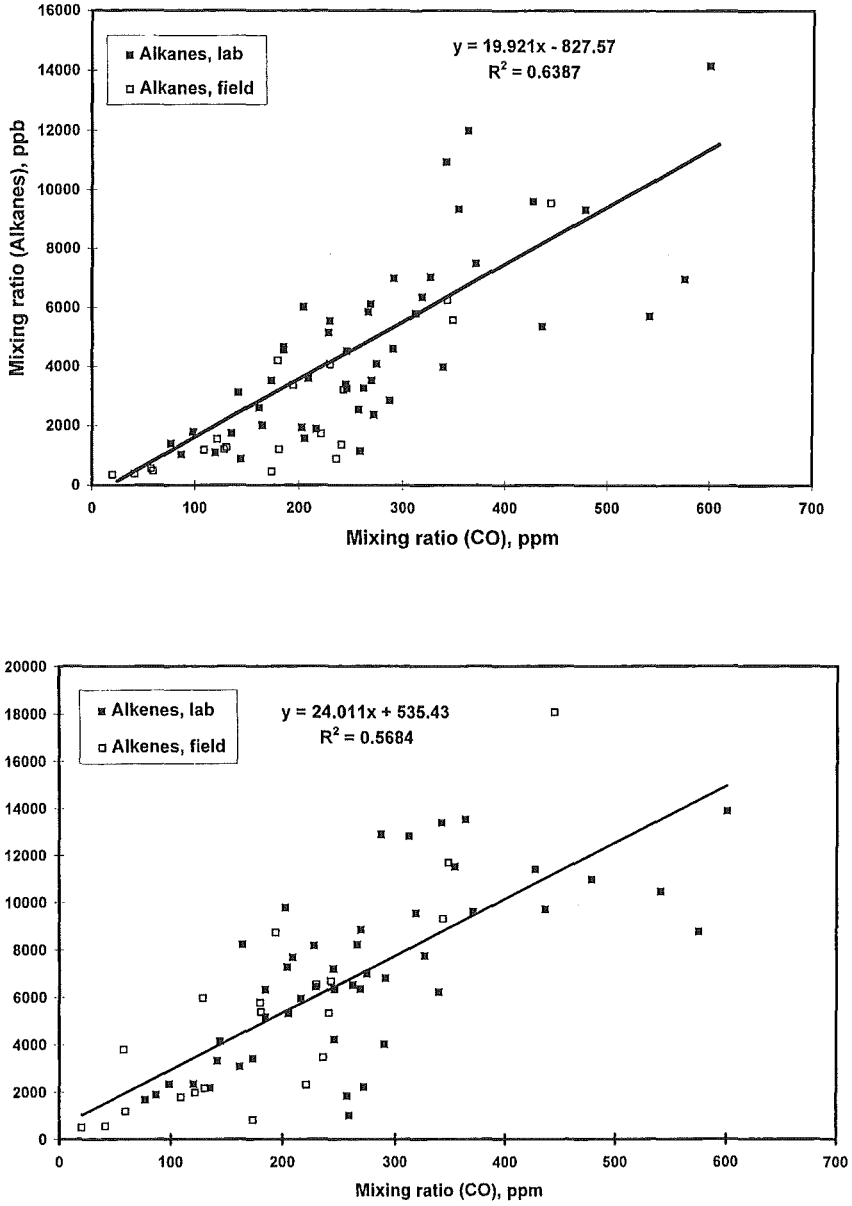

Figure 8. *Plot of alkane (top) and alkene (bottom) mixing ratios versus CO mixing ratios for all burning experiments under laboratory and field conditions.*

A comparison of emission ratios measured under laboratory and field conditions (Table 7) confirms that the general findings in laboratory studies hold true also for field studies, the comparability for individual fires is low. Averaging over a large number of fires, however, allows a comparison of emission factors of individual groups of VOC. Thus, knowing amount and typical water content of the fuel wood allows an estimate of the amount of VOC emitted. Including demographic studies of the fuel wood used per capita and year should make a rough estimate of global VOC emissions from these types of fire possible.

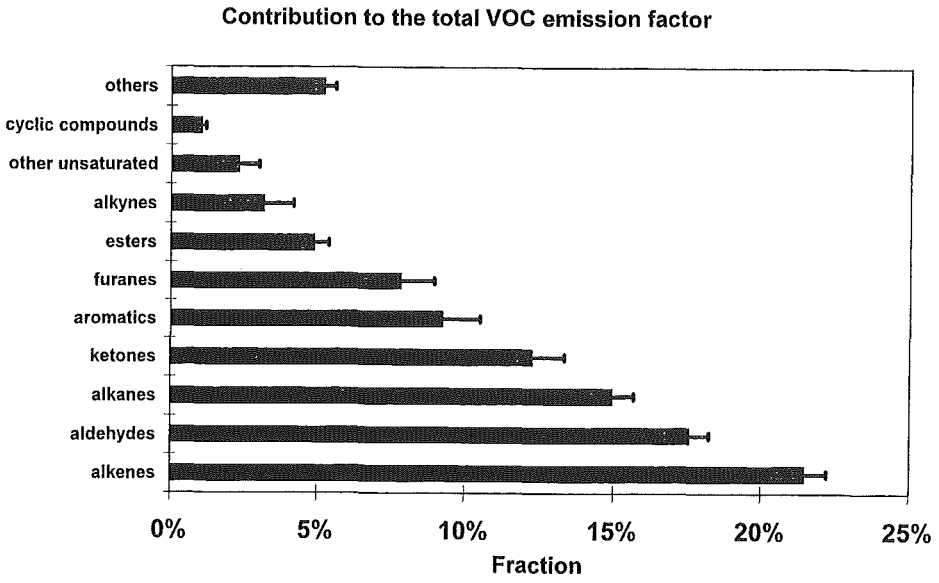

Figure 9. Contribution of different classes of VOC to the total VOC emissions for four laboratory fires .

6 Conclusions

In all samples collected in the plumes of biomass fires a large variety of organic trace gases is found. They include alcohols, aldehydes, ketones, carboxylic acids, esters, ethers, furanes and others. Biomass burning is thus a major source for VOC in the troposphere. The observed emissions show a considerable variation depending on the amount and type of fuel, water content of the fuel, the burning conditions and stages of the fires. Carbon monoxide, methane and most of the VOC are emitted during the smouldering phase of a fire and thus the emission of most organic compounds is correlated with the emission of CO. The emission ratio of the sum of light VOC is typically in the same order of magnitude or even higher than that of methane. About 40 % of the

emitted VOC are higher molecular weight hydrocarbons with more than five carbon atoms. With about 40 % oxygenated hydrocarbons are the predominantly emitted VOC. Unsaturated hydrocarbons contribute about 20 % to the total VOC emission.

Simple model calculations show that the formation of ozone in aging biomass burning plumes is substantial and has consequences for the global ozone budget. The simulation for the Drakensberg fire investigated during the SAFARI campaign shows a maximum excess ozone with and without taking into account the impact of VOC of 150 ppb and 85 ppb, respectively, leading to 65 ppb of additional ozone in the plume due to the impact of VOC. In this example the impact of VOC is responsible for about 40 % of additional ozone formed in the plumes.

The efficiency of ozone formation depends critically and in a complex way on the organic composition of biomass burning emissions and the dilution of the plume.

7 Outlook

Field experiments often can only investigate casual biomass burning events and thus can only be snapshots of the situation at a certain place of the earth. Future research should focus on an improvement of remote sensing data to gain information about fire frequencies and distributions, fuel loads and CO and other trace gas emissions. A compilation of more comprehensive data sets will lead to a better knowledge of the organic composition of biomass burning emissions, burning efficiencies and scaling of VOC emissions relative to CO. Based on these data a more precise estimate of the contribution of biomass burning emissions to the VOC budget should be available. The result should lead to a better understanding of the impact of these emissions an atmospheric chemistry and biogeochemical cycles.

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ORGANIC CHEMISTRY IN THE TROPOSPHERE

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Millions of tons of organic compounds are released into the atmosphere each year, from both natural and man-made sources. Some, such as methane, are relatively long-lived and can reach the upper troposphere and lower stratosphere, where they can affect global chemistry and climate. Others, such as the terpenes, have lifetimes of only a few hours, but their high reactivity means that they influence the local air quality close to their point of release. Hydrocarbons and other organic compounds are necessary components for the formation of elevated ozone concentrations in continental regions. Their chemistry leads to a large variety of short-lived organic oxy (RO) and peroxy (RO_2) radicals, and it is the subsequent chemistry of these radicals that governs the distribution of observed products.

Despite wide variations in the observed reactivity, the reactions of the atmospheric VOCs share many features in common, and the behaviour of larger compounds can to a large extent be predicted on the basis of smaller, simpler compounds, which are often better-studied. This abstract explores the reactivity trends observed in atmospheric VOCs and attempts to show how the elementary reactions of individual compounds influences the product distributions observed in the atmosphere. Although the emphasis is on general trends, it should not be forgotten that the information presented here is built up from laboratory studies of the kinetics and mechanisms of many individual reactions, too numerous to mention here. A detailed listing of many of the reactions pertinent to hydrocarbon oxidation is given, for example, in the review by Atkinson [1], while evaluations of some of the reactions of smaller hydrocarbons are provided by Atkinson *et al.* [2,3] and DeMore *et al.* [4].

The atmosphere is overwhelmingly oxidising in nature, and if it were allowed to come to equilibrium it would contain negligible concentrations of hydrocarbons. However, the presence of life in its various forms provides a steady supply of reduced compounds to the atmosphere, while the input of sunlight enables their oxidation (mostly through reactions with OH radicals and O_3). The oxidation of organic compounds in the atmosphere results in the incorporation of oxygen into the molecules, or molecular fragments, formed. The presence of oxygen leads to a further increase in reactivity, but also to an increase in solubility, which can tend to dampen the reactivity of the atmosphere through removal of the organic compounds. When the chemistry is considered on a global scale, all these factors have to be taken into account in order to fully assess the capacity of the VOCs to form ozone. The oxidation of a typical hydrocarbon is illustrated in Figure 1. Many of the reaction steps shown in this schematic will now be discussed in more detail.

1 Reactions of Alkanes

Alkanes are the least reactive hydrocarbons in the atmosphere. Alkanes, often written R–H, can be straight chain (so-called n-alkanes) or branched. Consisting of saturated C–C and C–H bonds, they are lost from the atmosphere by abstraction of a hydrogen atom by OH or Cl atoms. In general, the more heavily-substituted a carbon atom is, the weaker the remaining hydrogen atoms will be, and this affects the reactivity of the molecule dramatically. Both OH and Cl-atom

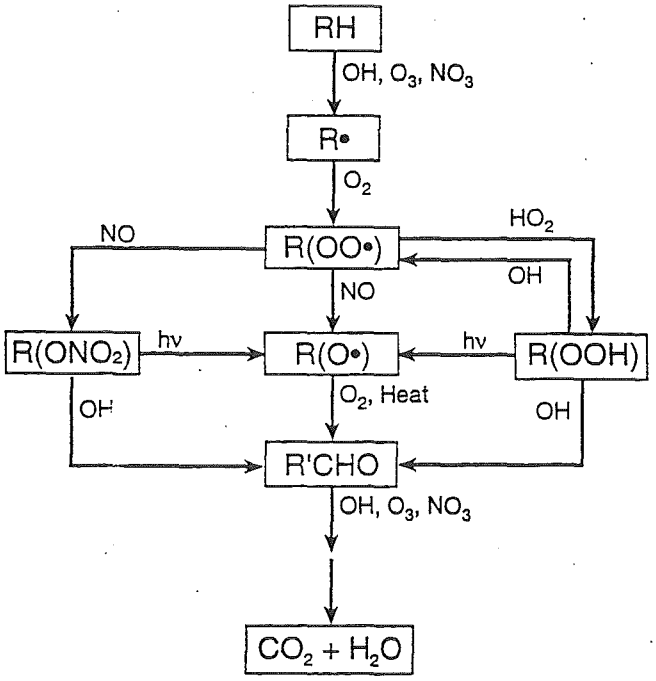

Figure 1. *Schematic flow chart for the oxidation of a hydrocarbon.*

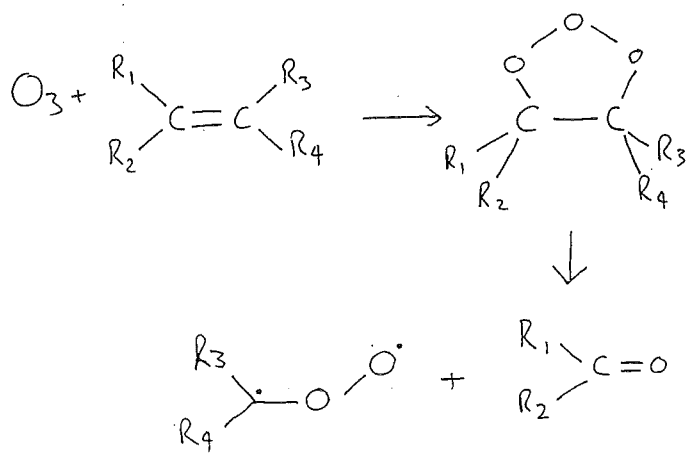

Figure 2. *Ozonolysis of alkenes. The 5-membered primary ozonide splits apart to give a carbonyl compound and a "Criegee" intermediate. The precise identity of the carbonyl and the Criegee depend on the substituent groups R_1–R_4. In general the formation of the Criegee containing the more substituted carbon atom will be favoured.*

reactions with alkanes have been well-studied, and predictive tools are available for the estimation of the rate coefficients [5–7]. These rules, or Structure Activity Relationships, are based on the idea that the rate coefficients for abstraction at similar sites in different molecules are the same. The reactivities are usually expressed as the rate coefficients for a particular "group", $-CH_3$, $>CH_2$ or >CH-, which are modified by factors to take account of the effects of substituents in the neighboring group. The method predicts the rate coefficients for most alkanes and many other organics to within a factor of two. For example, in the case of isopentane (2-methyl butane), for which the overall rate coefficient for reaction with OH is 3.7×10^{-12} cm^3 molecule^{-1}s^{-1} the following shows the rate of abstraction from the different sites.

$$OH + CH_3 - CH_2 - CH - (CH_3)_2$$

$$0.2 + 1.1 + 2.3 + 0.3 = 3.9 \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$$

As can be seen, the reactivity is dominated by the single hydrogen atom attached to the 2-site, while the three methyl groups combined contribute only 14% of the reactivity.

Abstraction of a hydrogen atom from each site in a given alkane gives rise to a unique product (alkyl radical), and so the structure activity relationships should also reflect the sites of abstraction, and hence the overall product distribution. In general, however, the observed product distributions are not as well-described as are the overall rate coefficients. Nevertheless, the general picture is that abstraction from weaker bonds occurs more rapidly than from stronger bonds, and this is also reflected in the products observed. Following hydrogen abstraction by OH or Cl, the alkyl radicals formed add O_2 to give alkyl peroxy radicals, the chemistry of which will be examined in detail later.

$$OH/Cl + R\text{-}H \rightarrow H_2O/HCl + R$$

$$R + O_2 + M \rightarrow RO_2 + M$$

2 Reactions of Alkenes

Alkenes contain unsaturated C=C linkages, which are subject to addition reactions with OH, Cl, NO_3 and O_3. The first three of these reactants simply lead to substituted alkyl radicals, which subsequently add O_2 to form the corresponding substituted alkyl peroxy radicals.

$$H_2C{=}CH_2 + X \rightarrow CH_2XCH_2\ (+ O_2 \rightarrow CH_2XCH_2O_2)$$

The addition reactions of OH with alkenes have lower activation energies than the abstraction reactions with alkanes and consequently occur much more rapidly. In larger alkenes, hydrogen abstraction by OH can occur, but this pathway does not usually compete with addition. For chlorine atoms, on the other hand,. the abstraction reactions are fast enough to constitute a considerable fraction of the total reaction [8].

2.1 Reaction of alkenes with O_3

The reaction of ozone with alkenes has long been a topic of research and continues to be a source of controversy. It is thought that ozone initially adds to the alkene to form a 5-membered cyclic ozonide in which the three oxygen atoms remain attached to one another [9,10]. This primary ozonide is then thought to decompose to a carbonyl compound and an unstable dioxo radical commonly known a Criegee intermediate (see Figure 2). The carbonyl compounds formed in the ozonolysis of many alkenes have been measured by Atkinson and coworkers [11,12] and by Grosjean and coworkers [13–15], and follow the simple mechanism shown. In general, for

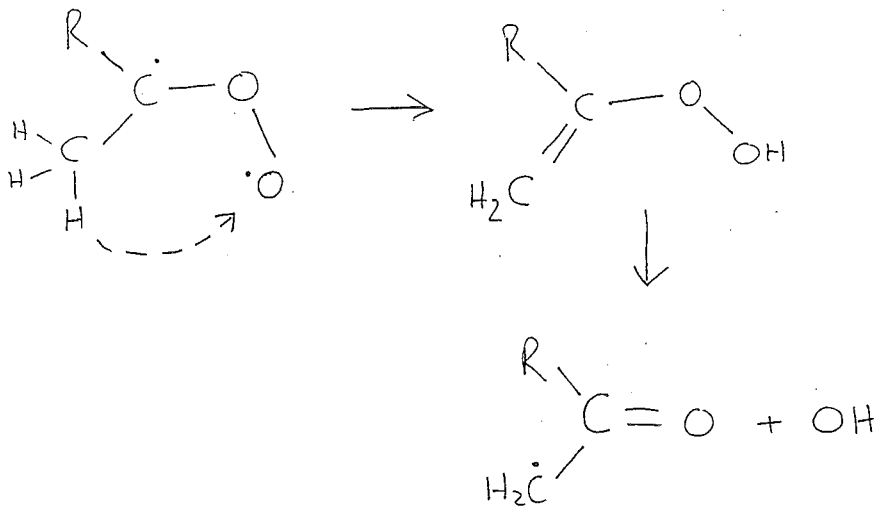

Figure 3. Proposed mechanism for the decomposition of a Criegee intermediate to give OH. The yields of OH are found to correlate with the number of methyl groups on the adjacent carbon atom, providing indirect evidence for the mechanism shown.

unsymmetrical alkenes, the less substituted carbonyl compound (co-product of the more substituted Criegee intermediate) is formed preferentially.

The Criegee intermediates are highly energetic and only a fraction are stabilised, with the fraction depending on the exact alkene involved. The majority (70–90%) decompose to smaller fragments, including both stable molecules and free radicals. Current research centers around identifying both the extent of the decomposition and the nature of the products formed, along with the further reactions of the stabilised species. In the case of the simplest Criegee intermediate (CH_2OO), formed from terminal alkenes such as ethene, propene, etc, the following pathways are thought to occur.

$$\begin{aligned} [CH_2O_2]^{\#} &\rightarrow H + H + CO_2 \\ &\rightarrow H_2 + CO_2 \\ &\rightarrow H_2O + CO \\ &\rightarrow OH + HCO \\ +M &\rightarrow CH_2O_2 \end{aligned}$$

The Criegee intermediates have never been identified in the gas phase. The German organic chemist Criegee postulated their existence in the 1950s from the study of liquid-phase ozonolysis reactions, and some of the larger species have been detected spectroscopically in solution [16]. Attempts to form the Criegee intermediates in the gas phase by means other than ozonolysis have provided evidence for the same decomposition pathways as those found in ozonolysis studies, but the energetic nature of the radicals has precluded their detection [17,18].

$$CH_2 + O_2 \rightarrow [CH_2O_2] \rightarrow \text{products}$$

$$CH_3O_2 + Cl \rightarrow HCl + [CH_2O_2] \rightarrow \text{products}$$

A current area of investigation is the possibility that larger Criegee intermediates can form OH directly [19]. If this is the case, then OH production can continue at night after sunset [20]. A good correlation is found between the yield of OH and the number of CH_3 groups adjacent to the COO group in the Criegee intermediates. A plausible mechanism is the transfer of a H atom via

5-membered ring inside the Criegee intermediates (see Figure 3). At present, though, the exact mechanism of the formation of OH is in some dispute [21–23].

The fraction of Criegee intermediate that is stabilised is thought to undergo further reaction, particularly with unsaturated compounds and hydroxy compounds such as H_2O or acids (see e.g., [24, 25]).

$$\begin{aligned} CH_2O_2 \quad + H_2O \quad &\rightarrow \quad HOCH_2OOH \\ &\rightarrow \quad HCOOH + H_2O \\ + CH_2O \quad &\rightarrow \quad ? \\ + HCOOH \quad &\rightarrow \quad HC(O)OCH_2OOH \\ + SO_2, NO_2, NO,... \quad &? \end{aligned}$$

These reactions lead to the formation of, for example, hydroxy- and hydroperoxy substituted esters, and substituted hydroperoxides. Many different compounds have been detected in ozonolysis reactions. Due to the wide range of detection techniques required, and the relatively low yields and high reactivity of some of the compounds, systematic studies are difficult, and this subject is a current active area of research.

2.2 Reactions of alkenes with NO_3

The nitrate radical, NO_3, is a further potential oxidant for alkenes, and warrants special attention. As a result of its rapid daytime photolysis NO_3 chemistry is mainly limited to nighttime [26–28], but this can be very important because of the very low levels of OH predicted to occur after sunset. The nighttime chemistry of NO_3 with biogenic hydrocarbons may turn out to be very important. NO_3 normally exists in equilibrium with NO_2 and N_2O_5 [29]. In the atmosphere this equilibrium limits the amount of NO_3 that can be present; in the laboratory, the decomposition of N_2O_5 is often used as a source of NO_3.

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$$

$$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$$

Nitrate adds to the double bond in alkenes in an analogous manner to OH, forming a substituted alkyl radical which rapidly adds O_2 to form a peroxy radical. The reactions of this nitrate substituted alkyl peroxy radical are analogous to those of the other peroxy radicals discussed later. Products formed in the laboratory include dinitrates and carbonyl nitrates [30]. However, as a result of the equilibrium above, large quantities of NO_2 are invariably present in reaction mixtures, so the products observed may not represent those formed in the atmosphere.

3 Reactions of Alkyl Peroxy Radicals

The oxidation of hydrocarbons - by OH, Cl, NO_3 or O_3 - inevitably leads to the formation of alkyl peroxy radicals, due to the rapid reaction of alkyl radicals (R) with O_2, and the vast abundance of O_2 in the atmosphere.

$$R + O_2 + M \rightarrow RO_2 + M$$

The presence of RO_2 radicals in the troposphere is critical to the formation of ozone. Under conditions of NO_x > 20ppt or so, typically encountered in the continental troposphere, the major fate of RO_2 is to react with NO, forming NO_2. The photolysis of NO_2 results in the formation of an O_3 molecule.

$$RO_2 + NO \rightarrow RO + NO_2$$

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

The net sequence results in the overall production of O_3 without consumption of NO + NO_2. As will be seen later, the reactions of alkoxy radicals (RO) lead to the production of HO_2 or a different RO_2, so the total number of RO_2 radicals is conserved. In the absence of peroxy radicals, however, the major conversion of NO to NO_2 occurs through the reaction of NO with O_3, and no net O_3 is produced. In the atmosphere, RO_2 radicals can react with NO, NO_2, HO_2 or other RO_2. Good summaries of the chemistry of peroxy radicals are given by Wallington *et al.* [31] and Lightfoot *et al.* [32].

3.1 RO_2 + NO reactions

The reactions of NO with RO_2 radicals have very similar rate coefficients, ranging fom about 5 x $10^{-12}cm^3molecule^{-1}s^{-1}$ for large alkyl radicals to about $2x10^{-11}cm^3molecule^{-1}s^{-1}$ for peroxy acetyl. The reactions also have weak negative temperature dependences, and are thought to proceed through weakly stabilised ROONO peroxy nitrite intermediates (which have, however, never been observed). Larger peroxy radicals do give a reasonable fraction of alkyl nitrates in their reaction with NO.

$$RO_2 + NO \rightarrow RO + NO_2$$

$$RO_2 + NO + M \rightarrow RONO_2 + M$$

The nitrate yields are dependent on both the size and the structure of the alkyl group present, and the total pressure [33]. Presumably a fraction of the peroxy nitrite complexes can be stabilised and then isomerise to alkyl nitrates. Most of the data available are for alkyl peroxy radicals; the yields of the substituted peroxy radicals formed, in the oxidation of alkenes are not as well-studied. For example, it is not known whether the oxidation of isoprene leads to the formation of β-hydroxy alkyl nitrates. A total nitrate yield of 10–14% has been inferred by Tuazon and Atkinson [34], although field measurements have not been successful in measuring these hydroxy nitrates [35]. Two fairly old but good general summaries of the chemistry of organic nitrates are those by Roberts [36] and Ridley [37].

3.2 RO_2 + RO_2 reactions

The earliest studies of RO_2 self reactions concentrated on the smaller alkyl radicals, whose self-reactions were found to be slow. More recent work on larger, substituted radicals has indicated much larger rate coefficients than previously thought, based on the alkyl species. If a C-H bond is present at the R-O_2 site, then the reactions can proceed by two pathways - one producing two alkoxy radicals, and one producing a hydroxy compound and a carbonyl compound, as shown below for the ethylperoxy radical.

$$C_2H_5O_2 + C_2H_5O_2 \rightarrow C_2H_5O + C_2H_5O + O_2$$

$$C_2H_5O_2 + C_2H_5O_2 \rightarrow CH_3CHO + C_2H_5OH + O_2$$

The relative yield of these pathways is dependent on the particular radical and on the temperature. No general rules are apparent to describe the yields. If no α-hydrogen is present, then only the first channel is available. Cross reactions between different alkyl peroxy reactions proceed along analogous lines. If one of the radicals is an acyl peroxy, $RC(O)O_2$, derived from the abstraction of an H-atom from an aldehyde or from photolysis of a ketone, then the second channel leads to the formation of an organic acid rather than an alcohol.

Reactions between RO_2 tend to be thought of as being limited in importance in the atmosphere, since the NO reaction usually dominates under continental conditions, and the HO_2 reaction dominates under clean, background reactions. However, when viewed as overall sinks for radicals the $RO_2 + RO_2$ reactions should not be neglected, particularly at low NO_x levels. Under conditions of high photochemical activity, the size of the radical pool is increased, and since the rate of such reactions goes as $[RO_2]^2$, these reactions can still be substantial radical sinks.

3.3 $RO_2 + HO_2$ reactions

The reactions of RO_2 radicals with HO_2 are important chain limiting reactions in the background atmosphere. For the smaller RO_2 species the products have been shown to be organic hydroperoxides, with greater than 90% yield [38,39]. Some substituted RO_2 are thought to lead to the formation of a carbonyl compound and water, also.

$$RO_2 + HO_2 \rightarrow ROOH + O_2$$

$$RO_2 + HO_2 \rightarrow R'CHO + H_2O + O_2$$

The organic hydroperoxides are lost from the atmosphere by reaction with OH, photolysis and by deposition with a lifetime of typically about a day or so. The OH reaction and deposition lead to a reduction in the number of radicals available to form ozone, and thus those pathways become very important in the background atmosphere.

4 Reactions of Carbonyl Compounds

Carbonyl compounds (aldehydes and ketones) contain a C=O double bond, which imparts an increased photochemical activity to the molecules in addition to their reactions with free radicals. The reactions of aldehydes with OH and Cl atoms are very fast, and often limit their lifetimes to a few hours. The reactions lead to the formation of acyl radicals, which add O_2 in an analogous fashion to the alkyl radicals.

$$RCHO + OH \rightarrow RCO + H_2O$$

$$RCO + O_2 \rightarrow RC(O)O_2$$

Ketones are not particularly reactive with OH or Cl and their rate coefficients are usually not different from those of the corresponding alkanes. Br atoms and NO_3 also abstract a hydrogen atom from aldehydes, but are largely unreactive with ketones.

As mentioned above, the carbonyl compounds all undergo photolysis in the troposphere. The photolysis rates depend on the exact compound, since the absorption cross sections and photolysis quantum yields all depend on wavelength. The rate of photolysis, usually designated j,

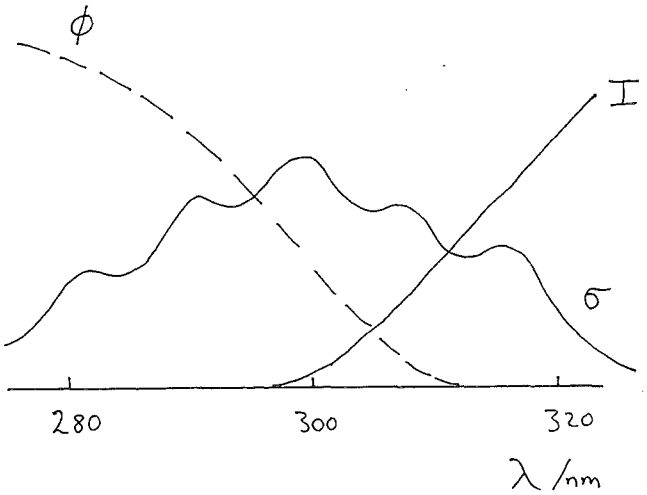

Figure 4. *The three factors governing the rates of photolysis of a carbonyl compound (or any other molecule for that matter) are the absorption cross section σ, the quantum yield ϕ, and the intensity of solar radiation I. The overlap of these three quantities determines the rate of photolysis. Note that the absorption cross section can vary as a function of temperature, while the quantum yield for a given channel can also vary with pressure due to quenching processes.*

is calculated from the product of the solar flux, the absorption cross section and the photolysis quantum yield integrated over all the wavelengths where all of these three quantities are non-zero, as illustrated in Figure 4.

$$j = \int I \bullet \sigma \bullet \phi \, d\lambda$$

The photolysis of carbonyls increases the radical pool in the troposphere and also accelerates the rate at which the carbon chain is shortened. Photolysis is one of the most important loss processes for formaldehyde, but it becomes less important for ketones. However, in the upper troposphere, where the dry conditions limit the amount of OH formed from ozone photolysis, the photolysis of ketones such as acetone can provide a major source of free radicals [40]. Multiple photolysis pathways are available for many of the carbonyl compounds. For example, for CH_2O, pathways to give H + HCO or H_2 + CO have been identified [41]. The photolysis of dicarbonyls such as glyoxal (CHOCHO) and methylglyoxal (CH_3COCHO) is facilitated due to the presence of conjugated carbonyl groups, which results in a fairly strong absorption around 400nm [42]. Although the quantum yields are rather small in this region, the abundance of solar radiation allows rapid photolysis to occur. Methylglyoxal is formed in the oxidation of isoprene, and its photolysis can be a large source of free radicals in isoprene-dominated areas.

It is worth emphasising once more at this point that the reactivity of a given organic compound is made up of the effects of all the constituent parts. For example, methacrolein, $CH_2=C(CH_3)CHO$, can be classed as an aldehyde and an alkene, and is subject to abstraction of hydrogen from the CHO group and addition of OH at both sites of the C=C bond, as well as photolysis of the carbonyl group. In some cases, the presence of one group can also substantially influence the reactivity of another due to the donation or withdrawal of electrons through neighbouring bonds.

The acyl peroxy radicals, $RC(O)O_2$, formed in the oxidation of carbonyl compounds are particularly important, since they are the precursors to PAN-type molecules (PAN = peroxyacetyl

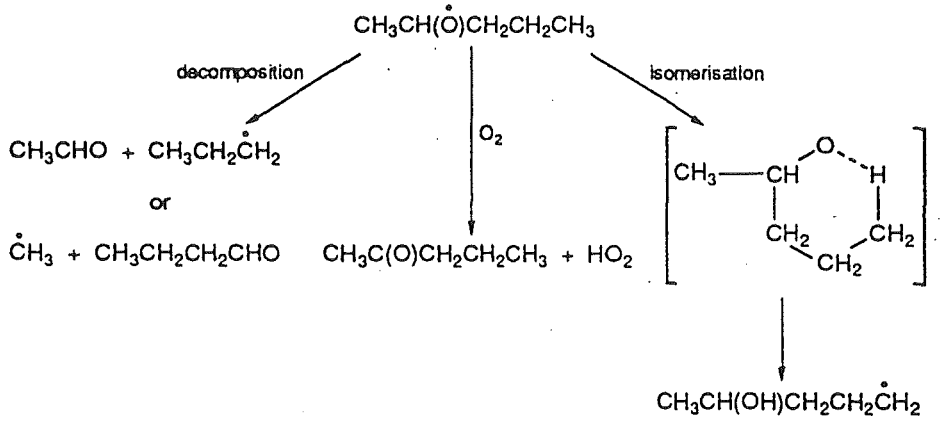

Figure 5. *Representation of the three reaction channels available for the 2-pentoxy radical. The competition between these pathways determines both the carbon number and the degree of oxygenation of the products formed. Figure from* R. Atkinson, E.S. Kwok, J. Arey *and* S. Aschmann, *Faraday Discussions* **100**, 23 (1995), Reactions of Alkoxyl Radicals in the Atmosphere.

nitrate or, alternatively, peracetic nitric anhydride). These compounds are thermally rather stable, and can transport active nitrogen from polluted areas to clean areas [36,37,43].

$$RC(O)O_2 + NO_2 + M \rightarrow RC(O)O_2NO_2 + M$$

5 Reactions of Alkoxy Radicals

Formed in the reactions of RO_2 radicals with each other and with NO, the alkoxy radicals are vitally important in determining the observed product distributions from VOC oxidation. In general, alkoxy radicals can react with O_2, decompose thermally or isomerise by internal hydrogen transfer, as illustrated in Figure 5 for the case of the 2-pentoxy radical. The competition among these pathways controls not only the length of the carbon chain, but also the degree of oxygenation of the molecule, which, as we shall see later, has important ramifications for the solubility of the molecule.

The O_2 reactions all have fairly similar rate coefficients. The reactions are actually quite slow, and do not necessarily dominate the chemistry of the alkoxy radicals, except in the case of simple alkyl systems. The reactions lead to the formation of HO_2 and a carbonyl compound.

$$CH_3CH_2O + O_2 \rightarrow CH_3CHO + HO_2$$

Alkoxy radicals are organic analogs of OH, and as such might be expected to abstract hydrogen atoms in a similar fashion to OH. However, due to the occurrence of the rapid reactions mentioned above, alkoxy radical abstraction reactions do not usually occur in the atmosphere, with the very important exception of internal isomerisation reactions. Isomerisation of alkoxy radicals is possible when 4 or more carbon atoms are present in a linear chain, and leads to the formation of a hydroxy alkyl radical (Figure 5).

The third mode of reaction for alkoxy radicals is thermal decomposition to give a carbonyl and an alkyl radical, in the case of an unsubstituted alkoxy. Substituted alkoxy radicals can lead to the formation of a carbonyl and an oxygenated radical (often acyl or CH_2OH).

$$CH_3CH_2CH(O)CH_3 \rightarrow C_2H_5 + CH_3CHO$$

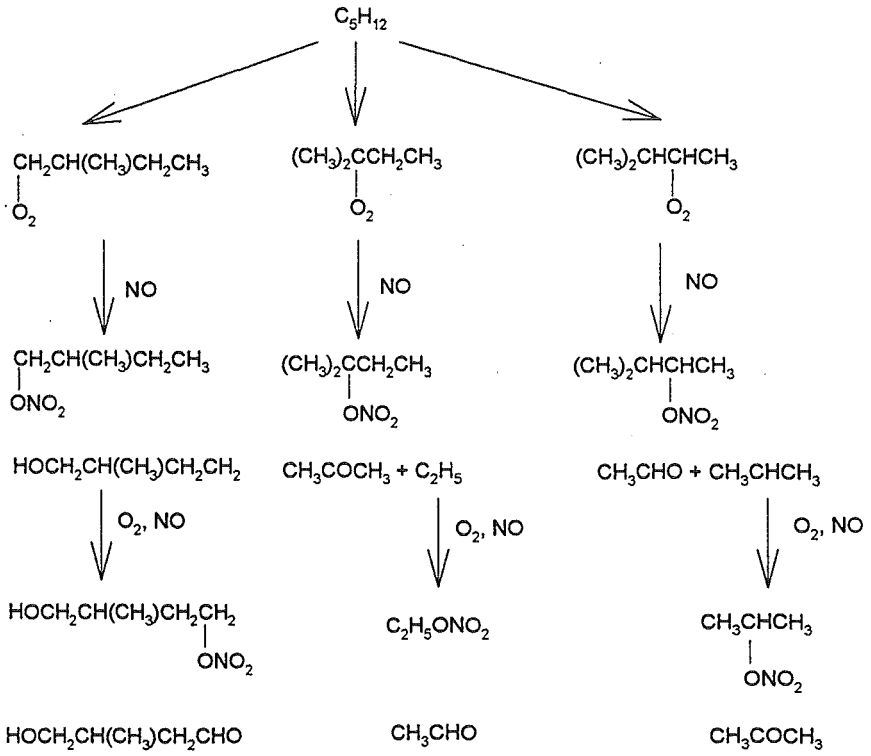

Figure 6. Schematic of the oxidation of 2-methyl butane (isopentane). The figure shows the formation of organic nitrates from the various initial alkyl peroxy radicals followed by the decomposition or isomerisation of the alkoxy radicals. A variety of carbonyl compounds and nitrates with between 2 and 5 carbon atoms are formed. Note that only one of the possible radicals resulting from abstraction at a terminal site has been drawn.

$$CH_3C(O)CH(O)CH_3 \rightarrow CH_3CO + CH_3CHO$$

$$CH_2(OH)CH_2O \rightarrow CH_2OH + CH_2O$$

The decomposition reactions are unimolecular processes, and may be expected to have strong temperature and pressure dependences. The rate coefficients for decomposition are governed mainly by the activation energy, which in turn is related to the enthalpy of decomposition of the alkoxy radical. The more endothermic the decomposition (less favorable) the higher the activation energy, and hence the slower the reaction. Atkinson has derived empirical expressions relating the activation energy to the enthalpy and, more recently, to the ionization potential of the radical formed in the decomposition [44,45]. These expressions can then be used to calculate a rate of decomposition. For many alkoxy radicals the fate in the atmosphere is determined by the competition between reaction with O_2 and decomposition, so it is usually of interest to know the ratio of these two processes, rather than the absolute rate of either. Conveniently, the ratio is also the easiest thing to measure in the laboratory, and a well-designed chamber experiment can provide much useful information on the fate of alkoxy radicals in the atmosphere. However, very few product studies have been carried out at temperatures below ambient. Since the decomposition reactions tend to be very dependent on temperature, while the reactions with O_2 are almost

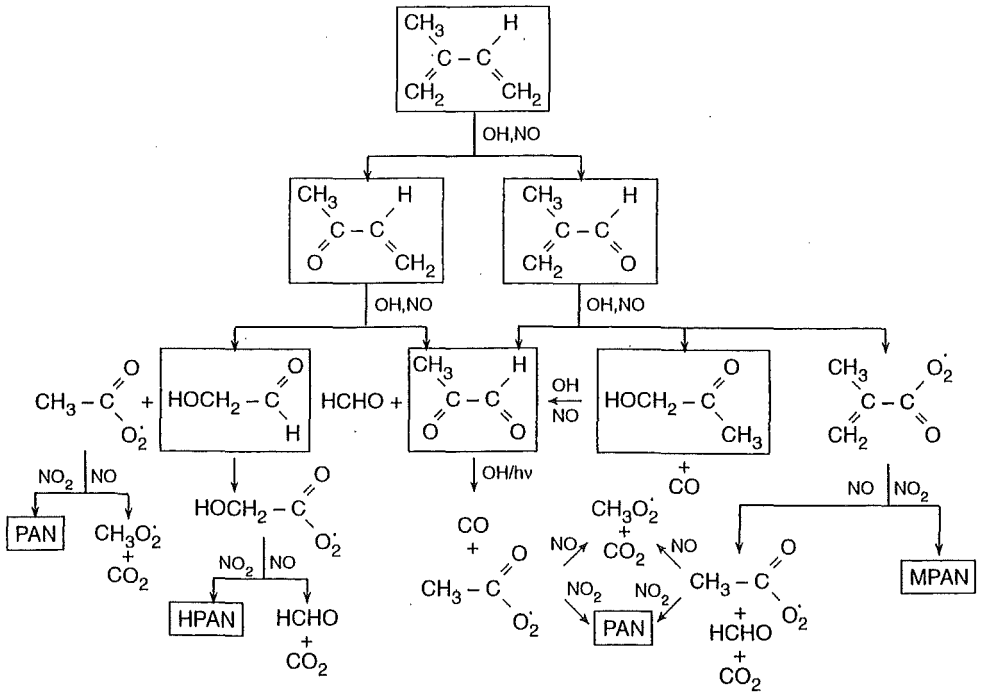

Figure 7. Schematic of the oxidation of isoprene in the presence of NO. The stable products shown inside the squares can in principle be measured using current techniques for carbonyl compounds. Minor products from reactions of peroxy radicals with HO_2 and from attack at other sites than the main ones are not shown. The reactions proceed along similar lines to those of simple alkenes (attack at either double bond, followed by formation of a peroxy radical, reaction of the peroxy radical with NO, and decomposition of the alkoxy radical). PAN, $CH_3C(O)O_2NO_2$; MPAN, $CH_2=C(CH_3)C(O)O_2NO_2$; HPAN, $HOCH_2C(O)O_2NO_2$.

independent of temperature, the ratio should also be strongly temperature dependent. Consequently, the mechanism of their oxidation should change with altitude in the troposphere.

The recently discovered effect of chemical activation may tend to reduce this temperature dependence. The reaction of RO_2 radicals with NO (the main route for the formation of alkoxy radicals in the atmosphere) is fairly exothermic, and the excess energy is usually deposited into the alkoxy radical. This is actually a consequence of the fact that the reaction proceeds through a long-lived intermediate, as discussed above in relation to the formation of organic nitrates. If enough internal energy finds its way into the alkoxy radical, it can decompose spontaneously, without having to overcome the barrier through collisional activation [46]. Currently, four or five systems have been identified in which chemical activation is thought to be important. One of them is ethene [47], which is a major emission from vegetation and biomass burning. As mentioned above, this is a relatively new field, and other cases will undoubtedly be discovered.

This discussion of the chemistry of simple alkanes and alkenes can be illustrated in Figures 6 and 7, which show schematic oxidation schemes for isopentane (2-methyl butane) and isoprene (2-methyl, 1-3-butadiene) respectively.

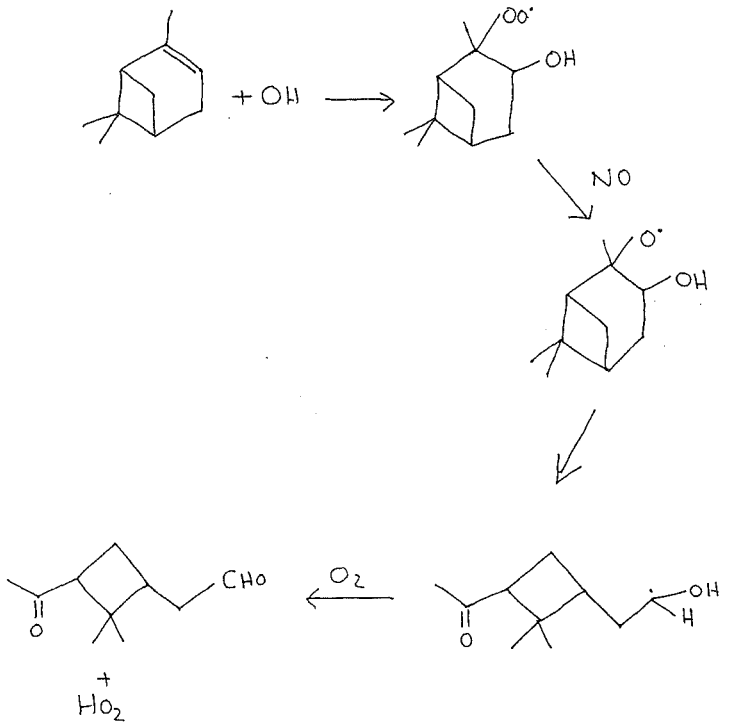

Figure 8. *Mechanism for the initial attack of OH at the double bond of α-pinene. The reaction is entirely analogous to that of propene. Note, however, that due to the complexity of the molecule, several other possibilities exist for the OH attack, such as hydrogen abstraction. The product formed, pinonaldehyde, is a difunctional compound.*

6 Biogenic Hydrocarbons

A rapidly emerging field is the study of the reactions of biogenic hydrocarbons (isoprene and the terpenes). Monoterpenes all have the chemical formula $C_{10}H_{16}$, while the sesquiterpenes are written $C_{15}H_{24}$; all can be derived from the isoprene structural unit. The terpenes are large, multifunctional alkenes which look at first intimidating, but their chemistry can be predicted on the basis of the simpler reactions considered already. As an example, take the oxidation of α-pinene, which has one double bond, and looks a lot like 2-methyl 2-butene to an OH radical (Figure 8). The initial oxidation steps can be written down by analogy to the simpler alkenes, and two carbonyl groups are formed from the two halves of the double bond [48,49]. Note, however, that since α-pinene is a ring compound, the two carbonyls are still attached to the same molecule, in contrast to the simple alkenes where two smaller carbonyls are formed. The fact that the resulting molecule is difunctional may have important consequences for the potential formation and growth of aerosols from biogenics, as described in the next section. The dicarbonyl product, commonly known as pinonaldehyde, is expected to react in an analogous manner to acetaldehyde, to form a PAN-like compound [50]. Although several studies of the oxidation of terpenes by OH, O_3 and NO_3 have been carried out, the mass balance of the products in general tends to be not very good, due to the increased number of products that can be formed in small yields, and the expected reduction in volatility of the products.

7 Heterogeneous Processing of Organics

The discussion so far has only considered gas-phase reactions. However, it is becoming increasingly apparent that multiphase (commonly referred to as heterogeneous) processes are important in most regions of the atmosphere. Water is present throughout the troposphere, and in many regions aqueous droplets are present that can affect both the physical partitioning and the chemistry of organic molecules. Furthermore, solid particles characteristic of urban conditions may also provide sites where organics may deposit. The two processes are intrinsically different, the first depending on solubility, and the second on vapor pressure.

The uptake of a molecule onto a particle is usually expressed in terms of an uptake coefficient α, which is the probability that the molecule sticks to the particle. The rate of uptake is given in terms of the rate of collisions of the particle and the molecule (derived from the kinetic theory of gases) and α. The rate of uptake of a molecule A on particles of surface area density (S/V) can be written,

$$-\frac{d[A]}{dt} = \frac{S}{V}\left(\frac{\alpha c}{4}\right)[A] = \alpha c \pi r^2 N_p [A]$$

where c is the mean molecular speed of the molecules. The second equality holds for spherical particles with number concentration N_p and radius r, since the surface area of a sphere is $4\pi r^2$.

The solubility of molecules in liquid droplets (usually aqueous in the atmosphere) is described by Henry's Law, which relates the liquid-phase concentration, or activity, to the gas-phase partial pressure in terms of a constant H (units of Mol L^{-1} atm^{-1}) according to:

$$H = \frac{a(aq)}{P(gas)}$$

Solubility increases dramatically with the presence of functionality, particularly OH groups, in a molecule. For example, consider the three alcohols derived from propane:

C_3H_7OH	$H \approx 160$ Molar atm^{-1}
$CH_3CH(OH)CH_2OH$	$H \approx 10^5$ Molar atm^{-1}
$CH_2(OH)CH(OH)CH_2OH$	$H \approx 10^8$ Molar atm^{-1}

Thus, in general, the process of oxidation leads to a pronounced increase in the solubility of the reaction products. Henry's Law coefficients have been measured for various carbonyls [51–53] and for multifunctional nitrates [54,55], while uptake coefficients are known for many carbonyl compounds, see for example, Jayne *et al.* [56] and references in Atkinson *et al.* [3] and DeMore *et al.* [4]. Uptake by clouds and rain-out has been shown to be important for many inorganic molecules such as H_2O_2 and SO_2 [57,58], and the same is expected to be true for soluble organic species [59,60]. Despite the high solubility of such molecules, the volume of aerosol in the troposphere is relatively small [61], so that the particles will saturate quickly, and the extent of physical uptake in aerosols may only be small. For the uptake to become significant, irreversible chemical reaction must occur inside the droplets. Possible mechanisms for such processes include reaction with free radicals such as OH, or catalytic reactions with transition metal ions, which may be present in fairly high concentrations in atmospheric aerosols [62,63]. The occurrence of such reactions can both affect the chemical nature of the organics present and reduce the amount of carbon in the gas phase if the reaction products are soluble enough to remain in solution.

Uptake on solid particles, which depends on the vapor pressure of the organic compound rather than its aqueous solubility, is thought to be important for larger organics. It is known that the secondary aerosol formed in urban regions results from the oxidation of aromatic compounds [64]. Also, the haze aerosol found in certain forested areas, e.g., the Smoky Mountains in the southeastern United States, is related to the presence of terpenes and/or their oxidation products. Currently, the mode of formation of such secondary aerosols remains an open question and an active topic of research. Also of interest is how the presence of organic molecules adsorbed onto the surface of particles affects the chemical and physical properties of the particles [65].

The question of aerosol formation and the nature of the transformations occurring on or in aerosol particles is clearly a topic requiring further study. The formation of aerosol has consequences not only for environmental issues such as visibility, but also for human health issues. Since the volatility of organic molecules is reduced by the amount of oxygenation, these compounds are the most likely to be deposited onto surfaces. Low volatility also causes these species to be the most difficult to measure by conventional sampling techniques.

The reactions presented here are not by any means exhaustive, but it is hoped that they give a flavour of how organic molecules react, and how the multitude of observed products can be formed. Presently, definitive and quantitative measurement techniques exist for only a small fraction of the organic compounds expected to be formed in the atmosphere. Until we can quantify organic species better any attempts to account for the flux of carbon through the atmosphere must be interpreted with caution. Also, our efforts to understand the global fluxes of hydrocarbons cannot succeed without some quantitative measure of the amount of carbon associated with particles.

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MODELLING THE VERTICAL DISTRIBUTIONS OF NON-METHANE HYDROCARBONS AND THEIR POTENTIAL IMPACT ON THE BACKGROUND ATMOSPHERE

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Introduction

It is well known that non-methane hydrocarbons (NMHCs) from anthropogenic and biogenic sources can play an extremely important role in the tropospheric chemistry. Anthropogenic NMHCs were hypothesized in early 1950's that they were a key component of O_3 precursors in the urban atmosphere (Haagen–Smit, 1952). It is now established that biogenic NMHCs are also important in the formation of pollutants, including O_3 and other oxidants, in both rural and urban atmosphere in the industrialized countries (Trainer *et al.*, 1987; Chameides *et al.*, 1988).

The major photochemical roles of NMHCs can be demonstrated by the following highly simplified reaction scheme.

$$\text{NMHC} + \text{OH} \rightarrow \text{R}^1\text{O}_2 \qquad (1)$$

$$\text{R}^1\text{O}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{HO}_2 + \text{CARB}^1 + \text{CARB}^2 \quad (1\text{-a}) \qquad (2a)$$

$$\rightarrow \text{R}^1\text{ONO}_2 \quad (a) \qquad (2b)$$

where (a) has a value ranging from 0% up to about 15% depending on the NMHC,

$$\text{CARB} + \text{OH} \rightarrow \text{R}^2\text{CO}_2 + \text{products} \qquad (3a)$$

$$\text{CARB} + h\nu \rightarrow \text{R}^3\text{O}_2 + \text{HO}_2 + \text{products} \qquad (3b)$$

$$\text{R}^2\text{CO}_2 + \text{NO}_2 \leftrightarrow \text{PAN} \qquad (4)$$

$$\text{R}^2\text{CO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{HO}_2 + \text{CARB}^3 \qquad (5)$$

$$\text{NO}_2 + h\nu + \text{O}_2 \rightarrow \text{NO} + \text{O}_3 \qquad (6)$$

where R's denote the organic radicals (superscripts denote different organic radicals), CARB for the carbonyl, and PAN for peroxyacetylnitrate. These reactions are intended only for presenting a simplified picture of the major reactions and products. For details, the reader should refer to reviews such as Atkinson *et al.* (1997). The advantage of showing the simplified scheme is that one can easily see the following important roles NMHCs play in the atmospheric chemistry. One is the production of O_3 shown in Equation (6). More than one O_3 molecule is produced for each NMHCs oxidized, because both HO_2 and RO_2 oxidize NO to NO_2. The second is production of organic nitrates, including PAN and $RONO_2$. PAN and O_3 are major surface level pollutants, especially in the urban areas. In addition, organic nitrates can act as a temporary reservoir for NO_x. Transport of organic nitrates, particularly $RONO_2$, can be an effective process of transporting NO_x because of a substantial longer photochemical lifetime of $RONO_2$ than NO_x. The third is the production of carbonyls. In many instances, the carbonyls can be transported over a significantly longer distance than their parent NMHCs, again because of their longer photochemical lifetimes, e.g. carbonyls of natural NMHC such as isoprene and pinenes.

Transport of $RONO_2$ and carbonyls over long distance would allow the influence of NMHCs to be extended over larger areas than the NMHCs themselves.

Most of the NMHCs are emitted over the continent. Anthropogenic NMHC emissions are relatively well known. A recent estimate indicates a global source of about 140Tg/yr (Bouwman, 1993). The largest source of NMHCs is from biogenic emissions. Their emission rate is about 1150Tg/yr (Guenther *et al.*, 1995). Another important source is emissions from biomass burning. Koppmann *et al.* (1997) gave a rough estimate that ranged from 25 to 48Tg(C)/yr. In comparison, the estimated sources of CH_4 range from 410 to 660Tg/yr (IPCC, 1994). For CO, the estimated sources are 770 to 1160Tg(C)/yr. Thus the sum of NMHC sources is about the same as the combined sources of CH_4 and CO.

Because the lifetimes of most of the NMHCs and their oxidation products, particularly those of the biogenic origin, are shorter than a day, the majority of NMHCs are oxidized in the continental boundary layer. Thus one can easily draw the conclusion that the sum of NMHCs and their reaction products is oxidized by OH in a larger quantity than the sum of CH_4 and CO oxidized by OH in the continental boundary layer. In other words, NMHCs play a more important role than CO and CH_4 in the photochemistry of the continental boundary layer. On the other hand, with lifetimes of about two months and 10 years, respectively, most of CO and CH_4 are transported and oxidized outside of the continental boundary layer. As a result based on the sources presented above, it is clear that CO and CH_4 are a larger sink than NMHCs for OH in the global troposphere other than the continental boundary layer. Indeed, observations of the concentrations of NMHCs over most of the remote troposphere suggest that the concentrations of NMHCs tend to be quite low such that they play a negligible role in the photochemistry of HO_x and O_3 (e.g. Davis *et al.*, 1996; Blake *et al.*, 1996). However, this conclusion does not apply to the effect of NMHCs in regard to the formation of organic nitrates and their potential impact on the reactive nitrogen photochemistry because CO and CH_4 are not directly involved in the production of organic nitrates. Furthermore, oxygenated hydrocarbons are usually not measured in the remote troposphere, thus their impact can not be evaluated from the observation. The only exceptions are acetone and methanol. Singh *et al.* (1995) reported that acetone mixing ratio ranges from about 200 to 500 pptv in the mid and upper troposphere. At these levels acetone can be a significant if not dominant source of PAN in the middle and upper troposphere. In addition, acetone can be an important source of HO_x in the upper troposphere and thus having a significant impact on the O_3 production.

Modelling the Impact of NMHCs on the Remote Troposphere

The above discussion suggests that it is unlikely that NMHCs can compete with CO and CH_4 in terms of acting as a sink of OH in the global troposphere other than the continental boundary layer. Thus, in order for NMHCs to have a significant impact on the tropospheric photochemistry beyond the continental boundary layer, some process similar to that of acetone has to happen. In fact, the impact of acetone on the mid and upper tropospheric photochemistry gives an excellent reference point to evaluate potential impact of other NMHCs. A simple method to obtain a quantitative evaluation of the reference point is to calculate the amount of acetone oxidized in the upper and mid troposphere. Assuming the median mixing ratio of acetone is 300pptv in the upper troposphere between 10 and 15km (assumed tropopause for summer conditions at mid-latitudes) and negligible amount of acetone above 15km, we can calculate a global average column oxidation rate of about 3Tg(C)/yr above 10km. Similarly, the column oxidation rate above 5km can be roughly estimated to be about 10Tg(C)/yr. Thus, in order for other NMHCs to have a

significant impact on the photochemistry in the mid and upper troposphere, similar amounts of these NMHCs have to be transported and oxidized in those regimes.

In the following, we will present a model study of the vertical distributions of NMHCs and their potential impact on the background atmosphere. The emphasis will be on the biogenic NMHCs and their products because, with their large emissions, they are most likely to be transported in a significant amount to the mid and upper troposphere. In addition, the model simulation will assume summer mid-latitude conditions when both biogenic NMHCs emissions and convection are at their seasonal maxima. Ideally, the model study would best be done in a three-dimensional global model that incorporate a realistic parameterization of the vertical transport processes, especially the convective transport which tends to be extremely efficient in transporting short lived species such as isoprene from the boundary layer to the upper troposphere. In addition, a relatively detailed representation of the photochemistry of biogenic NMHCs is needed because, as mentioned earlier, some important products of the oxidation such as carbonyls usually have significantly longer lifetimes than their parent NMHCs and thus can be transported out of the boundary layer in a larger quantity. So far there has been no published work that meets all the above criteria.

We will use a relatively simple one-dimensional model in this study. The model has a detailed treatment of the isoprene chemistry according to that recommended by Carter and Atkinson (1996). The vertical transport parameterization is a simple eddy mixing coefficient which is certainly not realistic and can not simulate convective transport. On the other hand, if a useful tracer can be found that can give a quantitative measure of the overall vertical transport rate (or time), an eddy coefficient can be derived from the tracer's vertical distribution and can be used for evaluating how fast and how much other trace species are transported vertically, even though eddy mixing is not the physically correct transport mechanism. A tracer that satisfies the above requirement is not difficult to find. For instance, ^{222}Rn and various NMHCs can be good tracers for vertical transport over the continent. However, extensive measurements of these tracers are usually not available.

Deriving a One-Dimensional Eddy Coefficient

Liu *et al.* (1984) used available data of ^{222}Rn over the United States to derive an eddy diffusion coefficient of about $40 m^2 s^{-1}$ under summer conditions, and about $20 m^2 s^{-1}$ for spring/fall conditions. These values are probably biased towards the lower side, particularly in the upper troposphere. The reason is that the prevailing westerlies in the mid and upper troposphere bring oceanic air with low ^{222}Rn concentration over the continent.

Davis *et al.* (1996) and Liu *et al.* (1998) took advantage of the observed vertical distributions of trace gases over the tropical Pacific during two Western Pacific Exploratory Missions (PEM-West A and B) to make a quantitative study of the atmospheric vertical transport processes. Among the trace gases observed during PEM-West, CH_3I and DMS are most useful for quantifying the vertical transport because they have relatively simple sources and sinks. Both are emitted primarily from the ocean (e.g. Andeae, 1990; Bates *et al.*, 1992). The predominant sink of CH_3I is photodissociation. This sink gives CH_3I a lifetime of about 3 days near the surface and two days in the upper troposphere under clear sky conditions. For DMS, oxidation by atmospheric OH radicals is the major sink and results in about one day lifetime in the boundary layer and two days in the upper troposphere under clear sky conditions.

Shown in Figures 1a and 1b are the vertical distributions of CH_3I observed in and near the tropics (< 20°N) during PEM-West A and B, respectively. The corresponding distributions of DMS are shown in Figures 2a and 2b. The data are segregated into six 2 km altitude intervals. The horizontal bar covers the range of all the data in the altitude interval; the rectangle denotes

data between the lower 25% and upper 75% values; and the vertical bar near the center represents the median value. From hereon we will refer to the lowest layer as the boundary layer because the predominant measurements in this layer were taken near 300 meters above sea level. The total number of points in each figure is on the order of 300 for CH_3I and about 100 for DMS. The data are not evenly distributed at each height interval as the flight patterns of DC-8 were designed to favor the upper troposphere (8km and above) and the boundary layer. Furthermore, during PEM-

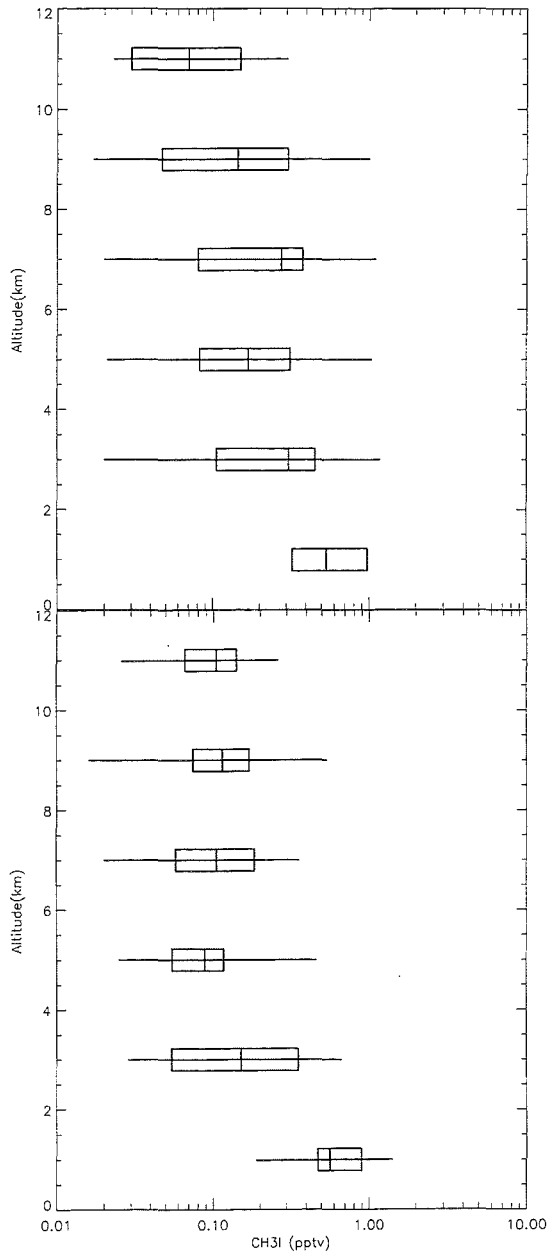
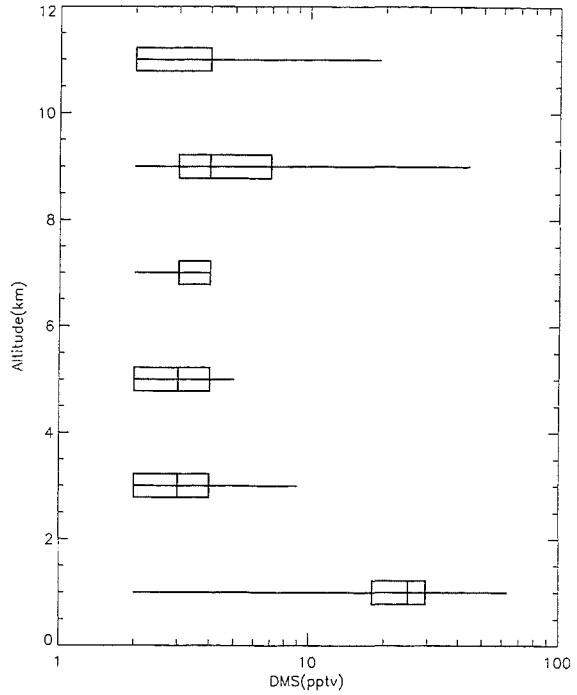


Figure 1. *Vertical distribution of* CH_3I *near the tropics (<20°N) for PEM-West A* ***(a)*** *and PEM-West B* ***(b).***

(a)



(b)

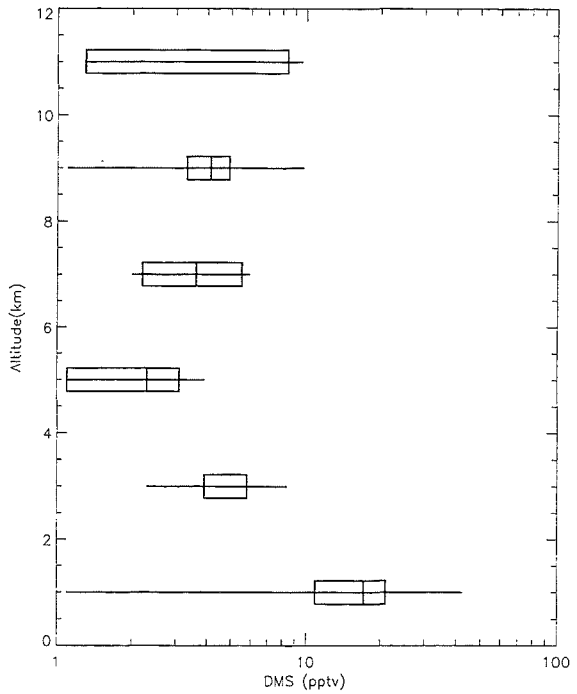


Figure 2. *Vertical distribution of* DMS *near the tropics (<20°N) for PEM-West A* ***(a)*** *and PEM-West B* ***(b).***

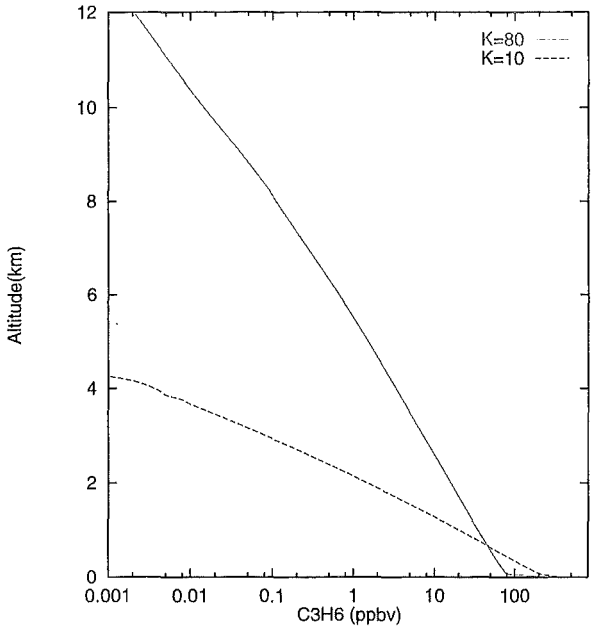


Figure 3. *The vertical profile of* C_3H_6 *concentration in polluted atmosphere for two values of the eddy constant, K=80 and K=10.*

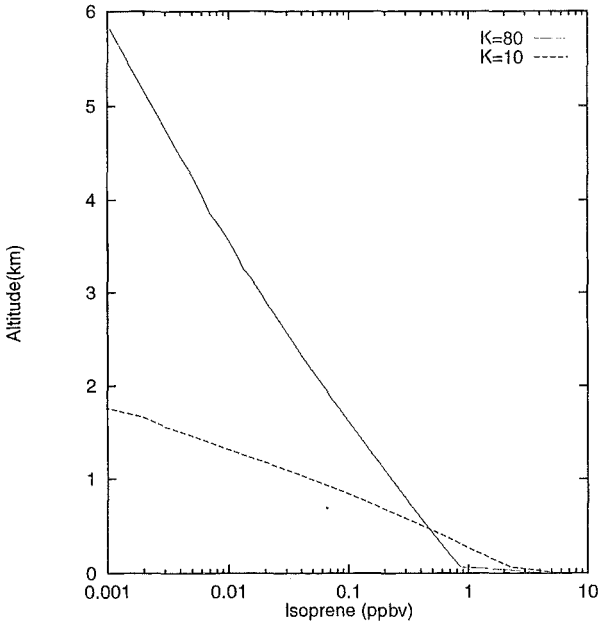


Figure 4. *The vertical profile of* Isoprene *concentration in polluted atmosphere for two values of the eddy constant, K=80 and K=10.*

West B a large number of DMS measurements are below the detection limit and are not included in the figures. Thus, statistically, the data are more meaningful or representative in the upper troposphere and boundary layer than the data at other altitudes. For this reason, in the following discussions emphasis will be put on the upper troposphere and the boundary layer.

An important feature in these figures is that when the profiles are normalized to a common mixing ratio in the boundary layer, the distributions of DMS are qualitatively and even quantitatively consistent with those of CH_3I in essentially every aspect. Because CH_3I and DMS were measured by independent methods, the consistency between the vertical distributions of the two species strongly supports that the relatively slow decrease of the mixing ratios of CH_3I and DMS from the boundary layer to the upper troposphere is the result of fast vertical transport. This notion is also supported by the fact that other relatively short lived trace species observed at low latitudes were also well mixed vertically. These species include O_3, NO, H_2O_2, and some NMHCs.

A three-dimensional model has been used to estimate the rate of vertical transport (McKeen *et al.*, 1998). Their results demonstrate that indeed the fast vertical transport can be attributed to the high frequency and large altitude extent of the convection in the tropics. Meanwhile, they suggest that on a scale that is substantially greater than the actual convection, the rate of vertical transport can be simulated by mixing processes, e.g., vertical eddy diffusion coefficient.

The spatial scales of the observations during both PEM-West A and B are about several thousand kilometers. This is many orders of magnitude greater than the scale of active convective activities along the flight tracks. Under these conditions, a one-dimensional eddy diffusion approach can provide valuable information about the vertical transport. By fitting a straight line between the median value of the boundary layer and that of the upper troposphere, we obtain an eddy diffusion coefficient of $87 m^2 s^{-1}$ for PEM-West A. For PEM-West B, an eddy diffusion coefficient of $202 m^2 s^{-1}$ is needed because the decrease in the mixing ratio of CH_3I between the boundary layer and upper troposphere is about a factor of two smaller than that of PEM-West A.

These eddy diffusion coefficients are much larger compared to the summer time eddy diffusion coefficient derived from ^{222}Rn over the United States. The reason is most likely the influence of oceanic air as discussed earlier. On the other hand, the eddy coefficient derived during PEM-West over the tropical Pacific is probably only representative of the convective vertical transport over the tropics and is most likely an overestimate for the convective vertical transport in mid-latitude summer conditions. Therefore, we will use a one-dimensional model with an $80 m^2 s^{-1}$ eddy diffusion coefficient, i.e., low PEM-West tropical value, to represent convective conditions in mid-latitude summer and a $10 m^2 s^{-1}$ eddy diffusion coefficient to represent non-convective conditions. Results from these two model calculations will be compared to deduce the importance of convective vertical transport on the distribution of NMHCs and their impact on the background atmosphere.

Model Results

In the model calculations, eastern United States summer conditions are assumed. Figure 3 shows the altitude distribution of a typical anthropogenic NMHC, C_3H_6. As expected, C_3H_6 decreases much faster with height for smaller eddy coefficient. With a total emission of only 140Tg/yr for the anthropogenic NMHCs, we estimate that, even for the large eddy coefficient case ($80 m^2 s^{-1}$), their impact on the photochemistry in the background atmosphere is small relative to acetone.

Figure 4 shows the altitude distribution of isoprene (the profiles are cut off when the decrease is more than three orders of magnitude). The decrease with height is even faster than that of C_3H_6 because isoprene's extremely short photochemical lifetime. For the large eddy coefficient case, isoprene decreases by more than 1000 from the surface to 5km. I.e., less than

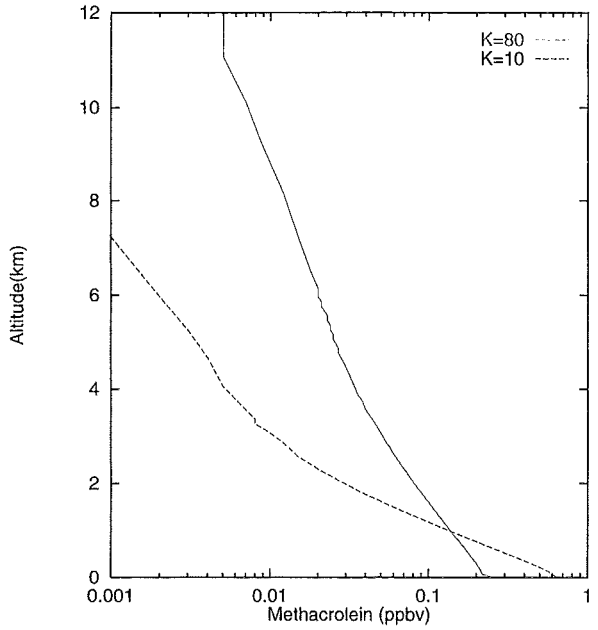


Figure 5. *The vertical profile of* Methacrolein *concentration in polluted atmosphere for two values of the eddy constant, K=80 and K=10.*

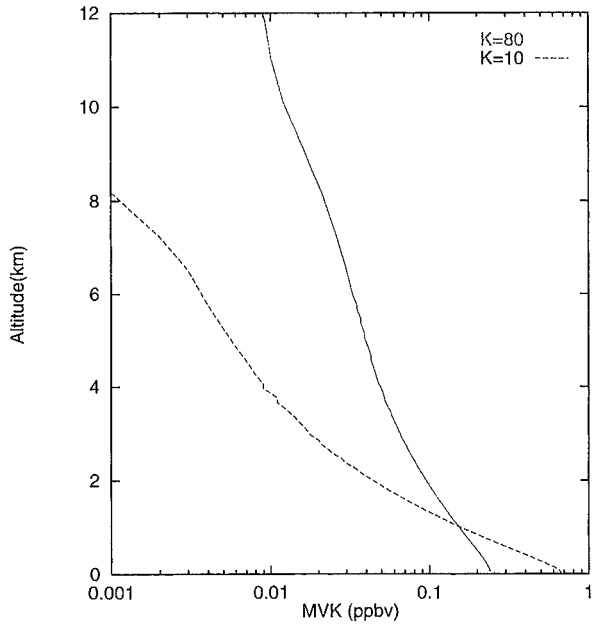


Figure 6. *The vertical profile of* Methyl vinyl ketone *concentration in polluted atmosphere for two values of the eddy constant, K=80 and K=10.*

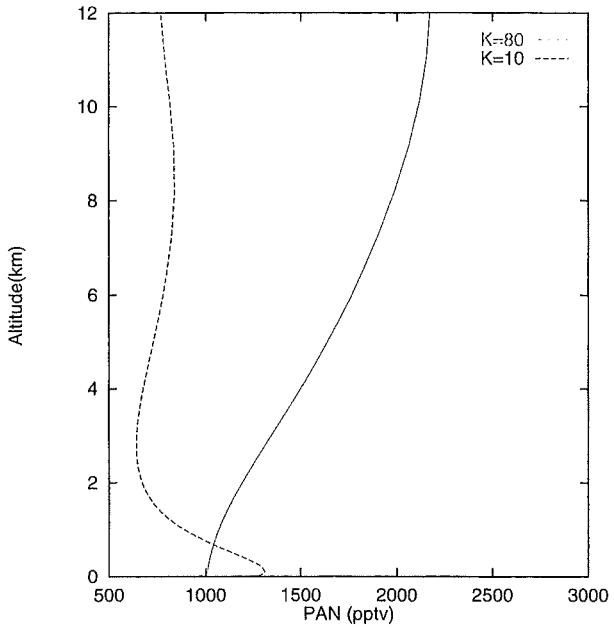


Figure 7. *The vertical profile of* PAN *concentration in polluted atmosphere for two values of the eddy constant, K=80 and K=10.*

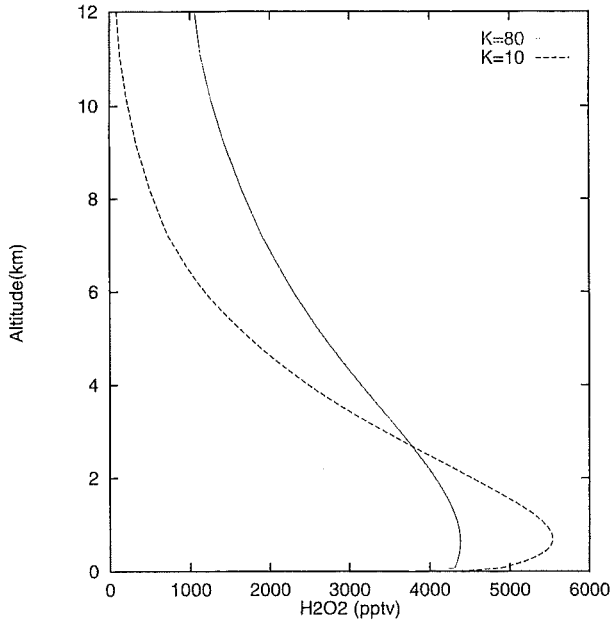


Figure 8. *The vertical profile of* H_2O_2 *concentration in polluted atmosphere for two values of the eddy constant, K=80 and K=10.*

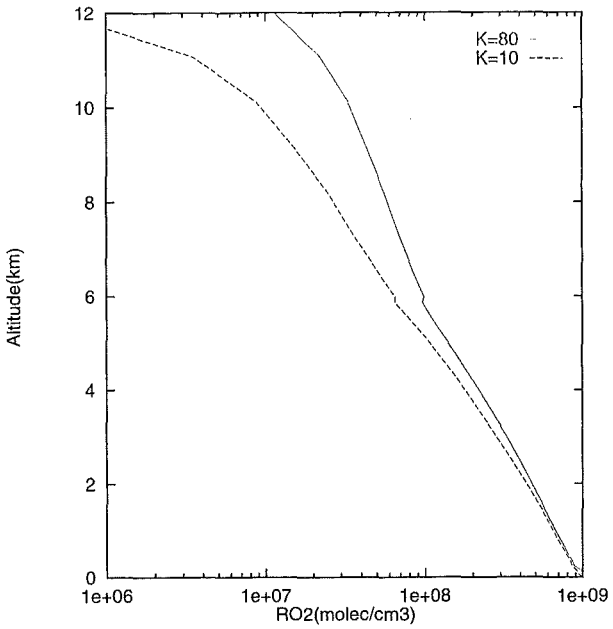


Figure 9. *The vertical profile of* RO_2 *concentration in polluted atmosphere for two values of the eddy constant, K=80 and K=10.*

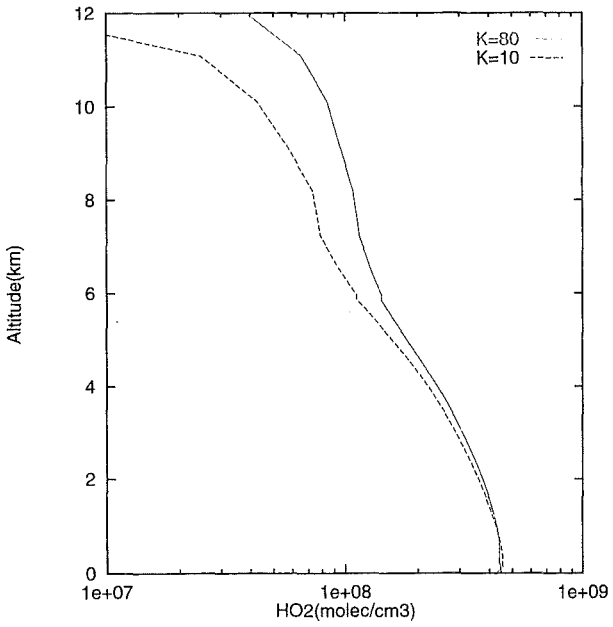


Figure 10. *The vertical profile of* HO_2 *concentration in polluted atmosphere for two values of the eddy constant, K=80 and K=10.*

0.1% of the isoprene is transported above 5km. Since isoprene is a good representative of biogenic NMHCs, we can conclude that less than 0.1% of total biogenic NMHCs are oxidized above 5km. Assuming half of the biogenic NMHCs are emitted in the summer, 0.1% corresponds to about 0.5Tg/yr. This value is about 20 times smaller than the 10Tg(C)/yr of acetone oxidized above 5km. Thus, similar to anthropogenic NMHCs, the direct impact of biogenic NMHCs on the photochemistry in the background atmosphere is negligible relative to acetone. However, this is not the case when we take into account of the secondary hydrocarbons of isoprene. Figure 5 and Figure 6 depict the altitude distributions of the major carbonyl compounds, methacrolein and methyl vinyl ketone (MVK), respectively. The decrease from the surface to 5km for the large eddy coefficient case is about 14 and 10 in number density for methacrolein and MVK, respectively. I.e., about 8% of the carbonyls are oxidized above 5km. If we make a reasonable assumption that about two third of the natural NMHCs are oxidized to carbonyls like methacrolein and MVK, then the amount of biogenic carbonyls oxidized above 5km is about 30Tg/yr. The corresponding number above 10km is about 6Tg/yr of biogenic carbonyls oxidized. These values are substantially greater than the 10 Tg(C)/yr of acetone oxidized above 5km and the 3Tg(C)/yr above 10km. Therefore, we expect that, in the case of large eddy coefficient, biogenic carbonyls will have a significantly larger impact on the photochemistry of the background atmosphere than that of acetone. For the small eddy coefficient case (10 m^2s^{-1}), the impact of biogenic carbonyls on the photochemistry of the background atmosphere is significantly smaller than that of acetone.

The impact of biogenic carbonyls on the photochemistry of the background atmosphere can be easily seen in the altitude distributions of PAN (and other organic nitrates, not shown here) and H_2O_2 (Figures 7 and 8). PAN in the upper troposphere is about three times in the large eddy coefficient case than the small one. The difference in H_2O_2 in the upper troposphere is even greater, about a factor of five at 10km. The effects on PAN and H_2O_2 can be directly traced to changes in RO_2 and HO_2 which are shown in Figures 9 and 10.

The changes in HO_2 and RO_2 will definitely affect the photochemistry of OH, NO_x and O_3. Our model calculations confirm a significant impact of biogenic carbonyls on the photochemistry of O_3, NO_x and OH in the background atmosphere when the eddy coefficient is large. However, the impact on these species depends critically on the vertical distributions of O_3 and NO_x which can not be simulated realistically in a one-dimensional model and thus is not shown here.

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EXPERIMENTAL DETERMINATION OF THE BALANCE OF HO_x RADICALS IN POLLUTED AIR

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During two field campaigns (SLOPE 92 and 96), simultaneous measurements of ozone and ozone precursors were conducted at Schauinsland in the Black Forest and in the valley north of Schauinsland that channels the flow of polluted air from the city of Freiburg to the site. From the decay of reactive hydrocarbons and NO_x between the two measuring sites and the known rate coefficients for their reaction with OH the average concentration of OH radicals in the air masses was estimated. The analysis yielded OH concentrations between $5x10^6$ and almost $10^7 cm^{-3}$, fairly large in presence of high NO_x concentration around 10ppb or more.

The analysis of the budgets of OH and HO_x shows that the relatively high OH concentrations can only be sustained if efficient recycling of OH via HO_2 is assumed to occur and that, based on the C_2–C_8 hydrocarbons measured during SLOPE 92, about two HO_2 molecules must be formed for each OH radical that reacts with a hydrocarbon molecule. Additional measurements of C_6–C_{15} hydrocarbons made during SLOPE 96 showed that the total hydrocarbon reactivity was about twice as large than that given by the hydrocarbons measured in 1992 and that biogenic hydrocarbons made up for a large fraction of the total reactivity. Because of the higher VOC to NO_x ratio, the amplification factor required to close the budget was less than 1.5 HO_2 for each OH radical consumed by reaction with a hydrocarbon. Measurements of ozone and ozone precursors from balloons and airplane were made to obtain information about a possible effect of mixing processes on the OH estimation.

Introduction

The transition region between urban and rural environs is important in understanding the fast photochemistry that leads to the build up of high concentrations of ozone and other photooxidants during so-called summer smog episodes. While the ozone balance at greater distances from the source regions is usually limited by the NO_x concentration, it is generally assumed that the ozone formation rate in urban air, rich in NO_x, is limited by the rate at which hydrocarbons (RH) and carbon monoxide (CO) are oxidised by hydroxyl radicals (OH) to yield peroxy radicals (HO_2 and RO_2).

$$RH + OH + O_2 \rightarrow RO_2 \qquad (R1)$$

$$CO + OH + O_2 \rightarrow HO_2 \qquad (R2)$$

At low NO_x concentrations, NO is the rate limiting factor in ozone production (R3a and R5) and controls the partitioning of HO_x (R5). At high NO_x on the other hand, reaction of OH with NO_2 (R7) is the major sink of HO_x ($[HO_x] = [OH] + [HO_2]$), and thus limits the production of RO_2 and HO_2.

$$NO + RO_2 \rightarrow NO_2 + RO \qquad (R3a)$$

$$NO + RO_2 \rightarrow RONO_2 \qquad (R3b)$$

$$RO + O_2 \rightarrow HO_2 + \text{Carbonyls} \quad \text{(R4)}$$

$$NO + HO_2 \rightarrow NO_2 + OH \quad \text{(R5)}$$

$$NO_2 + h\nu + O_2 + M \rightarrow NO + O_3 + M \quad \text{(R6)}$$

$$NO_2 + OH + M \rightarrow HNO_3 + M \quad \text{(R7)}$$

At high NO_x levels, HO_2 is almost completely recycled to OH and radical losses by HO_2 recombination reaction as well as that with organic peroxy radicals becomes insignificant.

Additional radicals can be formed from the photolysis of the carbonyl compounds formed in reaction R4, so that more radicals are produced from the hydrocarbon oxidation mechanism than are initially consumed (Jeffries and Tonnesen, 1994, Jang *et al.*, 1995). In addition, OH and RO_2 radicals are thought to be produced by reactions of alkenes with ozone (Becker *et al.*, 1990, Paulson *et al.*, 1992, Atkinson and Aschmann, 1993, Shu and Atkinson 1994).

Since the rate at which chemistry proceeds depends in a non-linear fashion on the precursor and product concentrations, which are influenced by chemical and physical processes such as radiation, advection, convection, and turbulence, coupling between chemistry and transport can have a large influence on the build-up of photooxidants in space and time. It is therefore interesting to investigate the radical budget experimentally under different atmospheric conditions.

We report here a budget analysis for HO_x radicals and ozone based upon two field campaigns (Slope 92 and 96) which were conducted in the vicinity of Freiburg (Black Forest in southwestern Germany).

The motivation for the SLOPE campaigns came from the long-term measurements made at Schauinsland as a part of the EUROTRAC sub-project TOR (Tropospheric Ozone Research). It was found that during weak synoptic conditions, a thermal up-slope wind system is usually established in the morning after the break up of the nocturnal inversion, and relatively fresh pollution from the nearby city of Freiburg is channeled to Schauinsland through the valley Großes Tal that extends from Schauinsland to the north (Volz-Thomas *et al.*, 1993).

Theoretical approach

The OH concentration is estimated by simultaneously integrating the rate of change of a set hydrocarbons. We consider the continuity equation for a molecule RH_i:

$$\frac{\partial[RH_i]}{\partial t} = P_{RH_i} - L_{RH_i} - \vec{u}\nabla[RH_i] + \nabla K \nabla[RH_i] \quad (1)$$

where $\partial/\partial t$ is the local rate of change, P and L are the local production and loss terms, $u\nabla[RH_i]$ and $\nabla K\nabla[RH_i]$ is the flux divergence due to advection and turbulence. It is the last term that renders the approach different from a laboratory system, i.e. a chemical flow reactor.

As has been discussed in several publications (McKeen *et al.* 1990, 1993, McKenna *et al.*, 1995, Kramp and Volz-Thomas, 1997), the approach relies on the fulfillment of a number of assumptions. First of all, it is assumed that reaction R1 is the major chemical loss process for the

hydrocarbons used in the analysis. It must be emphasized that the approach does not constitute a positive identification of OH in the atmosphere but rather relies on the wisdom about the role of OH in atmospheric chemistry. Secondly, chemical production and emissions of the considered hydrocarbons during transport must be negligible. The influence of emissions and mixing processes on the calculated OH concentrations from hydrocarbon ratios on a global scale is discussed by Ehhalt *et al.* (this volume).

Assuming that chemical losses are described by eq. 2,

$$L_{RH_i} = -\frac{d[RH_i]}{dt} = [RH_i] \cdot [OH] \cdot k_i \qquad (2)$$

and that the dilution is equal for all hydrocarbons and therefore the term $\nabla K \nabla[RH_i]$ can be described by a coefficient k_D. With these assumptions, the integration of (1) after transformation into Lagrangian coordinates yield:

$$\ln\left([RH_i]_{t_1} / [RH_i]_{t_2}\right) = \overline{[OH]} k_i \, \Delta t - \bar{k}_D \, \Delta t \qquad (3)$$

According to (3), the OH concentration can be estimated from the slope of a semi-logarithmic plot of the ratios of the individual hydrocarbons versus the respective rate coefficients with OH, k_i, and the dilution coefficient k_D is derived from the intercept with the ordinate. The ratios are formed from concentration pairs that are measured at Kappel at the time t_1 and at Schauinsland at the time t_2. Precondition for determination of the OH concentration from the slope is the knowledge of the traveling time $\Delta t = t_2 - t_1$ between the two points of measurement.

Experimental

During SLOPE 92, ground based ozone and precursor measurements were made in Kappel at the entrance of the valley Großes Tal and at Schauinsland. Both sites were equipped with instrumentation for NO, NO_x, NO_y, O_3, J_{NO_2}. For hydrocarbon analyses, Airmotec HC1010 GC-systems were used at both locations. This instruments were suitable to measure C_5–C_8 hydrocarbons with a time resolution of 30min. At Schauinsland, C_2–C_5 hydrocarbons were measured with a self-built GC-system with a time resolution of 3 hours.

During SLOPE 96, the Airmotec instruments were used with a higher time resolution of 20 min. C_2 to C_6 hydrocarbons were measured at both locations with a time resolution of 90min. Additionally to the in situ hydrocarbon measurements, samples on adsorption tubes were taken every 3h and evaluated with GC-MS for C_6 to C_{15} hydrocarbons. Figure 1 gives an overview of locations and measurements performed inside the valley during the SLOPE 96 campaign. Besides extensive meteorological measurements, also LIDAR measurements and balloon soundings were made at several sites as well as airborne measurements of O_3, NO_2, VOCs, and meteorological data by a small airplane.

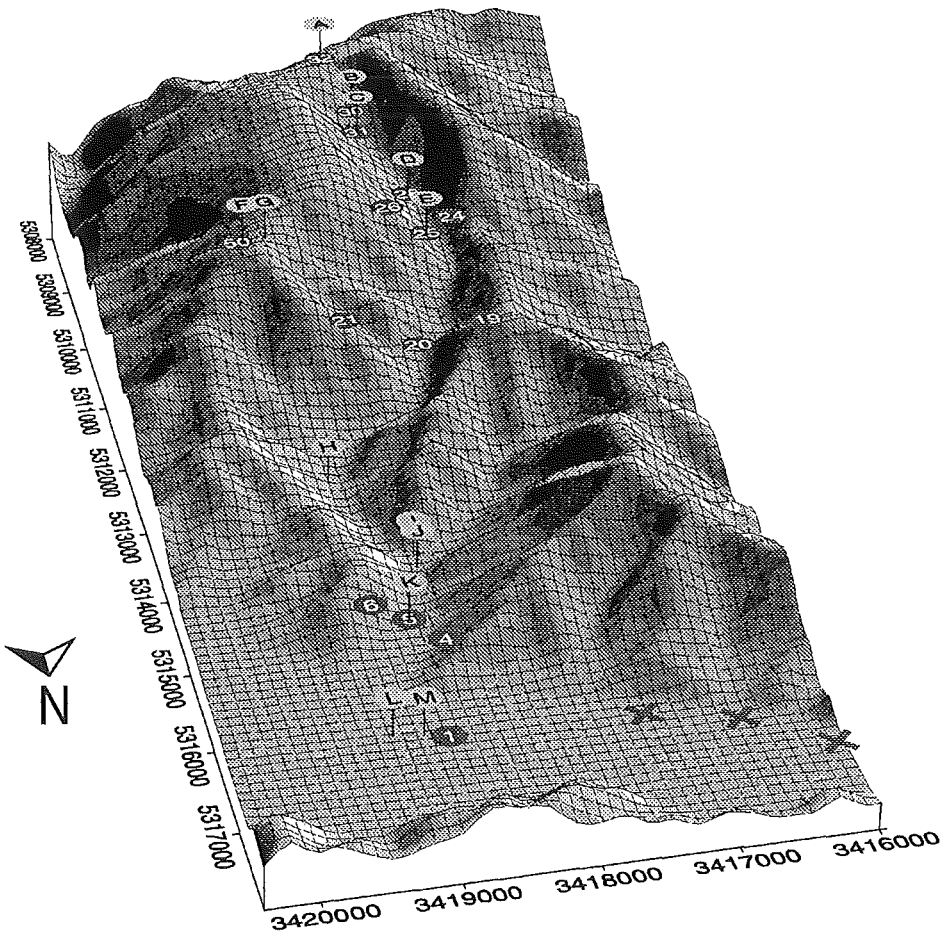

Figure 1. *Arrangement of the meteorological measurements, balloon sounding as well as sampling sites for the tracer experiments inside the valley Großes Tal during SLOPE 96. Encircled numbers: Locations of air samplers for* SF_6 *emissions.* **A–C, G:** *Meteorological measurements.* **D, H:** *Balloon soundings GKSS and ground based meteorological measurements.* **E:** *Mobile laboratory IFU.* **F, L:** *Sodar measurements.* **I:** *Zeppelin University of Stuttgart launching area.* **J:** *Balloon soundings University of Stuttgart.* **K:** *Monitoring site Kappel; mobile laboratory ICG-2, LIDAR measurements MPG Hamburg.* **M:** *Radio soundings KFK.*

Results and Discussion

Figure 2 shows the diurnal variation of the concentrations of NO_x and toluene at Kappel and Schauinsland observed at September 17th, 1992. The onset of the up-slope is marked by a change in wind direction, followed by a sharp increase in trace gas concentrations with a maximum

around 11 a.m. at the valley site. At Schauinsland, the peak concentrations were observed around 1.30 p.m., which corresponds to a transport time Δt of 150 to 180min. Additionally, Δt was treated as a free parameter in a range from 90 to 300 minutes and semi-logarithmic plots (Figure 3) were made for all sets $[RH_i](t_1+\Delta t) / [RH_i](t_1)$ that lie in the time interval where the up-slope persisted. Minimizing of the sum of squares obtained from linear least square fit analysis of the respective data (details are given in Kramp and Volz-Thomas, 1997) also resulted in a optimum value for Δt of 150 to 180 minutes.

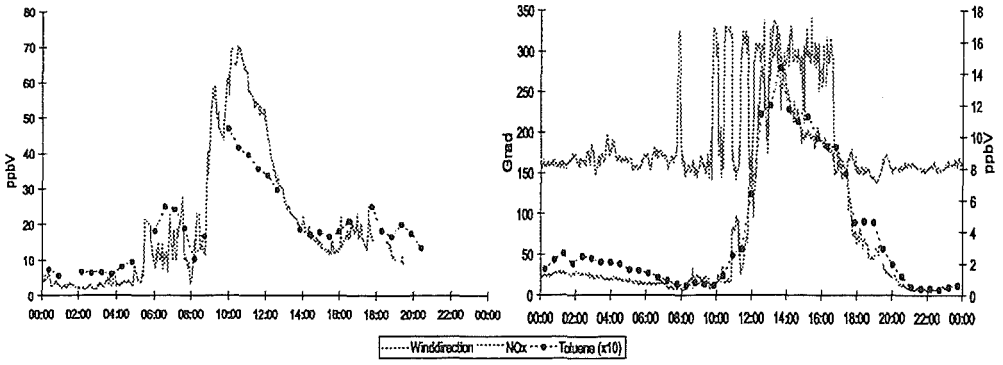

Figure 2. Diurnal variation of NO_x *and toluene at Kappel (left) and Schauinsland (right) in SLOPE 92.*

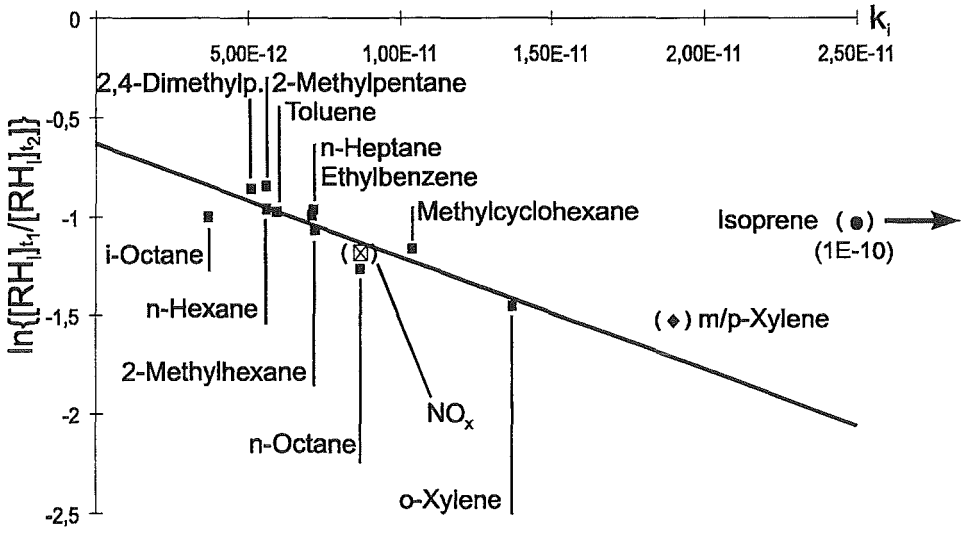

Figure 3. Semi-logarithmic plot of the ratios of hydrocarbons and NO *formed from the concentrations measured in Kappel at time* t_1 *and at Schauinsland at time* t_2*, with* $\Delta t = t_2 - t_1 = 150$*min..*

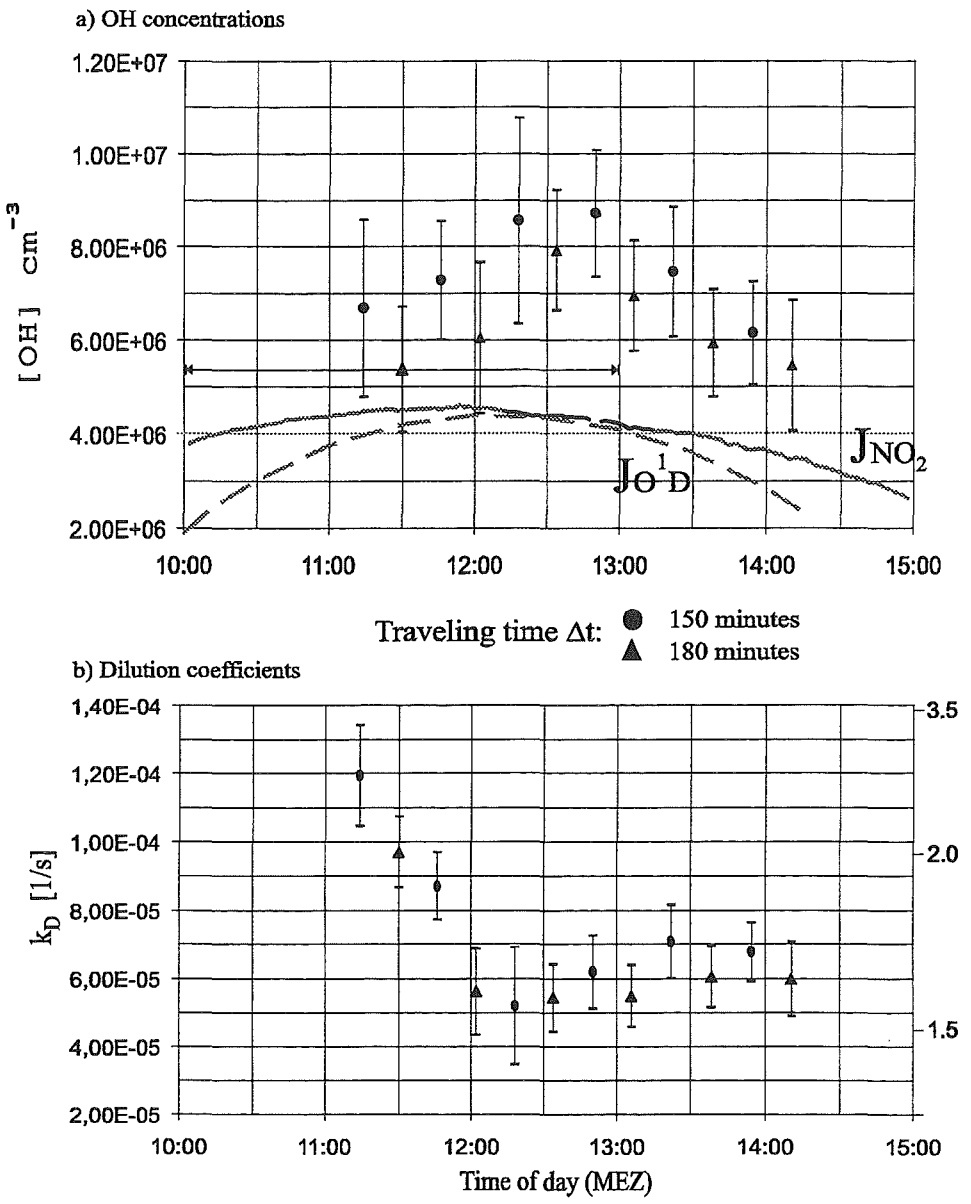

Figure 4. Diurnal variation of the average OH-*concentration between Kappel and Schauinsland as derived from Figure 2 for transport times* Δt *of 150 and 180min. The solid line gives the values of* J_{NO_2} *(x* $5 \cdot 10^{8}$*) and the broken line gives the estimated values of* JO^1D *(x* $1.5 \cdot 10^{11}$*). The lower panel shows the respective variation of the first order dilution coefficient.*

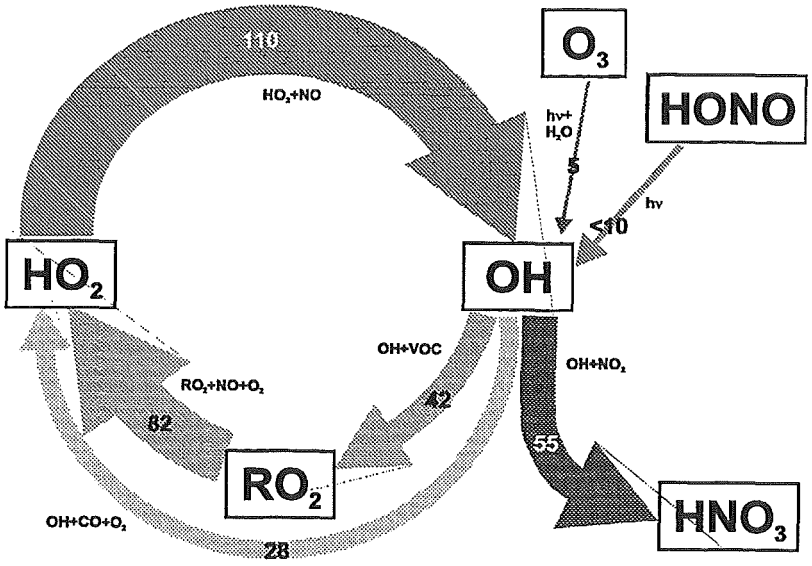

Figure 5. *HO_x budget calculated upon the measured concentrations of anthropogenic hydrocarbons, NO_x and carbon monoxide during SLOPE 92. The calculations relate to an air mass containing the peak concentrations of most of the measured ozone precursors. The employed concentrations were measured at Kappel at t_1 = 10:30 and Schauinsland at t_2 = 1:00. The respective concentrations (averaged over the sampling time of the GC's) were:* $[NO_x](t_1) = 68ppb$; $[NO_x](t_2) = 13.8ppb$; $[NO_2](t_1) = 33ppb$; $[NO_2](t_2) = 9.3ppb$; $[CO](t_1) = 842ppb$; $[CO](t_2) = 483ppb$; $\Sigma[RH](t_1) = 202ppbC$; $\Sigma[RH](t_2) = 61.6ppbC$; $[OH](\Delta t) = 7.3x10^6$ *molec* cm^{-3}; $k_D = 8.7x10^{-5}s^{-1}$. *The first order dilution coefficient translates into a volumetric dilution factor of 2.2. Number density:* $2.46x10^{19}$ *molec* cm^{-3} *at Kappel and* $2.25x10^{19}$ *molec* cm^{-3} *at Schauinsland.*

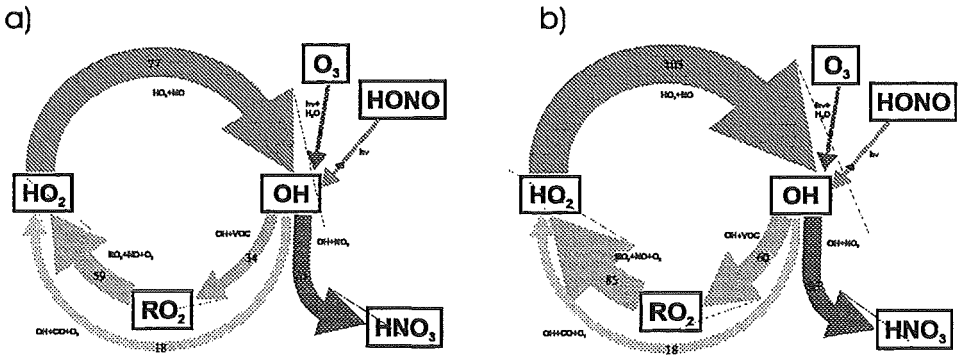

Figure 6. *Comparison of the HO_x budget obtained from the SLOPE 96 data set. In* ***(a)****, only the anthropogenic emitted VOC's were considered, whereas* ***(b)*** *includes the measured biogenic emitted organic compounds.*

Analyzing all pairs t_1 and t_2 with $\Delta t = t_2 - t_1 = 150$ min, respectively 180 min, within the period of up-slope gives the diurnal variation of OH concentration shown in Figure 4a. The concentration follows the photolysis rate of ozone, which is estimated from the measured values of J_{NO_2}. The enhanced values derived for OH in the afternoon are probably overestimated, since the assumption of negligible background concentrations for the hydrocarbons is not valid over the whole day. An indication for this is the decrease of the dilution coefficients before noon to a constant level in the afternoon (Figure 4b).

With respect to the heavily polluted airmasses that were transported through the valley, the estimated OH concentrations are quite high. The main loss process for OH radicals is the reaction with NO_2, CO and hydrocarbons. Since, in Kappel, only the hydrocarbons C_5 to C_8 were measured, the concentrations of the hydrocarbons C_2 to C_4 and carbon monoxide were estimated from the concentrations measured at Schauinsland by using the OH concentrations and dilution rates from Figure 4.

Considering all available data, the following balance of sources and losses of OH was obtained (Figure 5). The larger fraction of the OH losses in Figure 5 does not constitute a loss of HO_x but converts OH to HO_2 which, in the presence of high NO concentrations, is immediately recycled to OH in R5. Likewise, a fraction of the alkyl peroxy radicals that are formed in R1 react with NO in R3a to form alkoxy radicals. The fate of the alkoxy radicals is decomposition, reaction with O_2 or, in case of the larger molecules, intramolecular rearrangement (Atkinson, 1984, 1994). It is unclear at present how many HO_2 radicals are produced in the course of the degradation of an initial RO_2 radical under high NO_x conditions. The HO_x budgets can be closed by assuming that the reactions of OH with hydrocarbons lead to the generation of more HO_x radicals in the form of HO_2 than are initially consumed in the form of OH. The amplification factor f_a obtained from the budget is $f_a = (R_7 - P_{pr} + \Sigma R_1)/\Sigma R_1$, with R_7 and ΣR_1 being the rates at which OH radicals react with NO_2 and hydrocarbons, respectively, and P_{pr} being the primary HO_x production rate. The HO_x budget in Figure 5 requires a surplus of around 40×10^6 molecules cm^{-3} s^{-1}, and hence suggests an amplification factor of $f_a \approx 2$ (Kramp and Volz-Thomas, 1997).

The potential for radical amplification is an intrinsic feature in the oxidation of hydrocarbons, i.e. through the photolysis of carbonyl compounds that are formed in the reaction of the alkoxy radicals with O_2 (R4). Unfortunately, photolysis rates are known only for a limited number of carbonyl compounds. In the case of the measured C_1–C_4 carbonyl compounds their photolysis could only account for less than half of the HO_x surplus required.

The calculated amplification factor which is required to close the HO_x budget is sensitive to the ratio of hydrocarbons and NO_x. Approximately 75% of the total hydrocarbons from automobile emissions are accounted for by our measurements (Kramp *et al.*, 1995). Methane (CH_4) contributes only 3–5 % to the measured RH reactivity. Contributions from isoprene were included in our budget based on the measured concentrations. Unlike in other studies (e.g. Trainer *et al.*, 1987), isoprene made only a small contribution (15%) to the total VOC reactivity between Freiburg and Schauinsland. However, other biogenic hydrocarbons, e.g. terpenes, as well as internal alkenes which were not measured during SLOPE 92, could contribute significantly to HO_x production due to their decomposition after reaction with ozone (Paulson and Orlando, 1996). Depending on the relative rates and the surplus of HO_x generated from the oxidation of these hydrocarbons, the amplification factor required for the anthropogenic hydrocarbons could be significantly lower than the value of two derived above and would then be closer to what can be achieved via the photolysis of carbonyls.

Summarizing the results from SLOPE 92 it can be said that the uncertainties of the estimated OH concentrations and in the HO_x budget are chiefly given by:

a) Uncertainty in the transport time Δt,

b) Influences of mixing processes on the estimated OH concentrations, in particular after total development of the boundary layer,

c) Missing hydrocarbons, especially biogenic emitted species in the radical budget,

d) Contribution of ozone-olefine reactions to the radical budget.

Based upon the experience obtained in SLOPE 92, the measurements during SLOPE 96 were extended by vertical profiles and hydrocarbon measurements aboard an airplane. Transport time and volumetric dilution factor were obtained independently from a dispersion experiment with SF_6. Due to different meteorological conditions, the traveling time was shorter (Δt = 120 minutes) than in SLOPE 92 and the volumetric dilution factor was about 10, approximately a factor of 2.5 higher than in 92. Because of the larger dilution, the ozone precursor concentrations in the transported air masses were of about a factor of 2 lower than in 92.

From the airborne measurements, the background concentrations of hydrocarbons were determined. Including these in the analysis resulted in OH peak concentrations 1.0×10^7 cm^{-3}, only 10% lower than without the background correction (Kolahgar, 1998). The first evaluation of the data, therefore, gives no evidence that the chemical composition of the transported air masses was significantly changed by mixing processes during transport between Kappel and Schauinsland.

Figure 6 shows an comparison between the HO_x budget calculation excluding (a) and including (b) biogenic emitted organic compounds. To include these compounds in the budget calculations, their steady state concentration inside the valley was estimated by averaging the concentrations measured at a time t_1 at Kappel and $t_1+\Delta t$ at Schauinsland. Considering exclusively anthropogenic hydrocarbons, an amplification factor of 1.7 was calculated from the SLOPE 96 data set. Including the measured organic compounds of biogenic origin, the amplification factor needed to close the budget was reduced to <1.5 (Kolahgar, 1998). This must still be regarded as an upper limit since not all the hydrocarbons may have been measured and because of the potential of the ozone-alkene reactions to the HO_x budget.

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ON THE USE OF HYDROCARBON RATIOS FOR THE DETERMINATION OF TROPOSPERIC OH CONCENTRATIONS

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This paper explores a new approach to estimate atmospheric hydroxyl radical concentrations from regional measurements of a suite of hydrocarbons. The approach is guided by the study of a suite of synthetic tracers with uniform continental sources and constant but different lifetimes of 1, 2, 5, 20, 50, 100 days, whose global distributions are calculated from a three-dimensional chemical tracer model. With the help of the model we show that the monthly relative standard deviation, $\sigma_i / \overline{M}_i$ in a grid box is a unique function of the chemical lifetime, τ_i. In favorable cases, for instance in surface air within the domain covered by the PEM West-B campaign, that function takes a simple form: $\sigma_i / \overline{M}_i = A \cdot \tau_i^{-\alpha}$, with $\alpha = 0.48$, very close to 1/2.

An analogous relation is found between the alkanes, ethane through n-hexane, measured during PEM West-B campaign in the same domain, and their reaction rate constant with OH, k_{OH}. That relation has the form $\sigma_i / \overline{M}_i = B \cdot (k_{OH})^{\alpha'}$ with $\alpha' = 0.49$. Using the alkenes, ethene and propene, which also react with O_3, the dependence on $k_{OH,i}$ can be related to a dependence on τ_i.

This allows to estimate the regional OH concentration $6 \cdot 10^5$ cm^{-3}, with an error of roughly a factor of 2. This estimate is essentially based on empirical relations only and the assumption that the considered hydrocarbons have the same source distribution. As a byproduct we show that the α defined above is related to the slope in the (logarithmic) correlation plot between the mixing ratios of two trace gases with different lifetimes.

1. Introduction

The atmospheric distribution of trace gases is governed by three processes, namely production or emissions (and their geographical distribution), transport, and losses. Each one of these processes leaves its signature on the atmospheric distribution. In turn, measured trace gas distributions can be used to glean information about these three processes. Particularly useful for that purpose are the light hydrocarbons, because they possess similar source and destruction processes, yet a large range of destruction rates. Thus they can probe the processes at various time scales. Moreover, the techniques employed usually permit the measurement of a large suite of hydrocarbons from a sample, i.e., from the same air parcel. This has allowed a simple conceptual approach to extract information from hydrocarbon measurements, namely the use of ratios of hydrocarbon concen-

trations. Appropriate ratioing cancels some of the common dependencies (e.g., transport, source distribution) but retains the information on the other process e.g., the chemical loss rates of hydrocarbons. From it the concentration of OH, which is the major removal agent for hydrocarbons, can be eventually derived (see McKeen et al., 1996). The procedure has the added advantage, that its application does not require the measurement of complete hydrocarbon concentration fields but the measurement of time series at a few well selected sites suffice for the purpose. Beside OH in urban, rural, oceanic, and free tropospheric air masses (Calvert, 1976; Singh et al., 1981; Blake et al., 1993; Roberts et al., 1984; Bamber et al., 1984; McKenna et al., 1995; McKeen et al., 1996; Kramp and Volz-Thomas, 1997), the photochemical age of air masses (Nelson and Quigley, 1982; Roberts et al., 1984, 1985; Rudolph and Johnen, 1990) and the rate of dilution of polluted boundary layer air with background air (McKeen et al., 1996) have been determined by various methods of ratioing hydrocarbons. However, all these applications make a number of simplifying assumptions which introduce possibly large uncertainties in the desired results. So far no studies of these systematic uncertainties have been published and their magnitude remains unknown.

In this paper we propose an alternative approach to derive OH concentrations from hydrocarbon measurements - an alternative which requires fewer and different assumptions, and thus, when combined with the traditional methods, may provide an indication of the systematic errors involved in estimating OH. In the following we will first describe the assumptions underlying the traditional approach of ratioing. We then show that the assumption of diffusive mixing significantly changes the interpretations in some of the hydrocarbon correlations. Finally we use a three-dimensional chemical tracer model to derive an empirical relation between the local variance of a suite of tracers and their lifetimes. This relationship points to a new way in which hydrocarbon measurements may be used to derive OH concentrations without assumptions about the underlying physical model of mixing. To remain focused the study is limited to near surface air.

2. The use of hydrocarbon ratios to determine OH

The underlying assumption in the ratioing concept is, that the function, which relates the hydrocarbon mixing ratios at the point of measurement to that of a point upstream, depends only on transport (mixing) and chemical loss, and that it can be separated into a product of two terms, one solely depending on transport, T(t,x), the other solely depending on chemical loss, L(t,x) (McKeen et al., 1990).In all cases a Lagrangian approach is used with the further assumption that the chemical operator, L(t,x), is given by a simple exponential decay in time, i.e.,

$$M_i(t,x) = M_i(0,x) \cdot T(t,x) \cdot e^{-t/\tau_i} \qquad (1)$$

where M_i is the mixing ratio of species i, t is the time since last observation at time zero, x the geographical coordinates and t_i is the constant chemical lifetime. In some cases it is also assumed that

$$T(t,x) = e^{-t/\tau} \qquad (2)$$

where τ is the time constant for mixing or dilution with background air of vanishing trace gas concentrations. τ is assumed to be the same for all species and independent of the location. (cf. McKeen et al., 1996). Eq. (1) with (2) for the transport function is a solution of the simple differential equation

$$\frac{dM_i}{dt} = -\frac{M_i}{\tau} - \frac{M_i}{\tau_i} \tag{3}$$

An often used correlation of hydrocarbons species i with species j is the plot of $\ln(M_i)$ versus $\ln(M_j)$. Eq. (3) predicts that the correlation curve is linear, with a slope

$$\beta = \frac{1/\tau - 1/\tau_i}{1/\tau - 1/\tau_j} \tag{4}$$

Such a linear correlation is indeed found experimentally (McKeen et al., 1996). Another often used form is the correlation of the ratio of three hydrocarbon species: $\ln(M_i / M_k)$ versus $\ln(M_j / M_k)$. In this way the common dependence on mixing cancels. The slope of this curve, which is also linear, is

$$\gamma = \frac{1/\tau_i - 1/\tau_k}{1/\tau_j - 1/\tau_k} \tag{5}$$

If we allow for the fact that the hydrocarbons i, j, k react exclusively with OH and thus $\tau_i = k_i \cdot [OH]$, then

$$\gamma = \frac{k_i - k_k}{k_j - k_k} \tag{6}$$

where k is the rate constant for the reaction of species i, j, k. Obviously the simple model makes testable predictions about the correlation of hydrocarbons and of their ratios. If the background air, with which the observed parcel is mixing, has a finite mixing ratio, MB, instead of zero, the differential equation (3) changes to

$$\frac{dM_i}{dt} = -\frac{M_i}{\tau_i} - \frac{M_i - MB_i}{\tau} \tag{7}$$

And the solution (1) changes to

$$M_i(t) = \frac{MB_i}{1+\tau/\tau_i} + \left[Mi(0) - \frac{MB_i}{1+\tau/\tau_i} \right] \cdot e^{-t\cdot(1/\tau+1/\tau_i)} \tag{8}$$

The introduction of a finite background concentration changes the slopes β and γ considerably and the curves in general are no longer linear (see McKeen et al., 1996, for some special cases and numerical examples).

The physical model underlying diff. eqs. (3) and (7) is that of an airparcel with an initial content of species i being placed at time zero into an infinite reservoir of air with another but constant mixing ratio of species i. Both air masses are thought to be completely mixed internally and to exchange air between them at a constant rate defined by τ. The time t in eq. (8) and (1) can be replaced by a distance x, if the air parcel moves along a trajectory with the speed, v: Then $t \rightarrow x/v$. Thus, the approach can be used to follow the fate of an air parcel as it sits or moves along in a large reservoir of background air.

Eq. (8) allows to estimate the mixing time τ and the concentration of $[OH] = \tau_i^{-1} \cdot k_i^{-1}$, if the available set of hydrocarbon data meets certain requirements: Namely, a) that it contains enough clean air data to estimate the background mixing ratios; b) that the air parcels possess a range of

travel times, t, since the last contact with a source, and that t can be estimated, for example by trajectory analysis; c) that there are at least two species measured with different chemical lifetimes; d) that the airparcels encounter no source between time 0 and t.
The approach has the advantage that it is conceptually simple, that it defines useful parameters, and that it yields plausible values for [OH] and τ. McKeen et al., 1996, for example, have used it to derive [OH] and τ from hydrocarbon measurements obtained in the lowermost atmosphere during the PEM West A aircraft campaign. As these authors pointed out, however, there are disadvantages as well. One is that the variance and the errors in the estimates of [OH] and τ resulting from different pairs of hydrocarbons are large, another, that the assignment of background mixing ratios is difficult.
There is, however, also a more fundamental problem. The applicability of the model is limited to situations, where the simplifying assumptions are met by atmospheric conditions - at least approximately. On the other hand the concept of a two box model is a highly idealized description of atmospheric dilution. Thus, the scientific task is rather to demonstrate (i) where the model assumptions are met, or (ii) what systematic uncertainties are to be expected when they are met only approximately under the conditions of observations. To highlight this point we first demonstrate that the model predictions about β, γ and τ_i, depend on the model assumptions. To do so we consider two model cases where the mixing is provided by turbulent diffusion, i.e. we contrast the assumption of mixing between the required minimum of two reservoirs with the assumption of gradual mixing along a continuum of reservoirs. This also sets the stage for the later treatment including all modes of transport by a three-dimensional chemical tracer model.

3. 1-D Model

We first consider the case of one-dimensional vertical diffusion of a tracer with constant chemical lifetime, τ_i,. We assume an infinitely extended source at the surface, and zero mixing ratio at high altitudes, and a turbulent diffusion coefficient, D, which is constant with altitude. We also neglect the vertical gradient in air density, a reasonable assumption for short-lived species. The differential equation for the local material balance at steady state then is

$$\frac{\partial M_i}{\partial t} = D \cdot \frac{\partial^2 M_i}{\partial z^2} - \frac{M_i}{\tau_i} = 0 \tag{9}$$

with the solution

$$M_i(z) = M_i(0) \cdot e^{-z/\sqrt{D \cdot \tau_i}} \tag{10}$$

The mixing ratios at the surface, $M_i(0)$, can be calculated from a uniform surface flux, J,:

$$J = -D \cdot \left. \frac{\partial M_i(z)}{\partial z} \right|_{z=0} \tag{11}$$

$$= \frac{D \cdot M_i(0)}{\sqrt{D \cdot \tau_i}} \tag{12}$$

and

$$M_i(0) = J \cdot \sqrt{\frac{\tau_i}{D}} \tag{13}$$

The surface concentration scales as $\sqrt{\tau_i}$ and depends on D; the column integrated concentration, $J \cdot \tau_i$, scales as τ_i and is independent of D.
Obviously, eq. (10) does not allow the separation of the dependencies on transport and chemical destruction into two independent factors. This is a consequence of the diffusive transport term in diff. eq. (9). Other examples are the solutions of the diffusion equations for point and line sources reported by McKeen et al., 1990 (c.f. McKenna, 1997). Moreover, the chemical lifetime enters eq. (10) as $\sqrt{\tau_i}$ instead of τ_i as in eq. (1) - a consequence of the fact that diffusive transport enters as a second derivative in the local balance eq. (9). Both of these differences have consequences for the determination of [OH]. Finally, when we calculate the slope for the plot of $\ln(M_i(z))$ versus $\ln(M_j(z))$ we obtain

$$\beta' = \sqrt{\frac{\tau_j}{\tau_i}} \tag{14}$$

independent of the transport parameter, D. And the slope when plotting the ratios of the mixing ratios, $\ln(M_i/M_k)$ versus $\ln(M_j/M_k)$ becomes

$$\gamma' = \frac{\sqrt{1/\tau_i} - \sqrt{1/\tau_k}}{\sqrt{1/\tau_j} - \sqrt{1/\tau_k}} \tag{15}$$

or

$$\gamma' = \frac{\sqrt{k_i} - \sqrt{k_k}}{\sqrt{k_j} - \sqrt{k_k}} \tag{16}$$

when we replace τ_i^{-1} by $[OH] \cdot k_i$ (see above).The diffusion model also predicts straight lines for the relations of $\ln(M_i)$ versus $\ln(M_j)$ and $\ln(M_i/M_k)$ versus $\ln(M_j/M_k)$ respectively. But, when mixing is interpreted in terms of turbulent diffusion instead of exchange between two well mixed air masses, the slopes for measured hydrocarbon concentrations take on a drastically different meaning from the earlier ones from eq. (4) and eq. (5). Clearly, the predicted numerical values for the slopes β' and γ' are different as well. Interestingly, both, 3-D modeled tracers and measured hydrocarbons, show slopes, β', close to $\sqrt{\tau_j / \tau_i}$ within the PEM West domain (see Figure 6 below). Moreover γ' is close to $\frac{\sqrt{k_i} - \sqrt{k_k}}{\sqrt{k_j} - \sqrt{k_k}}$ for that domain.

4. 2-D Model

The next example approaches reality one step closer by including horizontal, meridional advection with a wind speed, v, uniform at all altitudes in addition to vertical eddy diffusion. Again we assume steady state, a constant vertical eddy diffusion coefficient, D, a constant chemical lifetime, τ_i, as well as constant air density. The resulting diff. eq. is

$$v \cdot \frac{\partial M_i(y,z)}{\partial y} = D \cdot \frac{\partial^2 M_i(y,z)}{\partial z^2} - \frac{M_i(y,z)}{\tau_i} \tag{17}$$

It is simple enough to have analytical solutions. With an initial vertical profile of $M_i(0,z) = M_i(0,0) \cdot e^{-z/\sqrt{D \cdot \tau_i}}$ (eq. (10)), and vanishing surface sources, we obtain the longitude and height dependent solution

$$M_i(y,z)=\frac{M_i(0,0)}{2}\cdot\left\{e^{-z/\sqrt{D\tau_i}}\cdot\left[1+erf\left(\frac{z\tau_i-2y\sqrt{D\tau_i}/v}{2\tau_i\sqrt{Dy/v}}\right)\right]+e^{+z/\sqrt{D\tau_i}}\cdot\left[1-erf\left(\frac{z\tau_i+2y\sqrt{D\tau_i}/v}{2\tau_i\sqrt{Dy/v}}\right)\right]\right\} \quad (18)$$

and for the surface mixing ratio

$$M_i(y,0)=M_i(0,0)\cdot\left[1-erf\left(\sqrt{y/(v\cdot\tau_i)}\right)\right] \quad (19)$$

where the error function $erf(x')=2/\sqrt{\pi}\cdot\int_0^{x'}e^{-x^2/2}dx$. Eq. (19) may be viewed as the surface distribution of a tracer in air flowing from a large polluted continent out over a large emission free ocean. It too depends on $\sqrt{\tau_i}$ rather than τ_i. Except for the initial mixing $M_i(0,0)$ (see eq.(13)), eq. (19) does not depend on D. The solution of diff. eq. (17) does, however, strongly depend on the vertical profile established over the emission region. With an initial vertical profile of constant mixing ratio the solution would have taken the form

$$M_i(y,0)=M_i(0,0)\cdot e^{-y/(v\cdot\tau_i)} \quad (20)$$

To consider a more realistic source distribution and to eliminate the influence of the initial profile diff. eq. (17) was solved numerically for an airmass circling the globe across two continents separated by two oceans. The longitudes of the continents are selected to represent the Eurasian and North American continent (and the Atlantic and Pacific Oceans) at 40° latitude. The mean wind speed, v= 8 ms^{-1}, corresponds to the climatological mean at that latitude during spring. The air mass circles the globe once in 40 days. The vertical eddy diffusion coefficient, D, is 20 m^2s^{-1}. The continents act as source with uniform surface emission rates of 10^{14} molecules $m^{-2}s^{-1}$ for each of the 3 synthetic tracers Rn5, Rn20, Rn100, with constant lifetimes, τ_i, of 5, 20, 100 days. The oceans have zero emissions (see lowest panel, Figure 1). There is no surface deposition of the tracers. Steady state was reached by allowing a spin up of 400 days corresponding to 10 cycles of the airmass around the globe. Figure 1 depicts the surface mixing ratios for each of the 3 tracers along the longitude. They exhibit some interesting features, namely: The decrease in mixing ratio, when the air moves out over the ocean, is non exponential: The rate of decrease is much faster in the first 5° of longitude downwind of the continents as evidenced by the curvature of the decay curves on a log scale. By the same token the increase when moving over the continent is much faster than the function $\left(1-e^{-t/\tau_i}\right)$. Maximum concentrations are reached at the end of the travel over the continents. Only in the case of Rn5 and the Eurasian continent the surface concentration approaches the steady state value for an infinitely extended source indicated by the dotted lines in Figure 1. For the others the lifetimes are too long compared to the travel time over the continents to reach steady state. These steady state values are proportional to $\sqrt{\tau_i}$ not τ_i (see eq. (13)). Thus the maximum values reached over the continents are also roughly proportional to $\sqrt{\tau_i}$.

The fast decay in the surface concentration, as the air moves out over the ocean can be easily understood when we remind ourselves that diff. eq. (17) can also be viewed as describing a Lagrangian air parcel - in the sense that the whole vertical column of air moves with the same speed. There is no mixing in the horizontal direction, that is, there is no mixing across the vertical boundaries of an air column. The total amount of tracer in the column decays as e^{-t/τ_i} (or since $y=v\cdot t$ *as* $e^{-y/(v\cdot\tau_i)}$), as the column moves out over the ocean and is no longer replenished from below. But there is diffusive vertical mixing and therefore vertical redistribution of the tracer. Coming from the continent, the mixing ratio in the surface layer is highest. Thus, vertical mixing

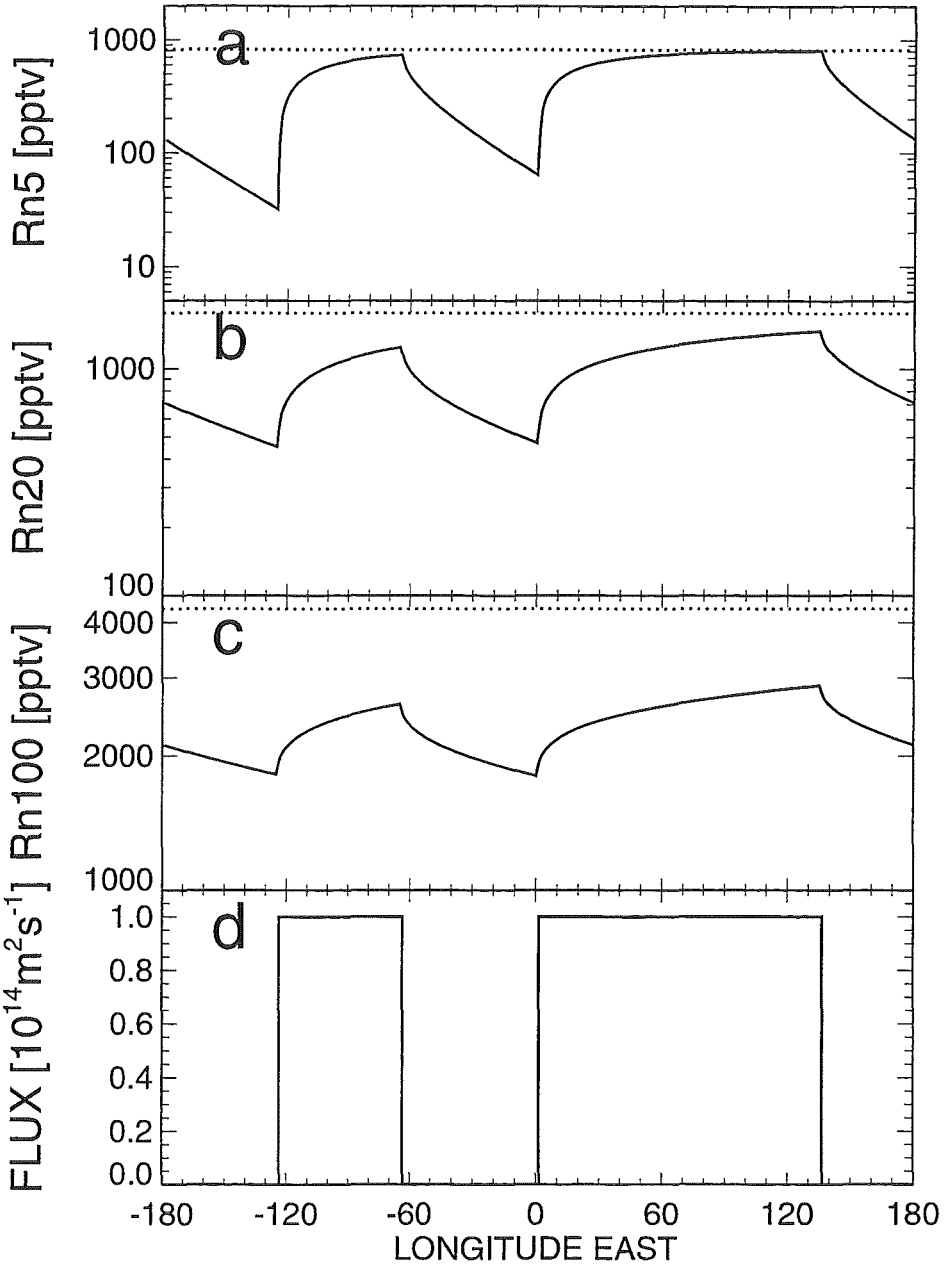

Figure 1: *Surface mixing ratios of the synthetic tracers Rn5, Rn20, and Rn100 as a function of longitude at 30°N - 40°N latitude during March calculated from a 2-D advection diffusion model. The dotted lines indicate the asymptotic mixing ratios reached after travel over a continent of infinite longitudinal extent. Panel d presents the position of the continental sources and the emission flux.*

removes tracer from the surface layer by upward transport in addition to the removal by chemical decay, and the total decrease becomes faster. Figure 2 illustrates this vertical redistribution as a sequence of Rn5 profiles spaced in steps of 1 day (691 km in length). To remove the chemical loss the actual profiles have been multiplied by e^{+t/τ_i}. Since Rn5 is relatively short lived, its vertical distribution when leaving the Eurasian continent is very close to its steady state distribution, eq. (10), as evidenced by the straight line when the mixing ratios are plotted on a log scale. Vertical transport alone reduces the surface concentration of Rn5 quite fast - a factor of 1.6 in the first day or a factor of 2.4 in the first 5 days. Consequently, vertical transport more than doubles the initial removal rate over that by chemical removal alone during the early travel over the ocean. At the same time vertical transport adds tracer to the higher altitudes, slowing the longitudinal decrease in concentration there below that expected from chemical decay alone. The compensation point of zero change varies with time; after the first five days it is at 3 km altitude. As a consequence of the vertical redistribution the vertical gradient decreases with the time and with it the rate of tracer removal from the surface layer by vertical transport. From day 25 to day 30 the surface concentration is reduced only from 240 to 220 pptv by vertical transport, i.e., by a factor of 1.1 over 5 days. Thereafter removal by transport becomes nearly negligible. However, over the finite oceans, see Figure 1, which are crossed in at most 11 days, vertical transport will always make significant contribution to the change in surface concentration even for Rn5. Figures 1 and 2 demonstrate quite clearly that the rate of dilution is not constant in time or space, as is assumed in eq. (1) and (8). It changes considerably not only over large distances, but also over short intervals when leaving the coast, i.e., the surface source. Moreover, it is important to note, that the rate of dilution depends on the vertical gradients which are a function of both chemistry and transport (see eq. (10)). Thus, dilution depends on the rate of chemical tracer destruction.

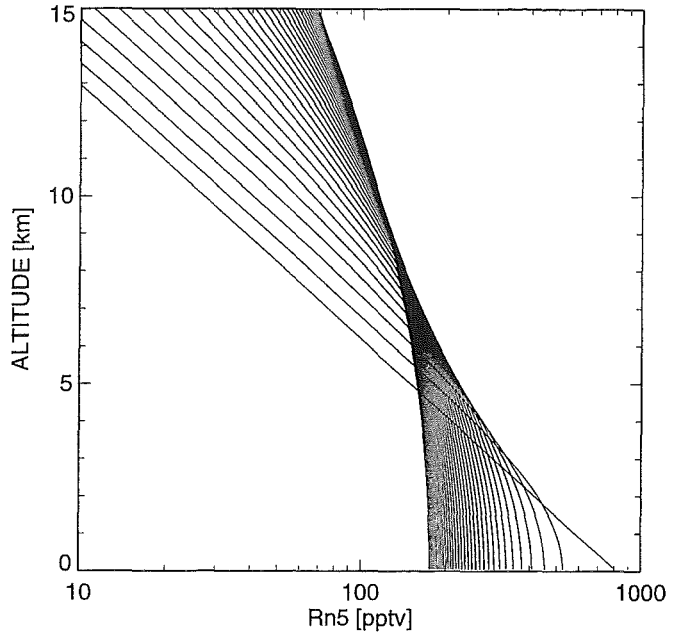

Figure 2: *Temporal redistribution of the vertical Rn5 mixing ratio after leaving the Eurasian continent, and moving over an infinite ocean. The profiles present the effect of vertical transport only (see text), and are given in time steps of 1 day beginning with the profile of the highest surface value.*

In the later analysis of tracer concentration ratios from the 3D model calculations we will utilize the slope, β, from plots of ln (Rn_i) vs ln (Rn_j). It should, therefore, be instructive to look at such plots for the Rn concentrations generated by the 2-D diffusion model. Figure 3 presents the results. It shows the slope $\ln(Rn_i)/\ln(Rn_j)$ calculated for a 10° longitude running interval - with Rn_j being the longer lived of the two tracers. A 10° longitude interval averages also over the discontinuities in slope at the coasts (see Figure 1). This generates distortions. Therefore, the portions of the curves placed at ±10° longitude around the coasts are disregarded.
As Figure 3 indicates β is reset to a value approximating $\sqrt{\tau_j / \tau_i}$ every time the airmass crosses the up- or downwind coasts of the continent. Over the continents β then decreases asymptotically towards zero. This is due to the fact that the shorter lived tracer approaches steady state faster, while the concentration of the longer lived tracer is still increasing (see Figure 1). Over the ocean β increases and would eventually reach a value τ_j/τ_i, but given the lifetimes considered here and the air mass travel time of at most 11 days over the ocean that value is not reached. Thus, the possible total range for β, 0 to τ_j/τ_i, is not assumed for the lifetimes and latitude considered in the 2 D diffusion model. Because β is reset to a value $\sqrt{\tau_j / \tau_i}$ at every transition of the airmass of the continental margins the range is significantly reduced. The exact reduction factor depends on the pair considered: for Rn20 and Rn100 the range is 1.3 to 3 instead of 0 to 5. A more structured distribution of emissions than that used here, which would cause more frequent resetting, would lead to an even narrower range in β.

5. 3-D Model

5.1. Model Description

The chemical tracer model, CTM, solves the continuity equations for a set of chemically reactive tracers over a global three-dimensional grid. The CTM is adopted from Prather et al. [1987]. In the present study the horizontal extension of a grid box is 8° in latitude and 10° in longitude. The atmosphere between the earth's surface and 10 hPa is divided into nine terrain following sigma layers on average centered at the pressure levels of 959, 894, 787, 635, 470, 322, 202, 110, and 40 hPa. The CTM uses a split-operator method to compute the separate effects of advection, dry and wet convection, large-scale diffusion, sources, and chemistry. The three processes of dynamical tracer redistribution are calculated with an 8-hour time step, while the time-step for sources and chemistry is one hour. The advective transport of tracer is upstream conserving the second-order moments of the tracer distribution [Prather, 1986]. The meteorological data which are used as input for the CTM are provided by the GISS general circulation model II [Hansen et al., 1983]. This data set contains 8-hour averages of mass flux, pressure fields, and convection frequencies as well as 5-day averages of temperature and detailed convection statistics for one year.
The three above mentioned tracers are also introduced into the 3-D model. These tracers have constant lifetimes of 5, 20, and 100 days, respectively, throughout the atmosphere and all seasons. Their source distribution is very simple: a uniform flux of 10^{14} molecules $m^{-2}s^{-1}$ over all land areas north of 60° S for all three tracers, and zero emissions elsewhere, in particular over the ocean. The emissions from coastal surface grid boxes are scaled to the proportion of land contained therein. Thus, the tracers behave like the radioactive noble gas Radon, which is the reason for calling them Rn5, Rn20 and Rn100, respectively. Radon has a lifetime of 5.5 days and essentially continental (though much smaller) sources. In first approximation the tracers also behave like the alkanes, butane, propane, ethane, which have also essentially continental (but not uniform) sources and comparable (but not constant) chemical lifetimes in the atmosphere. The fluxes mentioned above were selected to approximately match the global emission rate of ethane

[c.f. Rudolph, 1995] and amount to $7.1 \cdot 10^{11}$ moles/year. The model was run for one full year to reach steady state and was sampled the second year for the tracer distributions.

5.2 3-D Model Results

To build on our insights gained from the 2-D advection diffusion model we first consider the average surface concentrations generated by the 3-D model for the 32° N - 40° N latitude belt during March (Figure 4). This latitude and month were chosen for the eventual comparison of the 3-D model results with the hydrocarbon distribution observed during the PEM West B campaign. The continents are placed at approximately the same longitudes as in the 2-D case although the source distribution in the 3-D model (lowest Panel on Figure 4) is more highly resolved and due to the varying coastline more structured.

Just like the surface mixing ratios from the 2-D advection diffusion model the longitudinal distributions from the 3-D CTM show high values over the continents and low ones over the oceans. The maximum concentrations over the continents are slightly higher in the 3-D case, but also scale like the square root of the tracer lifetime. However, in the 3-D model the distributions over the continents (and correspondingly over the oceans) are much more symmetrical: when averaged over a month the changing wind patterns provide strong horizontal mixing which erodes the continental distribution from both ends, an effect, which is missing in the 2-D model. Despite the diffusive horizontal mixing, the concentrations over the remote oceans are significantly lower than in the 2-D case, indicating that in the 3-D case the air remains longer over the ocean. For each of the three tracers much of the horizontal gradients is concentrated in the coastal zones (about ±20° longitude with respect to the coast). This leaves a slightly ramped concentration plateau over the Eurasian continent and broad minima over the oceans, which divides surface air roughly into three categories: polluted continental air, background oceanic air, and air in the coastal transition zones.

Figure 5, which presents the corresponding slope β, shows also considerable deviations from the 2-D case. First, in the 3-D case β does not approach zero as was observed in the 2-D case over the large Eurasian continent; instead it hardly dips below 1. Second, its range is also significantly reduced with respect to the upper bound. At continental longitudes it varies between 1 and $\sqrt{\tau_j / \tau_i}$; the latter is indicated by the upper dotted line in the panels of Figure 5. Nevertheless, as in the 2-D case β is lower over the continents and higher over the oceans, where it clearly exceeds $\sqrt{\tau_j / \tau_i}$ The major gradients in β are located at the coastlines.

The numerical value of β tells us how important removal by mixing is with respect to chemical decay. A value of 1 indicates that the respective Rn concentrations correlate linearly.

This means that their concentrations change at exactly the same rate and thus that their removal from surface air is essentially due to mixing, which acts on both tracers at the same rate. In the 3-D case this mixing in the continental near surface air is essentially caused by the diurnal change in altitude of the boundary layer. At $\beta = \sqrt{\tau_j / \tau_i}$ transport and chemical removal act at about the same rate, as indicated by diff. eq. (4) for the 1-D diffusion, where transport by diffusion and chemical decay act on the tracer concentrations with the same rates as long as the system is in steady state. For $\beta > \sqrt{\tau_j / \tau_i}$ chemical decay is mostly responsible for local tracer removal.

The strong change of β in Figure 5 indicates that the plot of ln (Rn_i) versus ln (Rn_j) must be curved for concentrations sampled near the coastline. As Figure 6 shows this is indeed the case. Over the continental sources, high mixing ratios prevail with a slope β close to 1. So the upper parts of the correlation curves in Figure 6 have tangents of slope 1. Since the range of concentrations over the continent is limited that part of the curve is short.

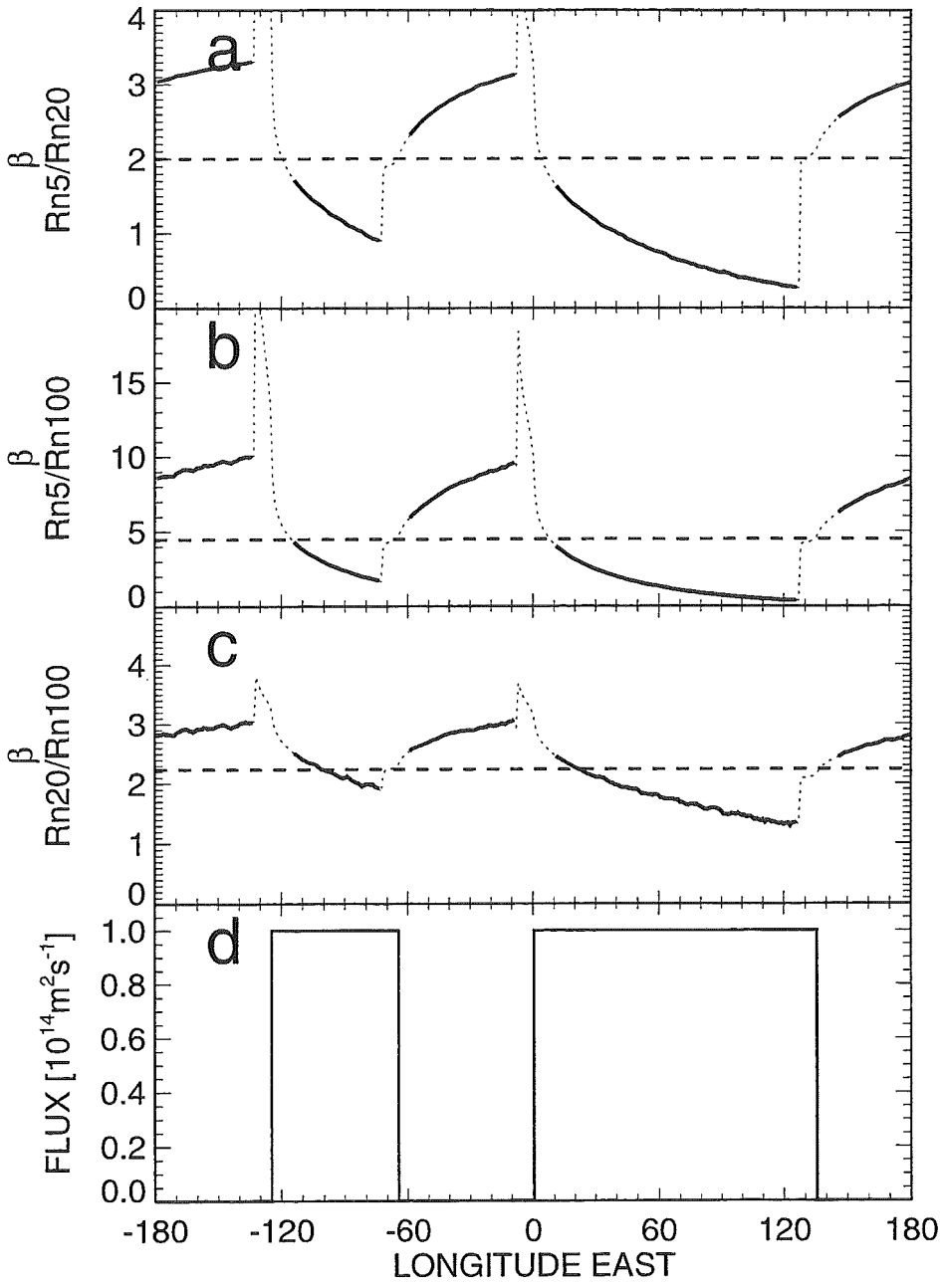

Figure 3: *Slope β for the three possible pairs of the Rn tracers as a function of longitude at 30°N - 40°N latitude during March calculated with a 2-D advection-diffusion model. The dashed lines represent* τ_j / τ_i *and* $\sqrt{\tau_j / \tau_i}$ *respectively with* τ_j *the lifetime of the longer lived tracer of the pair. Panel d indicates the position of the continents.*

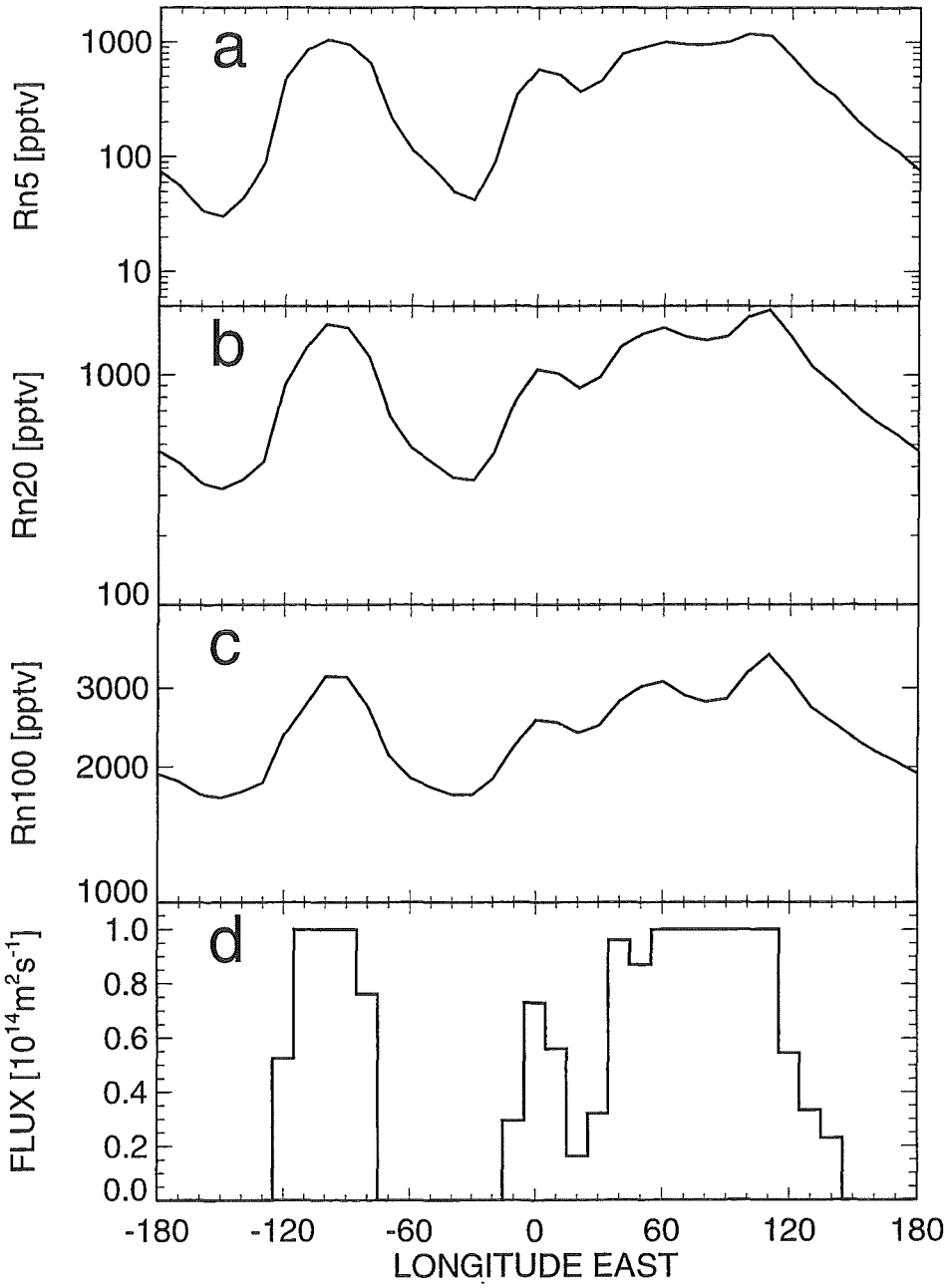

Figure 4: *Surface mixing ratios of the synthetic tracers Rn5, Rn20, Rn100 as a function of longitude at 32°N - 40°N latitude during March calculated from the 3-D chemical tracer model. Panel d presents the continental emission fluxes in that latitude band.*

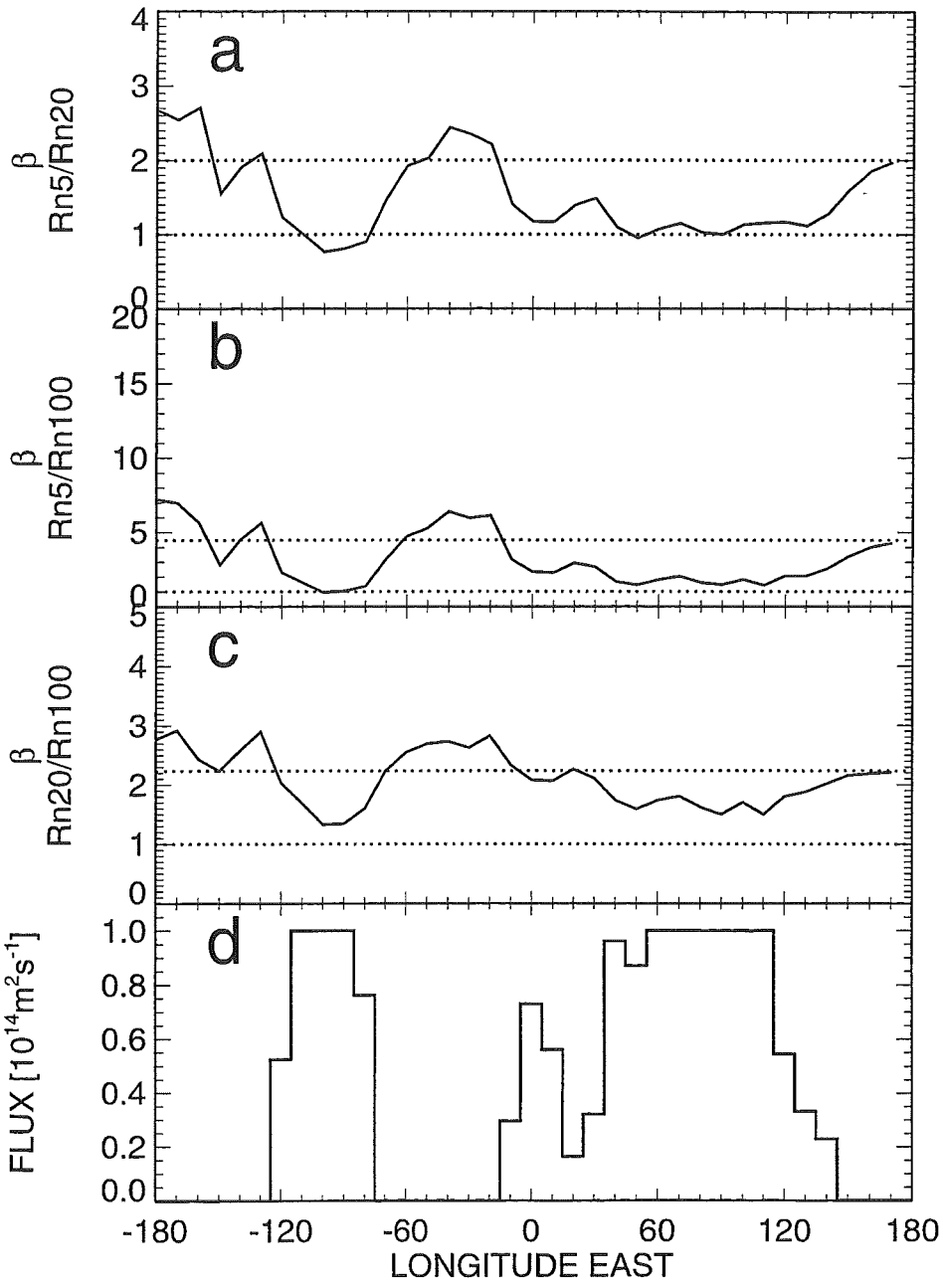

Figure 5: *Slope β for the three possible tracer combinations as a function of longitude at 32°N - 40°N latitude, and the surface (0-0.4 km) during March calculated from the 3-D chemical tracer model. The dotted lines mark β values of 1 and* $\sqrt{\tau_j / \tau_i}$. *The lines for* τ_j / τ_i *coincide with the abscissas above. Panel d indicates the continental emission fluxes.*

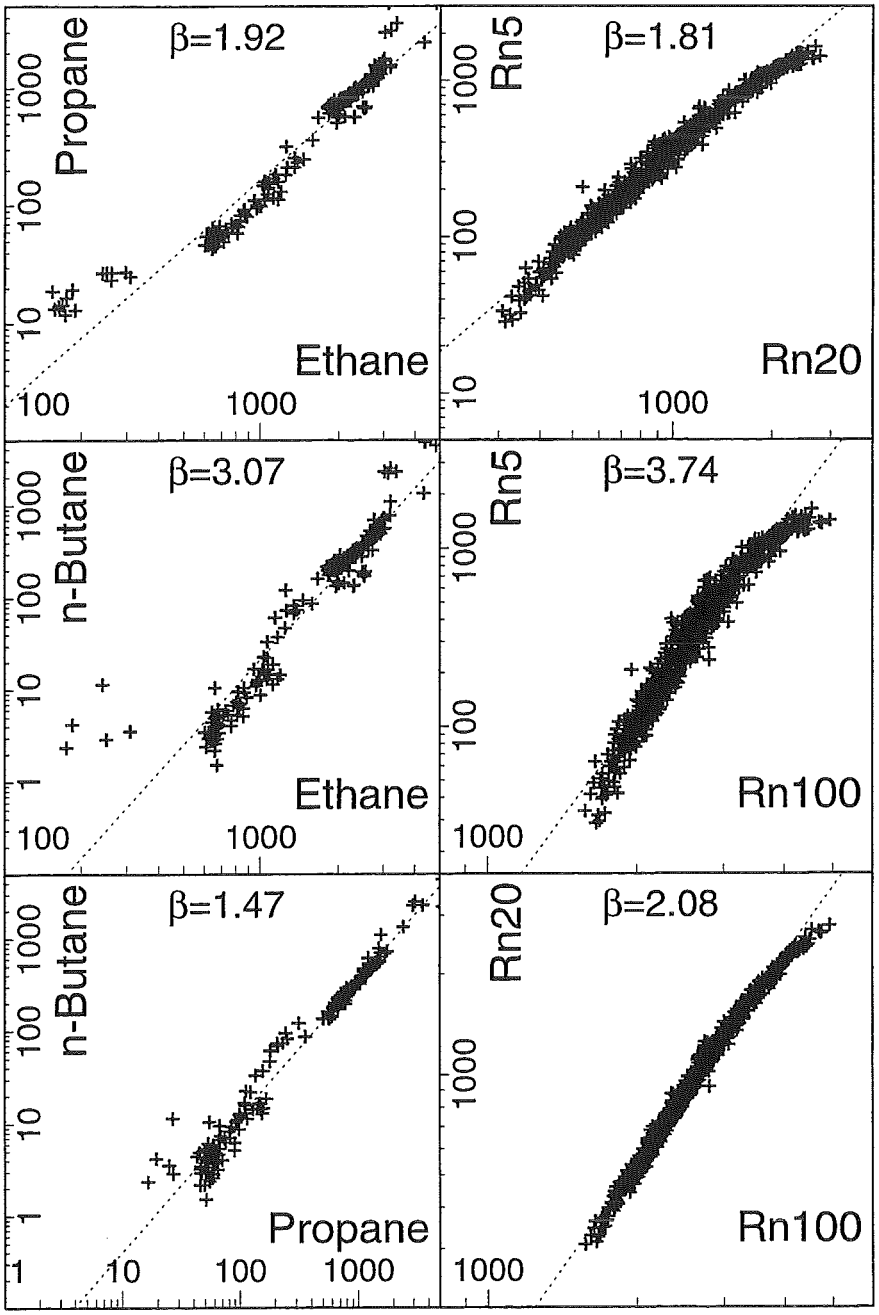

Figure 6: *Correlations between the measured surface (0-1 km) mixing ratios of ethane, propane, and n-butane in the domain 30°N - 50°N latitude, 115°E - 155°E longitude during PEM West B (left column) and those calculated by the 3-D CTM for the synthetic tracers in the same domain, but 0-0.4 km altitude during March (right column). The dashed lines represent a linear fit to all data. Their slopes, β, are indicated in the panels.*

The middle part of the curve covers the transition zone where most of the decrease in concentration occurs; in that part the slope $\beta \approx \sqrt{\tau_j / \tau_i}$,. Because the transition zone has the largest range of concentrations, that part of the correlation curve is relatively long. Over the remote ocean the concentration range becomes narrow again and approaches the slope $\beta \approx \tau_j / \tau_i$. That range forms the bottom part of the curve. An attempt of fitting linear regression lines to the full data ensembles is indicated by the dashed lines. The resulting slopes are close to $\sqrt{\tau_j / \tau_i}$. The lifetimes for the hydrocarbons are listed in Table 2 below. Incidentally, the slopes γ for the same data sets are 1.76 for the alkanes and 2.6 for the Rns in good agreement with the values $\frac{\sqrt{k_{nB}} - \sqrt{k_E}}{\sqrt{k_P} - \sqrt{k_E}} = 1.91$ and $\frac{\sqrt{1/\tau_{Rn5}} - \sqrt{1/\tau_{Rn100}}}{\sqrt{1/\tau_{Rn20}} - \sqrt{1/\tau_{Rn100}}} = 2.81$ expected from eq.(16) and (15).

The slopes β depend strongly on the absolute values of the tracer lifetimes which makes the direct comparison between the β from different tracer pairs difficult. To remove most of that dependency we normalize β to the ratio of the lifetimes by introducing

$$\alpha_{ij} = \ln(\beta_{ij}) / \ln(\tau_j / \tau_i) \tag{21}$$

or equivalently

$$\beta_{ij} = (\tau_j / \tau_i)^{\alpha_{ij}} \tag{22}$$

We note that a slope $\beta_{ij} = 1$ transforms into a $\alpha_{ij} = 0; \beta_{ij} = \sqrt{\tau_j / \tau_i}$ .into a $\alpha_{ij} = 1/2$ and $\beta_{ij} = \tau_j / \tau_i$ into $\alpha_{ij} = 1$ regardless of the pair of τ_j / τ_i.

5.3 The dependence of α on the chemical lifetimes

Already the comparison between the slopes β in Figure 5 indicate that α not only depends on the geographical location but that the local α_i must also depend on the chemical lifetimes of the two tracers considered. To investigate this point more closely, we consider the α within the area 32° - 40°N latitude and 125° - 145°E, i.e., an area comprising 2 grid boxes in our 3-D CTM. It was also sampled during both the PEM West A and B campaigns. The α for the various pairs of synthetic tracers are listed in Table 1. They refer to the month of March and include also the tracers Rn1, Rn2, Rn50 with lifetimes of 1, 2 and 50 days respectively, in addition to those already mentioned.

Table 1. *Values of $\alpha_{ij} = \ln(\beta_{ij}) / \ln(\tau_j / \tau_i)$ for all possible pairs of synthetic tracers Rni, Rnj in the domain of 32° - 40°N latitude, 125°S - 145°E longitude, and the month of March. j denotes the longer lived tracer.*

τ_j	τ_i					
	100	50	20	5	2	1
100		0.50	0.46	0.37	0.33	0.31
50			0.41	0.33	0.29	0.26
20				0.25	0.21	0.17
5					0.084	0.03
2						-0.05
1						

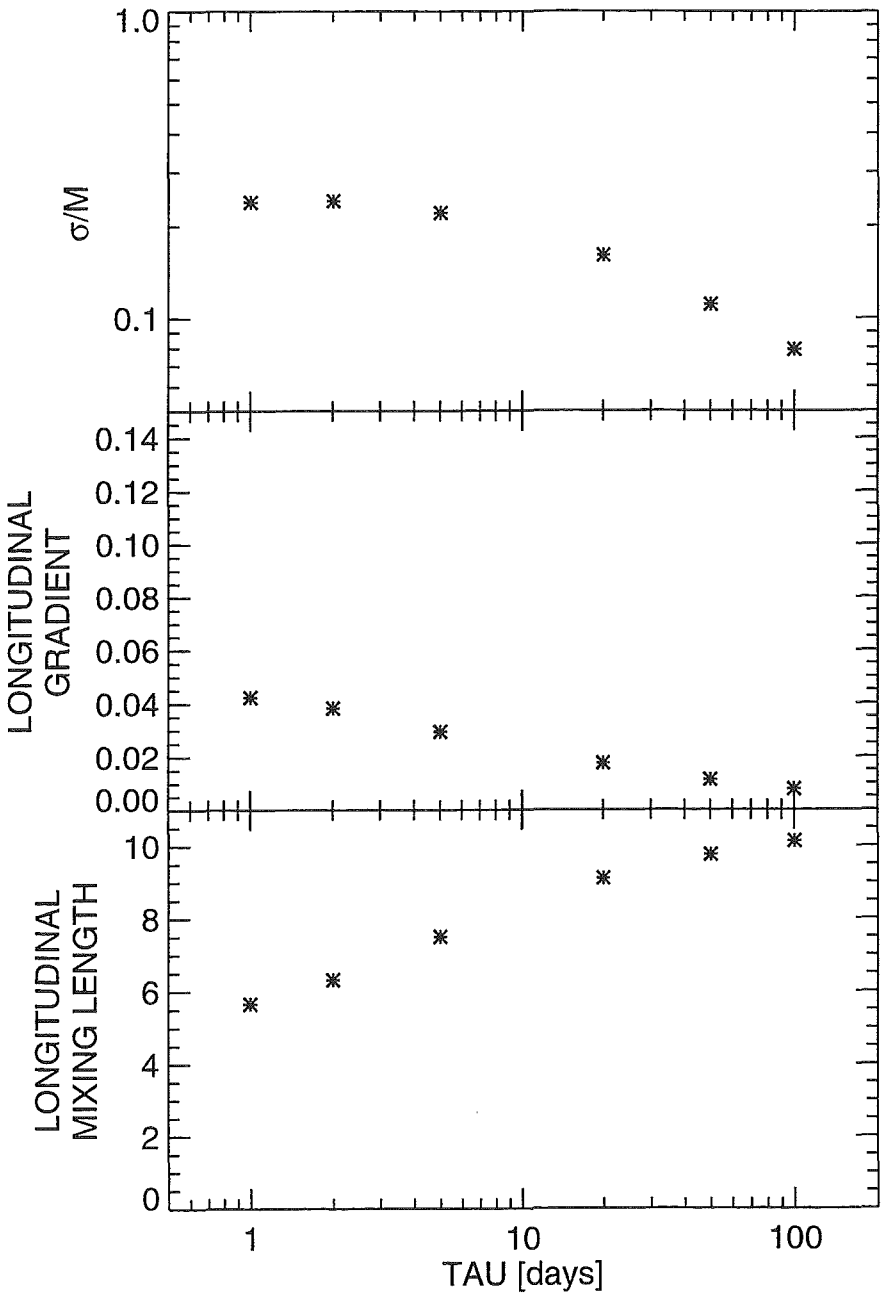

Figure 7a: *Average relative standard deviation of the synthetic tracers, relative longitudinal gradient (unit: Degree^{-1}) and longitudinal mixing length (in degree longitude) as a function of the lifetime τ for the domain 32°N - 40°N latitude, 125°E - 145°E longitude, surface, during March.*

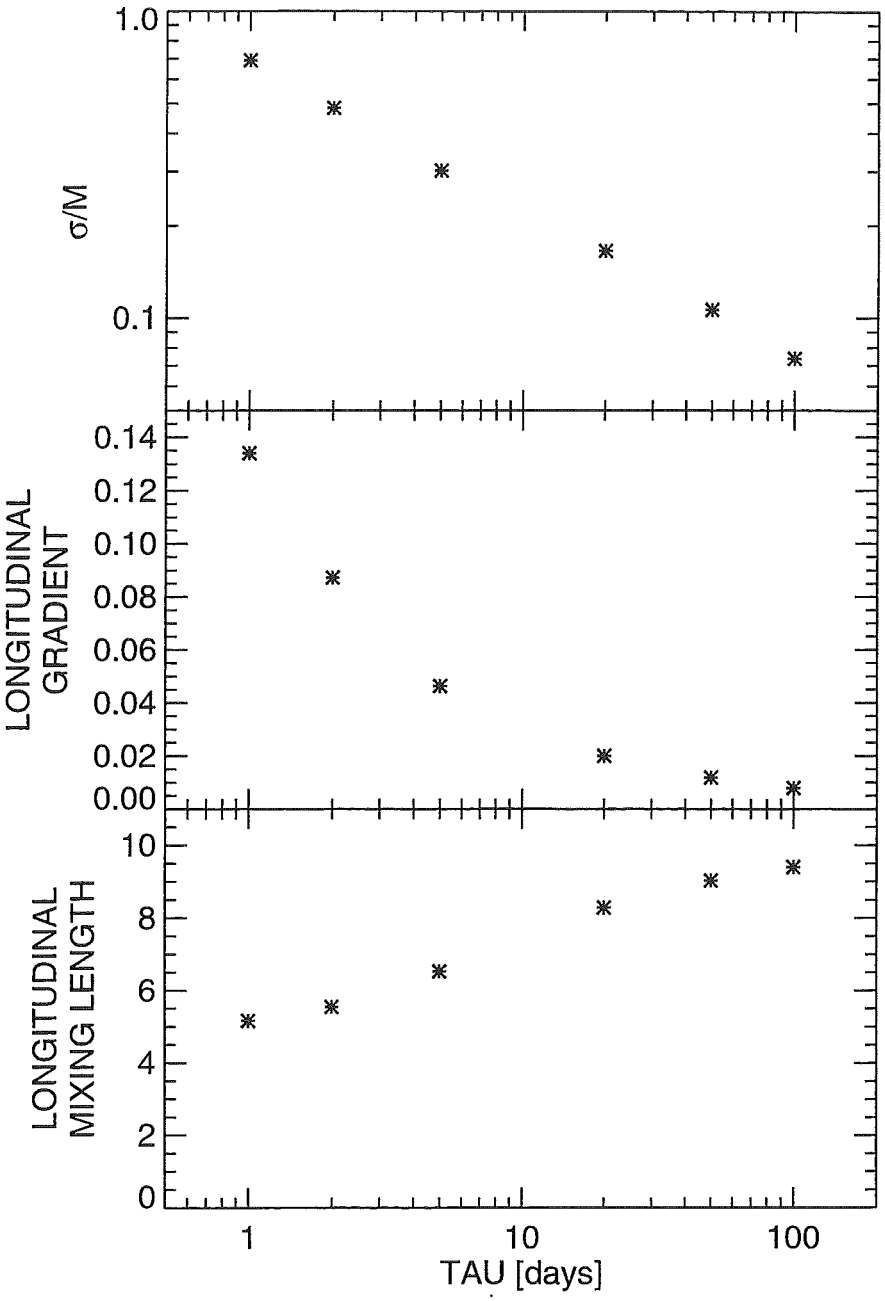

Figure 7b: *Average relative standard deviation of the synthetic tracers, relative longitudinal gradient (unit: Degree^{-1}) and longitudinal mixing length (in degree longitude) as a function of the lifetime τ for the domain 32°N - 40°N latitude, 135°E - 155°E longitude, surface, during March.*

Table 1 clearly demonstrates that the α_{ij} depend on the lifetimes of the tracers in a systematic way. The reasons for this systematic dependence become clearer when we consider the slope β in Figure 6. It is essentially given by the range of the values of $\ln(Rn_i)$ divided by the range of the values of $\ln(Rn_j)$. That range can also be characterized by the standard deviation of the Rn_i and Rn_j concentrations, σ_i and σ_j. For easier comparison we use the relative standard deviation, $\sigma_i / \overline{M}_i$, where $\overline{M}_i$ represents the mean of the Rn_i concentration in the domain, and investigate its variation with $\ln(\tau_i)$ (Figure 7a). Clearly, there is a pronounced and systematic dependence of $\sigma_i / \overline{M}_i$ on the chemical lifetime, τ_i. This dependence is related to that of α in the following manner: A straight line connecting any pair of data points in Figure 10a with τ_i and τ_j has the slope α_{ij} given in Table 1 - in close approximation. Thus, once it has been established that $\ln(M_i)$ and $\ln(M_j)$ correlate linearly, Figure 7a provides a more condensed representation of the information in Table 1. Figure 7a can also be interpreted more readily. In terms of the mixing length hypothesis, $\sigma_i / \overline{M}_i$ is given by

$$\sigma_i / \overline{M}_i = l_i \cdot \frac{\nabla M_i}{\overline{M}_i} \tag{23}$$

where l_i is the mixing length and $\frac{\nabla M_i}{\overline{M}_i}$ is the mean logarithmic gradient of Rn_i. Both depend on τ_i, but generally in opposite ways, which can generate a nonlinear behavior in $\sigma_i / \overline{M}_i$ such as that observed in Figure 7a. To illustrate that fact, the model derived longitudinal gradient, $\frac{\partial M_i / \partial y}{\overline{M}_i}$, which is the major component of the gradient, and the corresponding $l_i = \sigma_i / \frac{\partial M_i}{\overline{M}_i \cdot \partial y}$ are also shown in Figure 7a as function of τ_i. The dependency of the former is quite plausible: a tracer with a shorter lifetime will decay more rapidly with time and thus with distance from the source, and therefore exhibit steeper relative gradients. We note, however, that the region represented by Figure 7a does contain sources. Their longitudinal gradient, which is depicted in Figure 5, also acts on the concentration gradient, and may modify its dependence on τ_i. A similar argument holds for the mixing length. Because of decay, the concentration an air parcel carries upon arrival at the point of observation corresponds to that of a location nearer than its origin. Consequently the effective displacement length becomes smaller with shorter τ_i.

Since horizontal gradient and mixing length depend on the wind field, both vary in time and space and with them $\sigma_i / \overline{M}_i$. For example, the monthly average dependence of $\ln(\sigma_i / \overline{M}_i)$ on $\ln(\tau_i)$ at the same location but for September is stronger by about 50 % but has the same functional form. Locations further removed from the sources even show a different functional form. For example at 3 km altitude over the same area, and at the surface at 165° - 175°E longitude, 32° - 40°N latitude, $\ln(\sigma_i / \overline{M}_i)$ decreases nearly linearly with $\ln(\tau_i)$. More important, between 135° and 155°E, 32° - 40°N, the area with the highest density of surface samples during PEM West B, the modeled $\ln(\sigma_i / \overline{M}_i)$ over $\ln(\tau_i)$ shows an almost perfect linear relation (Figure 7b). The slope is - 0.48 ± 0.01. It appears that at a given time interval and location the modeled $\sigma_i / \overline{M}_i$ exhibits a unique relationship with τ_i. Thus, within the model framework the function $\sigma_i / \overline{M}_i$ (τ_i) can be used to determine the unknown lifetime τ_x of a tracer for which $\sigma_x / \overline{M}_x$ is known.

Obviously a plot of the relative gradient, $\frac{\partial M_i}{\overline{M}_i \cdot \partial y}$, versus $\ln(\tau_i)$, would serve the same purpose even better, because it is a monotonic function and would always yield a single value of τ_x for a given local value $\sigma_x / \overline{M}_x$ rather than two as in the first example. But the determination of a gradient requires sufficient data in at least two locations. These are often lacking when working

with experimental data. Thus we prefer to work with $\sigma_i / \overline{M}_i$, especially since for many experimental examples, the curve $\ln(\sigma_i / \overline{M}_i)$ over $\ln(\tau_i)$ is linear or at least monotonic (see below). It should be noted that Junge (1974) proposed a related approach. For globally averaged quantities he derived the relation

$$\sigma_i / \overline{M}_i = \alpha \cdot \tau_i^{-b} \tag{24}$$

where the symbols $\sigma_i, \overline{M}_i, \tau_i$, have the same meaning as before, and $\alpha = 2.16\ 10^{-2}$, when τ is given in years, b = 0.95, i.e. close to 1. The constant b is equivalent to our α. Clearly our regional analysis (see Figure 7a) can lead to a more complicated dependence of $\sigma_i / \overline{M}_i$ on τ_i than described by eq. (24). Moreover, even when we obtain a regional solution in the form of eq. (24) then the exponent b differs considerably from a value of 1. In the case of Figure 7b it has a value of 0.48, i.e. $\sigma_i / \overline{M}_i$ is very close to a square root dependence on τ_i.

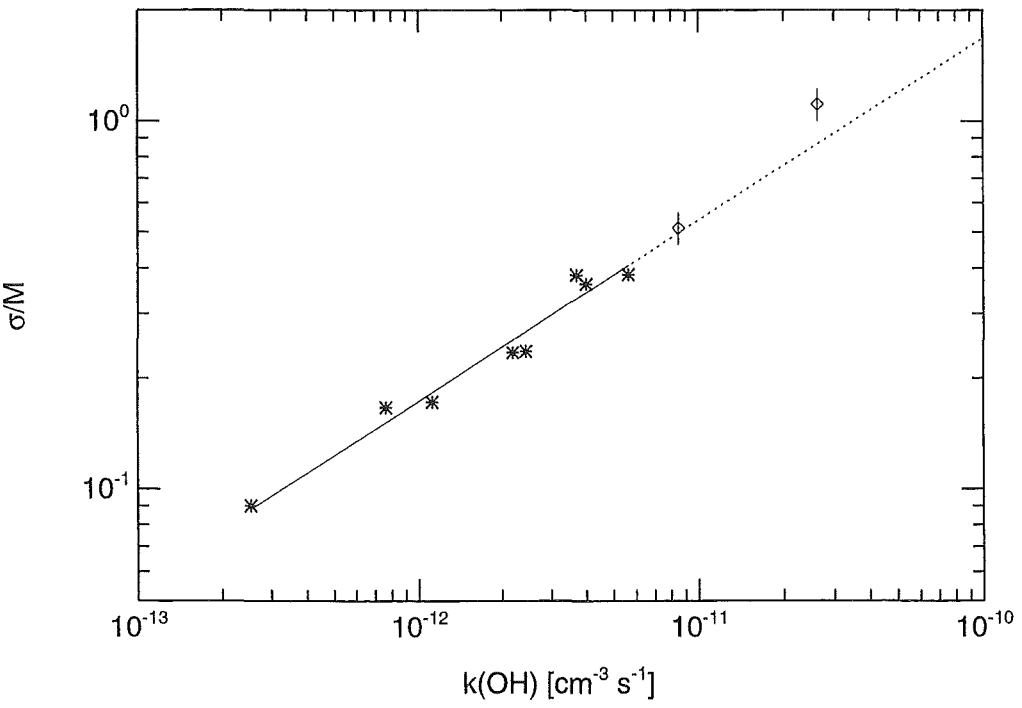

Figure 8
Average relative standard deviation of the hydrocarbons measured during PEM West B in the domain 30°N - 40°N latitude, 135°E - 155°E longitude, surface (0-1 km) as a function of their reaction rate constant, k_{OH}, with OH. The rate constants are given in Table 2. Triangles symbolize the alkenes, the crosses ethyne and the alkanes. The straight line represents a linear fit to the latter.

Table 2 Hydrocarbon species used in Figure 8 together with their rate constants, k_{OH}, for reaction with OH at room temperature (Atkinson, 1997), and an approximate lifetime against reaction with OH assuming an average OH concentration of 10^6 cm^{-3}.

Species	$k_{i,OH}$(298K) $10^{12}cm^3s^{-1}$	τ_i days
Ethane	0.254	46
Ethyne	0.767	15
Propane	1.12	10
i-Butane	2.19	5.3
n-Butane	2.44	4.7
i-Pentane	3.7	3.1
n-Pentane	4.0	2.9
n-Hexane	5.45	2.1
Ethene	8.52	1.4
Propene	26.3	0.44

Ethene and Propene react also with O_3; the rate constants at 298K are $1.59 \cdot 10^{-18}$ and $1.01 \cdot 10^{-17}$ cm^3s^{-1} respectively.

6. Application to PEM West B data

We will now try to apply the same principle to some of the experimental data from PEM West B. For that purpose we select the measurements of the hydrocarbons listed in Table 2 in the area 30° - 40°N latitude, 134.8° - 155°E longitude near the surface (0-1 km altitude). Excluding 6 highly polluted samples near Tokyo Airport our data set consist of 49 samples each with significant concentrations for each of the listed hydrocarbons. The relative standard deviation, $\sigma_i / \overline{M}_i$, of these hydrocarbons is plotted against their rate constant, $k_{i,OH}$, in Figure 8. In the logarithmic presentation of Figure 8 the data points for ethyne and the alkanes fall essentially on a straight line. The full curve is a least squares fit to these points. For these gases, which react exclusively or very nearly so with OH, Figure 8 also represents a plot of $\sigma_i / \overline{M}_i$ against the lifetime since $\log(\tau_i) = -\log(k_{i,OH}) - \log([OH])$, where $\log([OH])$ = const. merely provides an offset. Clearly, the experimental $\sigma_i / \overline{M}_i$ also exhibit a unique relationship with $k_{i,OH}$ and τ_i. Because $\log(\sigma_i / \overline{M}_i)$ over $\log(\tau_i)$ also forms a straight line, the exponent α as defined in eq. (15) assumes the same value for all pairs of hydrocarbons. $\alpha = 0.49 \pm 0.03$ and is identical with the slope of the full line in Figure 8. Unfortunately, because of the common and unknown factor [OH] the τ_i cannot be determined from this relationship alone. Additional information is needed, preferably in the form of simultaneous concentration measurements of a tracer with a known lifetime.

Natural ^{222}Rn with a radioactive decay time $\tau = 5.5$ days provides such a tracer. It has the added advantage that like the alkanes it has essentially continental sources, and thus we may assume a similar source distribution at least on a large scale. Knowing $\sigma_{Rn} / \overline{M}_{Rn}$ and using the fitted line one could assign a fictitious rate constant $k_{Rn,OH}$ to the Rn data point and from it calculate [OH]:

$$[OH] = \tau_{RN}^{-1} \cdot k_{Rn,OH}^{-1} \tag{25}$$

Unfortunately such Rn data are currently not available for PEM West B. Nonetheless, the combination of ^{222}Rn with hydrocarbon measurements appears to hold promise as a tool for deriving OH concentrations in future campaigns in similar geographic locations.

A presently workable approach to derive [OH] from $\sigma_i / \overline{M}_i$ is to include a trace gas whose lifetime depends partly on the reaction with ozone, such as the alkenes, ethene and propene which react with O_3 as well as OH, and which also have been measured during PEM West B. In analogy to the procedure for ^{222}Rn we first assign fictitious rate constants, k'_E, k'_P to ethene and propene pretending that the alkenes react only with OH. The values of these are read from the fitted straight line in Figure 8 at $\sigma_E / \overline{M}_E$, $\sigma_P / \overline{M}_P$. We then relate the fictitious reaction rate with OH, to the correct rate, which includes the reaction with O_3, e.g.

$$k'_E \cdot [OH] = k_{E,OH} \cdot [OH] + k_{E,O_3} \cdot [O_3] = \tau_E^{-1} \tag{26}$$

and deduce

$$[OH] = \frac{k_{E,O_3}}{k'_E - k_{E,OH}} \cdot [O_3] \tag{27}$$

With the rate constants given in Table 2, an O_3 concentration of 40 ppbv, and the fictitious rate constants $k'_E = \left(9.05^{+1.91}_{-1.73}\right) \cdot 10^{-12} cm^3 s^{-1}$ and $k'_P = \left(4.33^{+0.92}_{-0.82}\right) \cdot 10^{-11} cm^3 s^{-1}$ we derive the OH concentrations $3 \cdot 10^6$ cm^{-3} and $6 \cdot 10^5$ cm^{-3} respectively. We note, however, that the errors of these estimated OH concentrations are large, owing to the large errors in k'. These were obtained from the errors in $\sigma_E / \overline{M}_E$ and $\sigma_P / \overline{M}_P$ given in Figure 8, which in turn were estimated from the standard deviation of the alkane data from the fitted straight line. The error in the slope of the straight line contributes little to the total error. For the [OH] value derived from ethene the lower 1σ error bound is $6.5 \cdot 10^5$ cm^{-3}, the upper is ∞ (the nominal value is in fact negative). Thus ethene provides only a lower bound of $6.5 \cdot 10^5$ cm^{-3} for the expected [OH]. The errors for propene are less severe owing to the larger contribution of O_3 to the lifetime and thus a larger difference k'_P - $k_{OH,P}$ in the denominator of eq. (22). There the 1σ errors are $^{(+5.6)}_{(-2.0)} \cdot 10^5 cm^{-3}$. Thus propene does allow a significant estimate of the diurnally averaged [OH]. It is within the range theoretically expected for 35°N latitude and early March.

7. Conclusion and Summary

In the foregoing approach we essentially used measured data and empirical relations between the data. We tried to minimize the use of additional information or model assumptions in the hope to keep the systematic errors small. Thus, there is no need to postulate a mixing mechanism, nor to guess the background concentrations, as would be required for the traditional approach that leads to solutions (1) and (8) described above. This also reduces the possibility of systematic errors in the derived [OH] which are introduced by these assumptions. Nevertheless we had to make some assumptions. To derive the fictitious k' we had to assume that the straight line fitted to the alkane data extrapolated linearly to the larger k_{OH} (or shorter τ). As we showed for the modeled results, this does not need to be the case. However, the model data for the same area and month do yield an almost perfect linear relation between $\ln(\sigma_i / \overline{M}_i)$ and $\ln(\tau_i)$.

Moreover, the measured hydrocarbon data including the ethene and propene ones - the latter together with a reasonable assumption about the possible contribution from the reaction with O_3 to their lifetime - fall on a straight line. So we do not expect a large systematic error from that side. The other assumption is that of equal source distributions for the hydrocarbons. This is not strictly true, even if we assume the same continental source distributions for the considered hydrocarbons. The oceans are a minor but not negligible source of alkenes. This is much less so for the alkanes. Thus, the respective source distributions are not exactly the same, which might

become significant for samples taken over the remote ocean, where the oceanic source would tend to prevent very low values of the alkenes and thus reduce the variance in their concentration. This in turn would result in smaller fictitious rate constants and thus higher estimates in [OH]. Since the locations sampled here are sufficiently close to the very strong continental sources, we would expect their influence to dominate the variances observed and thus little influence from the oceanic source.

A similar effect can be caused by a possible contamination of the samples by alkenes generated at the walls of the sample flasks, a problem which has plagued early alkene measurements. From the linear correlations of the log of the ethene and propene mixing ratios against the alkanes it appears that this was not a source of concern for the present data. Nevertheless, generally speaking, the proposed new approaches to the estimate of the OH concentration from hydrocarbon measurements have their own sources of error and one has to scrutinize the available hydrocarbon data for any sign of natural or instrumental contamination, before utilizing them in a OH determination. This, however, is feasible again by correlation plots of the alkene and alkene/alkane mixing ratios. Since the assumption needed for the present approach are fewer and partly different than those needed for the traditional approach, it would be interesting to apply both techniques to the same data set. It would allow some insight in the magnitude of the so far unknown systematic errors introduced by the different assumptions of the various approaches. Since the latter also requires the knowledge of the average travel time from the coast to the point of observation as derived from trajectory analyses for example, which are at present not available to us, this remains a future task.

We investigated the average near surface distribution of trace gases with the same emission patterns but different atmospheric lifetimes. We showed that in the presence of diffusive mixing the rate of dilution depends on the chemical lifetime of the gas. In the 1-D and 2-D cases studied this dependence is explicit in the analytical solutions presented; in the 3-D case provided by a chemical tracer model this is shown implicitly by the fact that the horizontal mixing length depends on τ_i, which in turn will influence the rate of horizontal eddy diffusion.

This finding has several implications. First, for the cases studied the function describing the spatial and temporal distributions of the trace gases cannot be separated into two factors - one describing transport, the other describing the chemical loss. Second, it changes the interpretation of the slopes in the correlations of trace gas mixing ratios or of ratios of mixing ratios. Over a wide geographical range these ratios depend on $\sqrt{\tau_i}$. Third, in these situations the traditional way of determining τ and [OH] from pairs of hydrocarbons may fail.

Nevertheless, one can derive procedures to derive these quantities from sets of hydrocarbon measurements. The most simple is to relate $\ln(\sigma_i / \overline{M}_i)$ to $\ln(\tau_i)$. In the most favorable cases this leads to a linear relation, i.e. $\sigma_i / \overline{M}_i = A \cdot \tau_i^{-\alpha}$ where $\alpha \approx 1/2$. In any case this procedure leads to a unique function of $\sigma_i / \overline{M}_i$ of τ_i. To use this procedure for the determination of [OH] additional information is needed. In the present case this is provided by the alkenes, whose lifetime is partly determined by reaction with O_3 (of known concentration). Thus, we derived an OH concentration of $6 \cdot 10^5$ cm^{-3} for the PEM West domain of 30° - 40°N latitude, 135° - 155°E longitude during early March. The estimated 1σ error is a factor of 2. A major assumption remains, namely that of a similar source distribution for the tracers considered.

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Reports of the Working Groups

Report of working group 1

MEASUREMENT TECHNIQUES AND INTERCOMPARISON

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Introduction

The realization that VOC are of extreme importance for the atmospheric environment in general and the chemistry of the troposphere in particular has resulted in a tremendous progress in measurement techniques for VOC in the atmosphere during the past 10–15 years. Nevertheless, the existing techniques are not yet adequate for a comprehensive determination of tropospheric VOC concentrations. This working group identified a number of areas where further scientific work is needed. This is the consequence of several observations:

- The number of VOC that can be found in the atmosphere at relevant levels is substantial. This requires analytical techniques with high separation power or highly specific detection methods.
- A substantial number of atmospheric VOC are either highly polar or thermally unstable. This limits the use of conventional sampling techniques.
- It has been recognized that measurements of VOC are extremely useful to study important atmospheric processes. Consequently, interest in VOC measurements is not limited to VOC that are of relevance for the chemistry of the atmosphere or have otherwise significant impact on the environment. This results in a new level of required precision and sensitivity.
- The atmospheric lifetime of many VOC is short. Thus their temporal and spatial variability will be substantial. This requires measuring methods with good time resolution, especially for airplane based operation.
- The existing calibration techniques, including available standards, are not yet of sufficient quality for many important VOC.
- Quality assurance and quality control is just starting to develop. Up to now number and extent of intercalibration exercises is still very limited.
- A major portion of the tropospheric aerosol consists of organic matter. There is a need for measurements of VOC that contribute to particle growth or formation (e.g., substances with low vapor pressure or precursors for such compounds).

Existing techniques allow measurements of a broad range of VOC in concentrations ranging down to a few ppt, some specialized applications even allow measurements of concentrations well below 1 ppt. Nevertheless, the general consensus of all workshop participants was that further detailed studies and new developments are needed in several areas. The areas identified by the participants of the working group on measurement techniques were:

- Quality assurance and quality control including intercomparisons and reference gases
- Sampling methods

- Removal of water, carbon dioxide and ozone from the sample
- Field instrumentation including instruments for airplane operation
- Improved separations
- Detection methods with increased sensitivity
- Measurement techniques giving information on properties of specific VOC (e.g. isotopic composition, enantiomers)

Some of these points will be outlined below in some more detail.

Quality Assurance, Calibration, and Intercomparison

There is a wide range of issues that must be addressed with regard to quality assurance of VOC measurements. Among them are standards, sampling, intercalibration of measurement methods for VOC's, chromatographic separation and detection. Intercomparisons are vital and important because they help to establish reliable estimates of the uncertainty expected in measurements. Only with such an estimate observations and theory can be compared meaningfully, results from separate campaigns can be merged reliably into a global data base, spatial gradients from separate data sets can be characterized credibly, and time series from different networks can be used to establish long-term records.

VOC Standard Collection and Storage

The most common techniques for standard storage are in high pressure cylinders (usually around 2500psi), large pontoons (up to 500psi), or canisters (up to 100psi). A major issue concerning standards is their ability to maintain their integrity over time in these storage vessels. The most commonly used cylinders are aluminum with an interior surface treatment such as Aculife by Scott Specialty Gas. Pontoons and canisters are usually electropolished stainless steel that may have also undergone some sort of ambient air baking procedure to help ensure surface passivation and inertness towards the compounds of interest.

For nonmethane hydrocarbons (NMHC's), synthetic standards are most commonly prepared in the part-per-million by volume (ppmv) range in high-pressure cylinders by various manufacturers. These high concentration standards usually show very little change with time because small losses or growths will be negligible compared to the mixing ratio of the gas/gases in the cylinder. However, it should be noted that several participants in Working Group 1 had occasionally experienced large changes (10–20%) with the ppm level synthetic standards in high-pressure cylinders with time. Additionally, when the pressure becomes very low in the cylinders the mixing ratios drastically change.

Pontoons and canisters are used to dilute the ppm level standards down to the part-per-billion (ppb) or even the part-per-trillion (ppt) level. Artifacts and surface reactions from these particular containment vessels can become problematic at this stage. At lower mixing ratios, small changes in the standard can result in large calibration errors. The most common problem with the use of canisters (particularly at low pressures) for NMHC standards at low mixing ratios is the growth of the light olefins, growth or loss of benzene and toluene, loss of isoprene, and the

loss and isomerization of terpenes and of heavier aromatics. For oxygenated VOC's (OVOC), the only successful method for standard storage that seems to be acceptable at present is the use of high-pressure cylinders that contain ppm levels of these compounds. The working party members unanimously agreed that more work needs to be done for developing reliable, stable reference gases for OVOC.

Intercalibration of NMHC's

For calibration and intercalibration of NMHC's, different independent standards are desirable. In addition, a variety of standards differing in concentration and in composition are needed to check the linearity of the detection system and for identification of separation problems. It is also desirable to have whole air standards which have a similar matrix to the air sample, to test effects which are caused by the inlet system, sampling step and interference with other compounds (e.g. CO, CO_2).

For intercalibration procedures, it is critical to ensure that the standards have long time stability. It is known that NMHC standard mixtures in the upper ppb-range can be made that are stable for several years. However, there still is need to improve stability of low ppb and ppt mixtures.

For a number of applications permeation or diffusion tubes in combination with a dilution step is the presently best available calibration technique. Furthermore, diffusion or permeation devices can be absolutely calibrated and thus allow an independent check on other standards. However, the presently available systems are plagued by a varity of problems, especially for field operation. Work to improve permeation systems for easier and more reliable operation and absolute calibration is recommended.

Method comparison

In addition to formal or informal intercomparisons, it is highly recommended to use different methods for the analysis of VOC. Unfortunately, most methods are very similar, using GC in combination with a preconcentration step. Nevertheless, even slight modifications (e.g. the use of different columns for separation or changes in preconcentration methods) may reveal problems associated with one or the other step of the overall procedure. Systematic evaluations of this kind for both existing and newly developed methods are strongly recommended.

Separation and Detection

The tremendous improvements made during the past years in analytical chemistry in general and chromatography in particular had a visible impact on measurement techniques for VOC in the atmosphere. However, there is a certain time lag between developments in the field of chromatography in general and their application to atmospheric VOC analysis. This is only partly due to limited communication between the two different scientific fields "analytical chemistry" and "atmospheric chemistry." A considerable obstacle is the very specific nature of the sample matrix air. New developments in chromatography primarily are applied to liquid samples. Thus

the exploitation of new developments in chromatography for atmospheric measurements nearly always requires adjusting the "interfacing" steps needed to inject a gaseous, preconcentrated sample into the chromatographic system.

Separation

The complex composition of atmospheric VOC, and the necessity to provide detailed speciation of multicomponent mixtures, often dictates the use of high resolution capillary gas chromatography. Columns up to 100m length can provide adequate resolution of many major constituents of ambient VOC. A variety of columns of different polarity can be applied to the sample mixture to achieve selective separation and confirmation of certain target compounds. Furthermore, current column technology is producing internal surfaces of greater inertness than has been available in the past. This allows the analysis of more labile compounds such as peropxyacetyl nitrate (PAN), with improved detection and resolution. Other promising developments in the area of GC-columns are

- Chiral columns for the separation of enantiomeric compounds and improved separation of isomers,
- Improved inertness for the analysis of reactive compounds (e.g. PAN, acids, bases),
- New porous layer open tubular columns (PLOT) for the separation of volatile VOC with different selectivity compared to former plot columns (e.g., Gas Pro GSC, Pro Plot NMHCs, OVOC, Hal-VOC, Q-HT),
- Narrow-bore columns which combine the benefit of reduced analysis time with high resolution. Provided the appropriate injection techniques are available (e.g. on column focussing), the use of these columns also enhances detection limits due to reduced peak width.

Other separation techniques that deserve further development for VOC analysis are HPLC, ion chromatography, and capillary electrophoresis. Some of these techniques are presently successfully used for specific applications, they might potentially be very useful as part of two-dimensional separation methods, e.g. HPLC-GC. It should also be noted that derivatisation can be extremely useful not only to improve separation for specific compound groups, but also to improve chemical or thermal stability and detection limit.

Two-Dimensional Chromatography

In spite of the high separation efficiency of state of the art columns, resolution of peaks in extremely complex samples is still not always sufficient. Highly specific separations can be achieved by multidimensional chromatography. Although an established technique in chromatography, there are up to now only few applications of two-dimensional chromatography for analysis of VOC in air. As an extension of the currently utilized one-dimensional chromatographic techniques, two-dimensional chromatographic techniques are presently becoming more common in the study of atmospheric VOC's. However, their potential has not yet been fully exploited.

Isolation and further chromatographic separation by two-dimensional techniques offer improved results for highly complex samples, e.g from urban airsheds or other highly polluted regions where significant overlap of chromatographic peaks will occur. Other promising applications of this technique are separation of water and CO_2 from VOC. Considering that water

removal and CO_2 removal are supremely important for effective chromatography of VOC's, further development of two-dimensional techniques utilizing different column types should offer significant improvements to the measurement of VOC's.

Detection

Detector sensitivity is still an important point for VOC measurements in the atmosphere. In some cases, high detector sensitivity (e.g., the use of electron capture detection for the analysis of halocarbons or peroxyacetyl nitrate) allows to eliminate or at least substantially reduce problems connected with the preconcentration step or other steps of sample treatment before separation and detection. For some cases, enhanced sensitivity might even allow measurements without preconcentration step at all.

In addition to the commonly used GC-detector FID, ECD, and MS, there are more specialized detectors such as the reduced gas detector, atomic emission detector and photo ionization detector. For specific applications the use of such detectors can substantially reduce the lower limit of detection, sometimes also improve specificity. However, operation of these detectors is generally more demanding and their costs are higher.

The most promising detector for future developments and improvements is the mass spectrometer. Reduced costs and improved performance have already made it a very widely used detection method. Tailoring MS-detection to the specific needs for measurements of VOC in the atmosphere, e.g., the use of different ionization techniques, seems very promising.

Sampling and Sample Preparation

There are numerous sampling techniques, many of them include steps to remove potentially interfering substances such as ozone, water vapor and carbon dioxide. However, it was the general opinion that not sufficient systematic work is done and published to evaluate and compare the various sampling techniques which often are quite similar but nevertheless differ in details.

The combination of sampling on solid sorbents with solvent extraction and subsequent analysis, e.g., by HPLC or GC-MS, is presently mainly used for specific measurements, e.g., indoor air pollution. However, the method seems to be promising for more general applications. Adsorbents causing low blank values, high purity solvents and commercially available automated injection techniques for large volumes of solvents make this method readily available for laboratories which are not specialized in the analysis of air samples. Although this method may presently only be of limited value for background measurements, it seems to be a very promising technique for moderately or highly polluted air masses.

Dedicated Instruments

Most measurement techniques for atmospheric VOC aim at a general applicability, implying that one technique should be suitable for most purposes, e.g., monitoring at remote locations, campaign type studies or even indoor pollution. Although the methods are often adjusted for the specific problem (e.g., the expected concentration levels or the complexity of the sample composition) the basic principle very often is not changed.

However, there are applications which have requirements that are not met by "classical" VOC measurement methods. The main limitation for most established VOC measurement techniques is the limited time resolution. There are a few applications where the duration of several minutes to hours of most methods is not adequate, e.g., for airplane based measurements. Here a low temporal resolution translates, due to the high speed of the airplane, into a low spatial resolution. Both for scientific and economic reasons (high costs for flight hours) measurements with time resolution of minutes or less are highly desirable. Tunable diode laser spectroscopy has successfully been used for a few airplane-based measurements of a few selected VOC. However, the range of accessible compounds is very limited. Potentially more widely applicable are mass-spectrometry based methods, e.g., atmospheric pressure selected chemical-ionization mass spectrometry (APSCI-MS) or MS in combination with a two proton excitation/ionization step.

For some applications, less specific, but fast measurement techniques may be used. An example is measurement of isoprene by chemoluminescence for eddy correlation flux measurements.

Measurements of Properties of VOC

Traditional measurement techniques for VOC in the atmosphere aim at knowing their concentrations, e.g., to determine their temporal or spatial distribution. Very recently, techniques allowing to measure specific properties of VOC in the atmosphere are emerging. These properties are isotopic composition and identification of the enantiomers of optically active substances. These methods are sufficiently sensitive for relevant atmospheric concentrations. They do not supply direct information about the effect of the substances on the chemistry of the atmosphere or any other environmental impact. However, this type of information might be of extreme value to better understand the relevant processes that determine the abundance and distribution of VOC in the atmosphere.

Aerosols and VOC

A considerable fraction of the atmospheric aerosol consists of organic matter. The study of the atmospheric chemistry of aerosols requires therefore measurement techniques that are presently not available or only partly developed.

Measurement techniques for VOC that can contribute to the formation of multifunctional oxygenated products with low vapor pressure to some extent exist. However, for several groups of sub-stances, e.g., sesquiterpenes, no established techniques are available. Measurements of oxygena-ted VOC with low vapour pressure that form new particles and contribute to particle growth or formation present a serious challenge. The expected concentrations are small, and the substances may be lost by contact with surfaces, decompose or isomerize easily. For similar reasons the analysis of oxygenated VOC with high water solubility presents serious problems.

Sampling techniques using solid adsorption in combination with thermal desorption or solvent extraction and gas chromatographic analysis should be appropriate for most compounds. For the more reactive compounds extraction, where necessary followed by derivatisation or analyses by HPLC, seems most promising. The workshop participants shared the opinion that development of adequate techniques is needed.

VOLATILE ORGANIC COMPOUNDS: SOURCES AND DISTRIBUTIONS

Ralf KOPPMANN, Don BLAKE, Kristin von CZAPIEWSKI, Alex GUENTHER, Arnd HEIDEN, Holger HEIN, Laura IRACI, Bita KOLAHGAR, Robert KOTCHENRUTHER, Sadredin MOOSAVI, Jeffrey REID, Barkley SIVE, John SLATER, Jim SMITH, Jochen THELOKE, Lee VIERLING, and Jürgen WILDT

Introduction

The most complex group of trace gases in the atmosphere are volatile organic compounds (VOC). While OH radicals act as a cleansing agent initiating the photochemistry in the troposphere, VOC can be considered as the fuel sustaining the chemical reactions. VOC are present in the troposphere at relatively low mixing ratios ranging from less than one ppb to several ppt. Owing to their reactivity, VOC play an important role in atmospheric chemistry. VOC have been measured in a variety of atmospheric environments: from urban areas to the most remote areas over the oceans and in polar regions. Even with present techniques and methods which have been discussed intensively in Working Group 1, the organic chemical composition of the troposphere is by far not characterized. Depending on the measuring site, thousands of individual VOC can be found in ambient air.

The complex composition of VOC in the troposphere is a consequence of the large variety of sources and their distribution. VOC are emitted by both anthropogenic and natural sources. Additionally, the oxidation of VOC in the atmosphere leads to a complex mixture of short-lived and long-lived secondary organic compounds.

In order to apply model calculations to understand photochemistry in the troposphere, it is likely to know the sources and sinks, the distribution, the fate and the impact of VOC on the photochemical system.

The intent of this working group was to discuss the present state of knowledge about the sources, sinks and distribution of VOC in the troposphere, to raise open questions and identify possible fields for future investigations.

Availability of data

Discussing the present state of knowledge, the group shared the opinion that surveying the number of measurements, the measured compounds and published (or not yet published) data sets is as complicated as the organic composition of the troposphere. The discussion demonstrated a clear need for a centralized listing of available data sets, concurrent measurements and the format of the data. Further, a greater availability of the data taken but not widely distributed was requested. An enhanced publicity of availabe data sets to encourage their use was recommended.

Even in the case that measurements of VOC are available, it is apparent that there is a lack of consistent, responsible and thorough reporting of analytical methods, accuracy, precision, and calibration methods along with the data published in the literature and in data sets available to the community. It was pointed out that there are no common requirements for necessary information about quality assurance and quality control in published data sets.

Sources of volatile organic compounds

A compilation of sources for volatile organic compounds was discussed in detail. Table 1 summarizes the results. The listing shows that for a number of sources, essentially the most important ones, emission inventories are available. These inventories are, however, often on a regional scale, and extrapolations are difficult to achieve. The discussion determined that information is missing, especially for the developing countries in Africa and Asia.

For a number of sources, only a few or no measurements exist. Some of these sources have only local or regional impact. Nevertheless, concerning reduction strategies or legislative action, the emissions of VOC from those sources need to be known in much more detail than they presently are.

Table 1. *Compilation of sources for volatile organic compounds.*

Source	Importance	State of knowledge
Vehicular exhaust	*regional, global*	emission inventories available
Natural gas evaporation	*regional, global*	emission inventories available
Solvent evaporation	*regional*	production and sales data available
Fuel evaporation	*regional, (global)*	
LPG	*regional, global*	propane and butanes composition changes regionally
Oil refining	*regional*	
Power generation	*regional*	
Petrochemical processes	*regional*	
Landfills	*local, regional*	
Land conversion	*regional, global*	
Sewer	*regional, global*	
Oceanic emissions	*regional, (global)*	mostly at coastal areas connected with biological activity
Vegetation	*regional, global*	emission inventories available, emission algorithms for isoprene and some terpenes available
Soil	*?*	
Geogenic emissions	*?*	

Biogenic VOC

Another topic discussed were biogenic emissions of VOC which on a global basis seem to be much more important than anthropogenic emissions.

Although many measurements have been made globally concerning the emission of VOC from vegetation, compilations of emission rates and estimates of the contribution of biogenic VOC to the global VOC budget are still more or less uncertain. The group thinks that much more effort is needed to investigate this important source of VOC.

Information about plant physiology data bases should be combined with the input of atmospheric chemists to identify the specific issues of interest. Together with ecologists, emission experiments could be conducted on important landscape and economic species. Experiments should be carried out both in the USA and Europe to investigate species and climate differences and possible similarities.

In addition to that, stress factors have to be investigated such as enhanced ozone and VOC mixing ratios, nitrogen deposition, desiccation and increasing temperatures. All these investigations should lead to improved emission algorithms to account for the role of biogenic emissions in global model calculations.

Oxygenated volatile organic compounds

Oxygenated volatile organic compounds (OVOC) are important compounds for tropospheric chemistry. A compilation of source strengths of OVOC lead to the estimate that besides isoprene OVOC are the most dominant compounds emitted into the atmosphere (Table 2).

Our knowledge about these compounds is too fragmentary to understand their impact on photochemical processes in the troposphere. The regional and global distribution of OVOC is not known as are the sources and sinks. The lack of knowledge predetermine these compounds for future investigations. Even if more measurements are available, the interpretation of measurements in the troposphere leads to the problem of distinguishing between primary and secondary oxygenated compounds. The first group is directly emitted into the atmosphere by various processes, the second group is produced during photochemical oxidation of other volatile organic compounds. Obviously, the ratio of primary and secondary oxygenated hydrocarbons in the troposphere is one of the open questions concerning the organic composition of the troposphere.

Table 2. *Compilation of source strengths of volatile organic compounds*

Compound	Source	Emission rates in Tg/yr
Hydrocarbons	*anthropogenic*	50–80
Hydrocarbons	*biomass burning*	25–50
Isoprene	*natural and anthropogenic*	500
Terpenes	*natural*	150
OVOC	*natural and anthropogenic*	500 ?

Recent studies of emissions of OVOC from plants but also measurements in the ambient atmosphere suggest that important OVOC which should be investigated in much more detail are methanol, ethanol, methylbutenol, C_6 oxygenates, formaldehyde, acetaldehyde and acetone. For such studies a close collaboration between plant physiologists and atmospheric chemists is essential. An interesting question in this context is, how are these compounds produced in plants and why do plants emit these compounds into the atmosphere. From the atmospheric chemists point of view, the reaction pathways these compounds undergo in the atmosphere are important.

An additional open question that was raised is the heterogeneous chemistry of OVOC and their role in the formation of organic aerosols. This point is thought to be an important topic for future research.

Sinks of VOC

A further discussion addressed loss processes of volatile organic compounds from the atmosphere. All volatile organic compounds react rapidly with OH radicals, which is by far the most important sink for primary VOC. Unsaturated compounds react also with O_3 and during the nighttime with NO_3. The corresponding reaction rates are mostly known for a large variety of compounds.

There are, however, a number of loss processes which may have a considerable impact on the lifetime of VOC in the troposphere, which are not yet fully understood. The following list was compiled as the relevant sinks for VOC:

- reactions with OH, O_3, NO_3 and halogen atoms
- heterogeneous reactions
- dry and wet deposition
- aerosol formation
- thermal decomposition
- transport to the stratosphere
- microbial activity in soils
- uptake by plants

It was suggested that all of the sinks listed above need further investigations. Even for the most important sinks, the reaction with OH radicals, many rate constants are not yet measured. The reaction of methylcyclopentane with OH may hold as an example. Very little is known about heterogeneous reactions, aerosol formation and deposition processes.

Open questions

During the discussion in the working group and in the written comments of the participants, the following questions were identified as open questions in the field of sources and sinks of volatile organic compounds in the troposphere:

- Which VOC can be used as a tool for indirect measurements of other compounds, e.g. radicals?
- Can we close the VOC budget from biomass burning?
- Can we set up a budget for acetone?
- What role do oxygenated hydrocarbons play in atmospheric chemistry?
- Are there unidentified organic compounds, which may play an important role in atmoshperic chemistry?
- How much of a sink for volatile organic compounds is represented by secondary aerosol formation and subsequent deposition?
- What are the oxidation pathways of biogenic VOC?
- Which and how many of the oxygenated VOC are photolysed and how does this affect the ozone formation?
- How do oxygenated VOC affect plants?
- What is the relative importance of primary versus secondary VOC in the troposphere?
- What role does heterogeneous chemistry of VOC play in the troposphere?
- What is the fate of isoprene in the troposphere?
- Is there a night-time radical production (OH) from the oxidation of biogenic VOC?
- What is the role of VOC with two or more functianal groups in atmospheric chemistry?
- Can we define groups of VOC as fingerprints of different sources?
- Which VOC have a tendency to form secondary aerosols and how is their budget affected by this behaviour?
- What are the baseline emissions from biogenic sources of methanol, ethanol, formaldehyde, acetaldehyde, acetone, C_6 oxygenates, methylbutenol?
- How do biogenic sources respond to environmental changes?

This collection of questions, which has no claim to completeness, includes at least some of the problems that deserve attention in the near future. Although it is possible that a number of important questions are missing, the group hopes to have initiated further discussions on the importance of VOC for the understanding of photochemical processes in the troposphere.

Report of Working Group 3

DATA ANALYSIS, INTERPRETATION AND MODELING

Geoff TYNDALL, Shaw LIU, Ludger BENNING, Harald BERRESHEIM, Dieter EHHALT, Frank FLOCKE, Greg FROST, Tom JOBSON, Dirk POPPE, Bjørn RAMACHER.

Priorities of research should be given to major areas of uncertainty in the modeling and interpretation of VOC observations. Currently, the modeling and data interpretation of VOC measurements is limited by a large number of outstanding problems related to the emissions, chemistry, transport and removal processes, particularly for biogenic VOCs. In the following, we highlight some of the major uncertainties that may be amenable to study in the near- to mid-term future.

The discussions of Working Group Three centered around the modeling of ozone formation in rural areas (illustrated in a presentation by Greg Frost regarding ROSE data) and the extraction of OH concentrations from ratios of hydrocarbons (following from Dieter Ehhalt's talk, and illustrated by Tom Jobson). Further areas that were touched upon were the vertical mixing of VOCs into the free troposphere via convective processes (as described in Shaw Liu's talk) and the use of factor analysis to identify sources of air masses by their hydrocarbon signatures.

1 Chemistry of VOCs in rural areas

Ozone formation in rural areas is influenced to a large extent by organic peroxy radical production and loss terms. However, these are often the reactions for which there remains a good deal of uncertainty in the rate coefficients and product yields. The peroxy radical chemistry at the ROSE Experiment has been discussed by Cantrell *et al.* (1992, 1993) while the site location and VOC measurements have been described by Montzka *et al.* (1993). Figures 1 and 2 (courtesy of Greg Frost) illustrate the major gas-phase photochemical production and loss terms for radicals and ozone as a function of the time of day.

The following questions were identified as being areas for future research. All can in principle be tackled in the near- to mid-term, although ideal experimental techniques may not always be available at the moment.

1.1 Reactions of peroxy radicals with NO

These reactions are the "engine" by which NO is converted to NO_2, the photolysis of which forms ozone in the troposphere (Liu *et al.*, 1987).

$$RO_2 + NO \rightarrow RO + NO_2$$

$$NO_2 + h\nu\ (+ O_2) \rightarrow NO + O_3$$

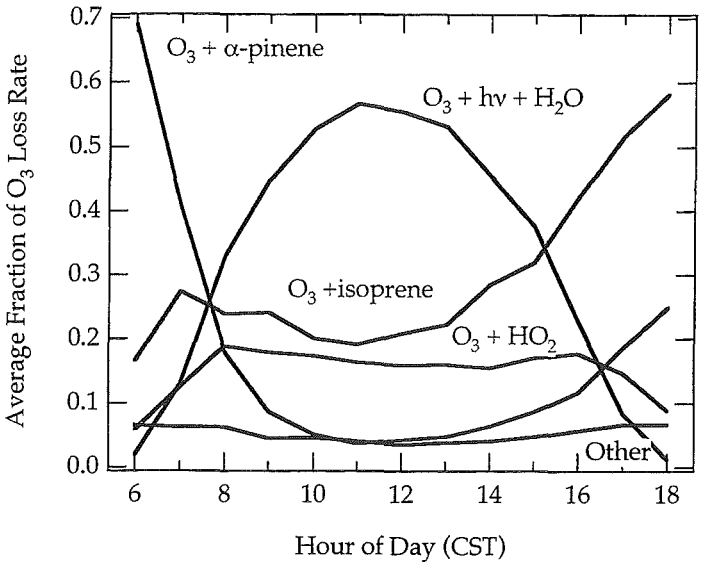

Figure 1. *Plot of the average radical production and loss terms as a function of time of day at the ROSE study, which took place in July 1990 at Kinterbish Alabama (Greg Frost).*

However, the rate coefficients for many of the reactions, particularly those involving the peroxy radicals derived from biogenic VOCs, have never been measured. The reactions also involve a pathway to give organic nitrates.

$$RO_2 + NO + M \rightarrow RONO_2 + M$$

This pathway leads to a net loss of radicals, and so reduces the potential to form ozone. Furthermore, the nitrates themselves are a marker for photochemical activity (Flocke *et al.*, 1991). The yields of organic nitrates from these reactions remain a major uncertainty, particularly from alkenes.

1.2 Reactions of peroxy radicals with HO_2 and other peroxy radicals

The reactions of peroxy radicals with HO_2 are known to be important losses for peroxy radicals in remote areas. However, they also serve as one of the major losses in continental areas, due to the elevated radical density in regions of high photochemical activity. Laboratory studies of the rate coefficients for these reactions for peroxy radicals derived from isoprene and aromatics are required, as are measurements of the product yields.

The reactions between different organic peroxy radicals are usually considered to be less important than the reactions with HO_2, but can themselves play a part in limiting ozone formation when the RO_2 concentration is high. Again, further laboratory studies of the rate coefficients and product branching ratios would be useful for modeling, and would enable predictive rules to be formulated for reactions that have not been measured.

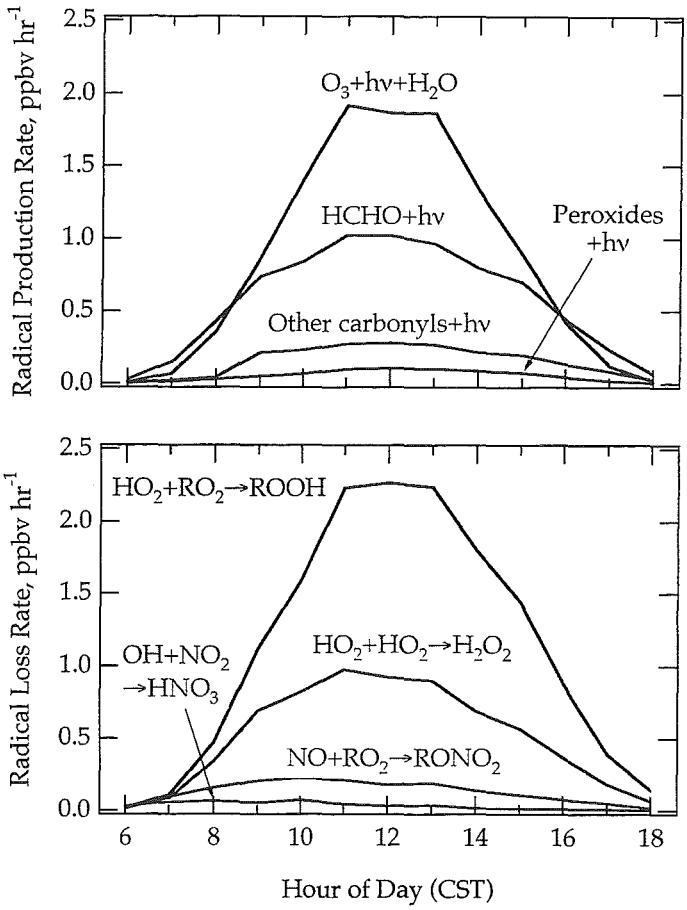

Figure 2. *Plot showing the various chemical loss terms for ozone as a function of time of day at the ROSE study (Greg Frost).*

1.3 Hydroxyl yields from ozonolysis

This topic is very much in the current interest. While it has long been known that a multiplicity of pathways occurs in the ozonolysis of alkenes, including both radicals and stable products, the formation of OH as a direct product in the reactions of larger alkenes has only recently received a lot of attention. The direct formation of OH is in principle very important, since sources of OH at night are very limited. The extent of OH formation is currently subject to both uncertainty and also a degree of controversy (Schäfer *et al.*, 1997; Paulson *et al.*, 1997). Direct evidence of the formation of OH has recently become available (Donahue *et al.*, 1998); however, experimental techniques capable of achieving unequivocal evidence for this pathway are not readily available, nor are they easily imaginable, due to the complexity of the reaction mixes and the slowness of the ozone-alkene reactions. Many alkenes are known to give hydrogen atoms on reaction with ozone, and the reaction of H with ozone leads to the rapid formation of OH. Further experimentation required!

1.4 Photolysis rates of carbonyls

Both laboratory measurements of absorption cross sections and photolysis quantum yields, and in situ measurements of the photolysis rates of carbonyl compounds in the field are required to accurately model radical production rates. The quantum yields are in particularly bad shape, with only formaldehyde and acetaldehyde having been studied in detail as a function of wavelength, temperature and pressure.

1.5 Aerosols

The role of aerosols in the chemistry of VOCs in the troposphere has not yet been completely established, although several known examples clearly point to a potentially large impact. The major links between VOCs and aerosols can be summarized as:

- Formation of aerosols from VOCs and their oxidation products
- Removal of VOCs onto existing liquid or solid aerosol particles
- The processing of VOCs on or in particles, to form new products

The presence of organic aerosol in areas heavily impacted by VOCs has been established for a long time - the observation of "blue haze" over forested areas appears to be related to the emission of terpenes by the trees, and aromatic compounds formed from automobile exhaust are often found on urban aerosol. However, the identity of the compounds required to form *new* particles is not known at present.

Low-volatility organic compounds might be expected to deposit readily onto surfaces, and aerosol particles in the atmosphere clearly provide such a surface. In the case of solid particles with an organic character, the tendency for large organic molecules to deposit will probably be very high. However, it is not known how much loss of organics occurs onto liquid (aqueous or sulfate) particles. Cloud particles are known to scavenge soluble material very efficiently, but the volume of aerosol in the troposphere is several orders of magnitude smaller than that encountered in a typical cloud. It is not known whether reactions can occur within the aerosol that are rapid enough to convert the organic molecules before they leave. Such processing could lead to more soluble products that remain in the particles, or new products that are released into the gas phase, but which otherwise would not be formed. The observation of organic acids, particularly difunctional acids, in the particulate phase is strong evidence of the processing of organic matter in aerosols - currently, very few mechanisms are known to produce these acids by homogeneous gas phase reactions. However, until further work is carried out, the extent of processing of organics by aerosols remains speculative. Possibilities for both short-term (exploratory) and long-term research are clearly present, but one general equation appears to be true:

$$\gamma(\$)_{\text{aerosols}} \approx 1$$

where the left hand side of the equation represents the probability for funding to attach itself to an aerosol project!!

Despite all the chemical questions related to ozone and photochemistry, several physical processes may actually be the most uncertain in the determination of ozone production. During the night, ozone can be depleted in the boundary layer by dry deposition. Entrainment of (ozone-rich) air from the mixed layer into the ozone-poor boundary layer, can at times actually be the major source of ozone in the boundary layer. The dry deposition of various oxygenated species, particularly carbonyls, nitrates and radicals, has not been studied to any degree. The paramaterization of the above processes is not in particularly good shape at the moment.

Thus, many unanswered questions remain concerning the processes controlling observed levels of ozone in the boundary layer. Before a full assessment can be made of the impact of VOCs on human and plant populations, these questions will need to be addressed fully.

2 Find an analytical or numerical way of extracting chemical (i.e. [OH]) and dynamical information from observed hydrocarbon patterns

Light hydrocarbons such as the C_2–C_6 alkanes, acetylene and benzene share similar sources and are removed from the atmosphere by OH-initiated oxidation over a wide range of rates depending on the reactivity of the hydrocarbon. This makes them ideally suited for measuring photochemical processing in urban and regional plumes since a range of chemical timescales can be employed to probe the plumes as they disperse. Estimates of OH concentrations have been made by following hydrocarbon concentration changes within plumes spreading from urban areas (Calvert, 1976; Roberts *et al.* 1984; Blake *et al.*, 1993) and other hydrocarbon sources (McKenna *et al.*, 1995). In general, this analysis approach has limited applicability since atmospheric dispersion can blend air with different degrees of photochemical processing. A common observation attributable to mixing influences is for the more reactive hydrocarbon species to yield the lower estimate of [OH]. The influence of dispersion on hydrocarbon aging trends has been investigated numerically by McKeen *et al.* (1990) and analytically by McKenna (1997). Both papers address the question of whether separability of chemistry and transport can be assumed given the chemical and diffusive timescales for boundary layer hydrocarbon oxidation.

The consensus from working group 3 is that chemical and dynamical information is contained in observed hydrocarbon patterns, but that a rigorous mathematical solution, either analytical or numerical, is needed to show that time averaged [OH] can be extracted with known certainty. One possible approach is to investigate the observed relationship between hydrocarbon concentration variability and lifetime. For example, Junge (1974) showed that the global spatial variability of a number of trace gases appeared to be inversely proportional to lifetime as shown in Figure 3 (courtesy of Tom Jobson). Well correlated variability-lifetime relationships are also observed on the regional level, but with a weaker dependence on lifetime than that given by Junge. A physical model that explains why trace gases display this behaviour is still awaited. However, from such trends, it seems possible that estimates of average OH concentrations relative to those of ozone could be reliably made by comparing alkene and alkane variability.

Some time was also given to the discussion of the effects of halogen chemistry on hydrocarbon distributions. While the contributions to hydrocarbon loss made by chlorine atoms are thought to be minimal at mid-latitudes, both chlorine and bromine can play a role in the Arctic troposphere. While many of the rate constants are known at room temperature, the reaction rates and particularly the products are less certain at the cold temperatures encountered at Northern high latitudes.

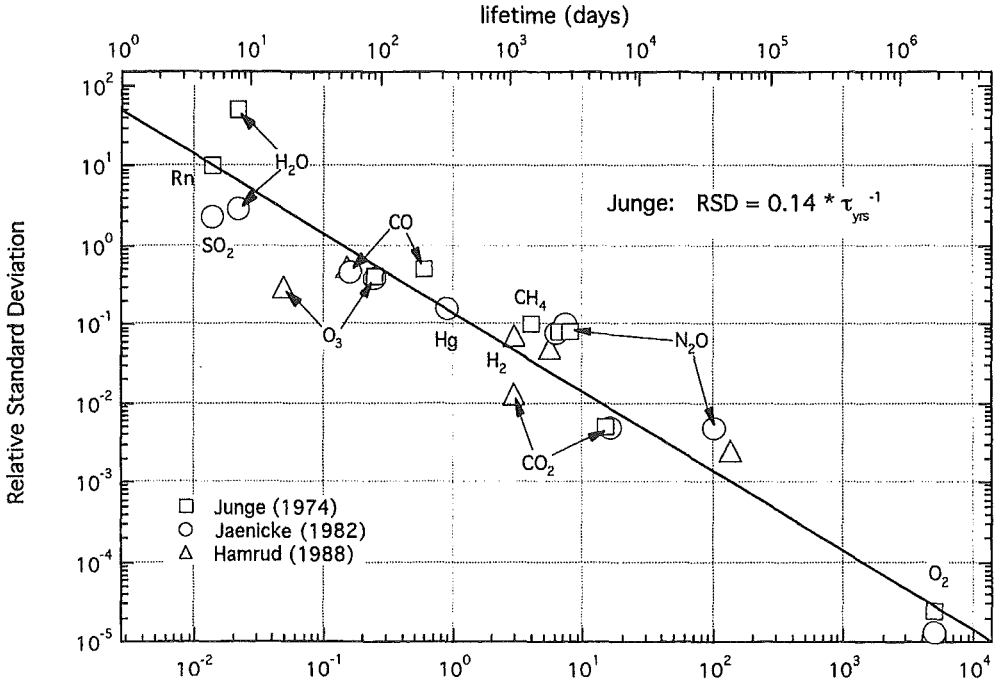

Figure 3. Plot showing the spatial variability of various atmospheric trace gases (expressed as the relative standard deviation of measurements) versus the atmospheric lifetime (Tom Jobson). Note that the three principle contributors have all their data displayed at once (so one can see how estimates of lifetime and variability have changed over the years).

3 Hydrocarbon source fingerprints

While there is some published work on the composition of major hydrocarbon sources such as auto exhaust and various fossil fuels, it was felt by the working group that more should be done in this area. Different countries utilize different types of fuel and pollution control measures and this imparts a hydrocarbon "fingerprint" characteristic to that urban area. Potential differences between North American, European, Asian, and South American city "fingerprints" may be useful for interpreting hydrocarbon data collected from remote sites. On a regional scale, comparing urban source "fingerprints" from measurements to those expected from emission inventories is an extremely useful first step for evaluating model input for regional ozone modelling studies.

4 Hydrocarbon tracers for vertical transport into the upper troposphere

Rapid vertical transport associated with thunderclouds may be an important mechanism for introducing relatively reactive hydrocarbons into the upper troposphere which could significantly influence the otherwise hydrocarbon-poor photochemistry of the upper troposphere. Candidates for tracers would be those hydrocarbon species that have strong vertical gradients but which also have lifetimes substantially longer than the timescales associated with convective cloud transport.

The modeling of convective events can pose particular problems, since these events occur on much finer spatial scales than most chemistry models can handle. However, the effects of the redistribution of chemicals can impact a regional area. Since a major fraction of the global hydrocarbon emissions occur in the Tropics, where convective activity is the strongest, effective modeling or parameterization of convective transport is vitally important in the coming years.

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THE GERMAN-AMERICAN ACADEMIC COUNCIL FOUNDATION (GAAC): SPANNING GERMAN AND AMERICAN SCIENCE, SCHOLARSHIP, AND TECHNOLOGY

1 Political Objectives

The objective of the German-American Academic Council Foundation (GAAC) is to strengthen German-American cooperation in all fields of the sciences (including the natural, physical, medical, and social sciences and engineering) and humanities, particularly by integrating younger scientists and scholars and supporting policy studies on topics of mutual interest to both countries. Such collaboration should contribute to keeping German-American cooperation and partnership as alive and dynamic as they have been in the past 40 years.

The GAAC is an independent organization. By bringing together and utilizing the experience, expertise, and personal commitment of its members and by sponsoring selected activities it complements the activities of existing institutions and programs that support cooperation between Germany and the US in the fields of science, scholarship, and technology.

The GAAC is affiliated with seven scientific and scholarly institutions. On the U.S. side these are the American Academy of Arts and Sciences (AAAS) in Cambridge, MA, the American Council of Learned Societies (ACLS) and the Social Science Research Council (SSRC) in New York, and the National Academy of Sciences (NAS) in Washington, D.C. In Germany, the institutions are the Alexander von Humboldt-Stiftung (AvH), the Deutsche Forschungsgemeinschaft (DFG) in Bonn, and the Max-Planck-Gesellschaft zur Förderung der Wissenschaften (MPG) in München.

The GAAC

- serves as a forum for transatlantic dialogue concerning the fundamental issues confronting modern industrial societies;
- encourages and supports young German and American scientists and scholars in developing and maintaining permanent networks of cooperative activities;
- uses the interdisciplinary expertise available in Germany and the US to conduct policy studies of mutual interest to decision makers in both countries, in particular studies relating to science, technology, and higher education.

2 Structure, Tasks, and Modes of Operation

The GAAC has the following organizational structure:

- The Council - Members of the Council make all decisions regarding research topics and work program. The Council consists of up to fifteen German and fifteen American members. Council members serve for three years, but may be reelected for a second term. The work of the Council members is honorary;

- The Executive Committee - The activities of the Council are supported by an Executive Committee, made up of the Chairperson, the Deputy Chairperson, and six other Council members (three German and three American);
- The Chairperson and Deputy Chairperson - Both are elected by the Council members and serve three-year terms;
- The Kuratorium - In accordance with German foundation law, the Kuratorium supervises the legal and efficient management of public funds. It is composed of up to six German and six American members.

The work of the Foundation is supported by a small office, headed by a director. The main office is located in Bonn and a subsidiary office in Washington, D.C.

The experience and views of the Council members constitute the most important contribution to the discussions and intellectual work of the GAAC. On the one hand, Council members can draw on the potential of the institutes, institutions, and organizations to which they belong and on the other influence the strategies that these take through their experience in the Council.

The Council is proactive in setting its program priorities. It initiates policy studies and projects addressing issues that have crystallized out of Council discussions and then seeks out the appropriate research partners to implement these activities. The GAAC accepts proposals for network-building activities and policy studies particularly from its seven affiliated organizations. It also accepts proposals submitted jointly by other qualified German and American organizations. In addition, it promotes scientific and scholarly cooperation between the two countries through public symposia, publications, and the exchange of ideas. It does not consider itself to be purely a funding agency.

The GAAC's assets consist of funds granted annually from the budget of the German Bundesministeriums für Bildung, Wissenschaft, Forschung und Technologie, BMBF, (1996: 4.8 million DM). In the medium to long range, it is intended that the GAAC's activities will be financed jointly by public and private European and American sources. Not until third party funds are secured can the Council broaden its working basis. Individual projects and other activities that meet the objectives of the foundation are thereby be managed and financed in cooperation with other institutions. Currently additional 0.5 to 1.0 million DM are mobilized for specific projects and programs from external sources annually.

Participation shall - according to GAAC statutes - also be open to scholars and scientific organizations from other European and North American countries in due course.

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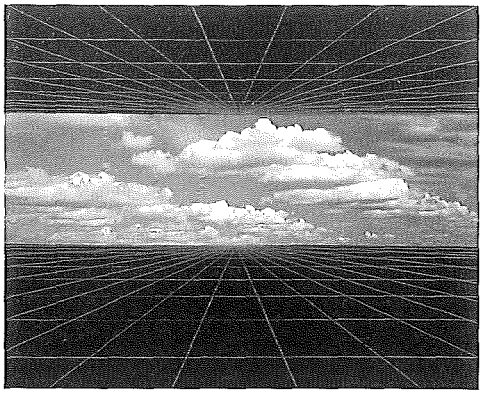
Atmospheric chemistry is a fast developing field. An important component is the research on volatile organic compounds, VOC. Volatile organic compounds have a large impact on atmospheric chemistry. Furthermore, they can be used as diagnostic tracers for transport, chemical pathways and distribution of sources. Along with the need for interdisciplinary research this makes a very attractive topic for young scientists.



This book presents lectures held at the workshop 'Volatile Organic Compounds in the Troposphere', an activity within the project 'Network of Young Scientists in the Field of Atmospheric Chemistry'.

The main topics of the presented lectures:

measurement techniques and intercomparison
sources, sinks and distribution of volatile organic compounds in the troposphere
data analysis, interpretation and modeling.

This book also contains the reports of three study groups, in which young scientists, with the help from senior attendees, summarized some of the current issues and open questions in the field of VOC research.

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