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A Note From the IGAC Chair: *Guy Brasseur*

Space Observations of Tropospheric Chemical Composition: Is the Scientific Community Ready?

One of the major challenges for the atmospheric chemistry community in the next decade will be to retrieve, analyze and interpret new data obtained from space. After having emphasized dynamical and chemical processes in the stratosphere, primarily in relation to the ozone depletion problem, the major space agencies (NASA in the US, ESA in Europe, and NASDA in Japan) are developing an ambitious program to investigate the chemistry of the global troposphere. Observations from several NASA satellites (TOMS, SBUV, SAGE) have already provided opportunities to derive the abundance of ozone in the troposphere. GOME, a European space instrument, has given promising information on the tropospheric abundance of several compounds including nitrogen dioxide, bromine oxide and formaldehyde. After the MAPS experiment from the Space Shuttle, the IMG instrument, which flew on the Japanese ADEOS satellite, reported nearly global observations of tropospheric carbon monoxide. Additional CO measurements as well as observations of methane are soon expected from the Canadian-US MOPITT experiment as part of the NASA Earth Observing System.

Additional space experiments are currently scheduled and will provide a large amount of new data. SCIAMACHY, MIPAS and GOMOS on board the European ENVISAT Spacecraft as well as TES, HIRDLS and MLS on board EOS/CHEM, scheduled to be launched in the early 2000's, will focus on tropospheric and lower stratospheric chemical compounds. In addition, PICASSO will use a spaceborne lidar to derive the vertical distribution of atmospheric aerosols.

As large amounts of new data become available, one should ask the question: Is the community ready for the analysis and interpretation of these data? How will we maximize the scientific return of these large technological investments?

Different new approaches are necessary including the improvement of retrieval schemes and the development of advanced assimilation algorithms applied to complex interactive chemical systems. Further, the community involved in ground-based or airborne observations and the space science community will have to cooperate better and recognize the complementarity of their respective approaches. Similarly, modelers and experimenters will have to work more closely together. Finally, it is important that international organizations like IGAC and SPARC, as well as the funding agencies, recognize the new opportunities for the scientific community and that they strive to make access to the new data as easy as possible.

6th IGAC Scientific Conference

Summary of Conference

Contributed by **Sandro Fuzzi** (fuzzi@atmosphere fisbat.bo.cnr.it), *Institute for Atmospheric and Oceanic Sciences, Bologna Research Establishment, National Research Council of Italy*

Details of the Conference organization

The 6th IGAC Conference was held in Bologna, Italy, from 13-17 September 1999 at the Conference Centre of the CNR Bologna Research Establishment. The Conference was sponsored jointly by IGAC, CNR's Institute for Atmospheric and Oceanic Sciences (ISAO), and the European Commission, DG XII-JRC. Three hundred and seventy-six scientists from 38 countries spanning 5 continents took part (Figures 1 and 2).

The Conference was organized according to IGAC's three main foci:

- Biosphere-atmosphere interaction
- Atmospheric aerosols
- Atmospheric photooxidants

with the additional topic of:

- Atmospheric chemistry-climate interactions

The Conference format consisted of background review papers for each session presented by invited speakers, as well as contributed papers selected by the Conference Program Committee. A total of 54 oral papers was presented, including an opening lecture, "Atmospheric Chemistry: Developments During the Past Three Decades, and a Look Ahead", presented by Nobel laureate Paul J. Crutzen. John Miller, Head of the Environment Division of the World Meteorological Organisation, gave an invited lecture on the perspectives of the Global Atmosphere Watch program and its connections with IGAC. The majority of contributions were presented as posters, with a significant fraction of each afternoon devoted to poster sessions. These were always lively and well attended. A total of 298 posters were on display during the Conference, divided among the four above topics.

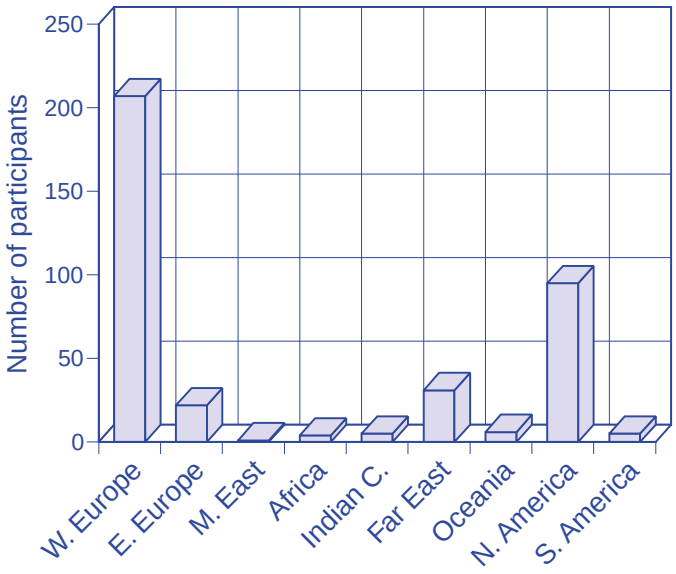

Figure 1. Distribution of participants in IGAC '99 among different regions of the world.

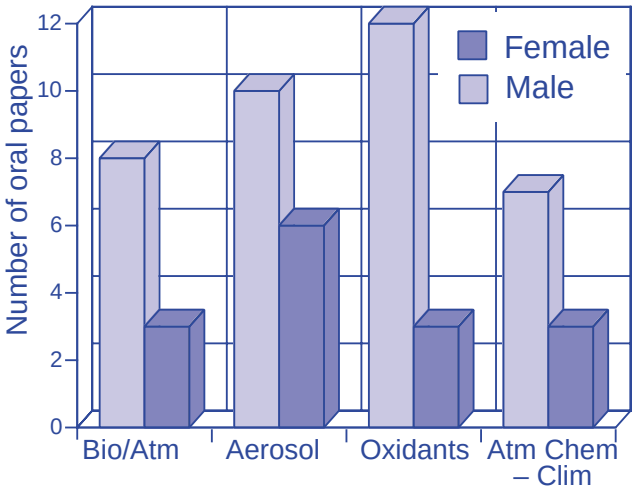

Figure 2. The 52 oral contributions divided by session and gender of the presenter.

Session reports

Session 1: Biosphere-Atmosphere Interactions (contributed by P. Ciccioli and A. Guenther)

A wide range of topics was presented in this session's oral and poster portions. The fundamental objective of the oral presentations was to assess the state of knowledge regarding exchanges of trace gases (mainly VOC, NO_x, NH_3, CO_2, CH_4) between the atmosphere and terrestrial and marine ecosystems and how these compounds play a fundamental role in global change through radiative forcing, ozone formation or acid deposition. Some oral presentations focused on methodological aspects related to flux determination by advanced techniques (such as micrometeorological methods, isotopic ratio analysis and inverse modeling). The possibilities afforded by these techniques were reviewed through critical analyses of recently collected data. Gaps to be filled in by ongoing and future research were clearly identified. Large emphasis was given to biogenic VOC due to their different photochemical ozone production potential and the possibility that they may act as a significant source of secondary aerosols. Presentations and discussions demonstrated that the role of biosphere-atmosphere interactions as a component of IGAC has expanded greatly in recent years from a few trace gases (CH_4, N_2O, isoprene, etc.) to a wide variety of compounds (acetaldehyde, acetone, toluene, selenium, NO, etc.). Another important direction has been a greater interaction between IGAC and other disciplines. Each of the other themes

(aerosols, photooxidants, climate) had presentations that touched on the biosphere, which in turn had a number of presentations connected with the other three themes. Thus the biosphere work has advanced from being primarily studies of trace gas fluxes to investigations of the implications of these fluxes on atmospheric chemistry.

Session 2: Atmospheric Aerosols (contributed by S. Fuzzi)

This session had the highest number of submitted contributions, an indication of this issue's increasing importance in the wider context of atmospheric chemistry. After spending much effort over the last decades on the study of gas phase processes, the role of multiphase processes in the atmosphere is now being fully recognized. The contributions at the Conference closely reflected the different areas of aerosol research: gas-to-particle conversion, aerosol–cloud interaction, aerosol source characterization, direct and indirect aerosol climate forcing. More than half of the presentations concerned field studies, while the rest were mainly modeling contributions, with only a few concerning laboratory studies. Efforts should be made in future conferences to involve a larger number of research groups from the laboratory community. Besides a majority of modeling and experimental contributions dealing with trends of aerosol concentrations and properties at different spatial scales, five subjects emerged as important components of international aerosol research: aerosol optical properties (mostly in relation to climate change), cloud processes, organic aerosol characterization and properties, mineral dust, biomass burning aerosol. These will certainly be the fields over the next few years where aerosol research will see major advancements. Also, at the time of the Conference the first important results of the ACE-2 experiment were being finalized for publication and several contributions were presented from this specific IGAC field campaign. A highly exciting future is to be expected for the whole field of multiphase atmospheric chemistry.

Session 3: Atmospheric Photooxidants (contributed by S.A. Penkett and H. Akimoto)

The session on photooxidants contained some very interesting presentations describing progress over the past decade towards understanding the behavior of ozone in the troposphere, much of it with an IGAC label. Papers were presented describing the situation in Europe, over the North Atlantic, over the Pacific, and in Asia. The coverage was therefore truly global. Highlights included the close agreement between predicted and measured fields of ozone and its precursors in pollution incidents, similarities in ozone seasonal behavior at many sites across the Northern Hemisphere, and the use of satellites to study detailed aspects of ozone production and dispersion in large pollution episodes. The change of the tropospheric ozone budget between 1860 and 1990 was discussed based on the new modeling results. Universal consensus now exists that most of the ozone observed in the troposphere is formed there by chemical processing rather than being transferred from the stratosphere. Though there have been many advancements in our understanding of sources and sinks of tropospheric ozone, revealed in both modeling studies and perhaps a more accurate estimate of emissions of precursor compounds into the atmosphere, significant areas of uncertainty remain. Both these features were highlighted in the invited papers, one of which was entitled, "Indications and Extent and Cause of Global Ozone Pollution", drawing attention to the extensive long-range transport of continental air pollution now taking place, and another entitled, "Tropospheric Chemistry of OH and Ozone: New Developments and Challenges," which showed that in the upper troposphere, at least, our understanding of the free radical chemistry is far from perfect. In particular, attention to the heterogeneous loss of HO_2 and NO_3 on aerosols was called for. The need for further research for a quantitative understanding of tropospheric photochemistry was clearly recognized during this session.

Session 4:Atmospheric Chemistry-Climate Interactions (contributed by J. Fishman)

This session reflected the growing complexity of the problems related to atmospheric chemistry. The overview paper was presented by Dr. Jeff Kiehl of the National Center for Atmospheric Research (USA) and highlighted how climate processes might respond to changes in atmospheric composition. The hydrologic cycle and how it is impacted by the surrounding chemistry is an important link in relating the climate system to atmospheric chemical composition and behavior. In particular, changes in clouds and precipitation can alter aqueous phase chemistry and the wet removal of species. Conversely, changes in convective activity can alter the vertical transport of chemical species. Just as natural modes of variability exist for the climate system, such modes exist for the chemical state of the atmosphere. An example of this was discovered in INDOEX. Due to the ENSO mode of variability in atmospheric circulation, there were significant shifts in the chemistry and aerosol effects in this region. Papers in this session illustrated the challenge in atmospheric chemistry to extrapolate local measurements to the global scale, and then assess what impact such perturbations have on the earth-climate system. Several papers highlighted findings from field programs spanning diverse spatial and temporal scales in regions from the temperate North Atlantic to the tropical Indian Ocean. Within the vertical domain, it was seen from the papers that composition changes at the surface may not be as important as chemical perturbations induced from subsonic jet aircraft flying at typical tropopause altitudes. In addition, the effects of aerosol composition on radiative transfer have added a new complexity to the role of aerosols in perturbing the climate. Lastly, the point was made that other links between modes of variability impacting the chemical and climate states need to be considered, as is the case with the exploration of any new research frontier.

Best poster awards

Four distinguished scientists (one for each session) had the task of selecting the best posters by young scientists (under 35 years old). The reviewers reported that the selection was not easy, since many posters were well prepared and contained new and very interesting results. At the end, the four selected posters were:

Session 1: Biosphere-Atmosphere Interactions

Scientist: **Xu Xiaobin**, Institute for Meteorology and Geophysics, J.–W. Goethe Univ., Germany

Poster title: Measurement of the exchange of COS and CS_2 between the atmosphere and a forest using the relaxed eddy accumulation technique

Co-authors: H. Bingemer and U. Schmidt

Session 2: Atmospheric Aerosols

Scientist: **Alena Kubatova**, University of Antwerp, Dept. of Pharmaceutical Sciences, Belgium

Poster title: Carbonaceous aerosol characterization in the Amazon basin, Brazil

Co-authors: R. Vermeylen, M. Claeys, J. Cafmeyer, W. Maenhaut, G. Roberts and P. Artaxo

Session 3: Atmospheric Photo-Oxidants

Scientist: **Katja Riedel**, Alfred-Wegener-Institute for Polar and Marine Research, Germany

Poster title: Variability of peroxides and formaldehyde in the Antarctic troposphere

Co-authors: R. Weller and O. Schrems

Session 4: Atmos. Chemistry-Climate Interactions

Scientist: **Myke Zachariasse**, Royal Netherlands Meteorological Institute, The Netherlands

Poster title: The influence of large-scale transport on the vertical ozone distribution over the Indian Ocean during the 1998 winter monsoon

Co-authors: P.F.J. van Velthoven, H.G.J. Smit & T.Mandall

It is worth noting that three of the four young scientists awarded prizes for best posters are women. All winners received a certificate and mementos.

The future of atmospheric chemistry

Roughly ten years have passed since the IGAC project was initiated by the Commission on Atmospheric Chemistry and Global Pollution (CACGP) and adopted as a Core Project of the International Geosphere–Biosphere Programme (IGBP). Presently the IGAC community is engaged in an integration and synthesis review to assess progress over the last decade. During the Conference a discussion was initiated of the future direction of global atmospheric chemistry research. Two panel discussions were organized, the first led by Hajime Akimoto and Leonard Barrie (President and Vice-President, respectively, of CACGP) and the second by Guy Brasseur (Chair of the IGAC Scientific Steering Committee). Leading scientists were asked to summarize their opinions before the floor was opened for discussion. Some major items were recognized as important gaps in knowledge to which renewed research efforts should be devoted in the future. A summary of these future needs for research in the field of atmospheric chemistry is given below.

Enhanced observation capability (for process study and trend detection)

- Satellites for troposphere constituents
- Networks (including vertical profiles and ancillary meteorological data)
- Instrument development (e.g., sensitive, robust devices to measure NH_3, NO_2, real time VOC, size-distributed particle properties, etc., including chemical sondes)
- Standardization and QC / QA internationally
- Data processing, interpretation and archiving

Atmospheric chemistry–cloud interactions

- Chemical controls on cloud processes
- Cloud impact on chemistry

Gas–surface heterogeneous processes (involving ice, aerosols and Earth's surface)

- Gas–particle conversion
- Physico–chemical equilibria
- Reaction mechanisms / kinetics

Near–tropopause studies

- Troposphere / stratosphere exchange
- Chemistry in upper troposphere / lower stratosphere

Regional emphasis

- Atmospheric chemistry in tropics & sub-tropics
- Continental effluent interaction with marine systems
- Eurasia
- Boreal Forest
- Role of urban complexes in regional / global chemistry

Atmospheric chemistry–climate feedbacks

- Carbon cycle and changing atmospheric chemistry
- Ozone tropospheric budget
- Aerosols

Organic chemistry of the troposphere

Education and communication

Final remarks

Participants unanimously expressed their pleasure at having been part of the IGAC Conference in Bologna. Several elements contributed to this appreciation: the high level of the presentations and posters, as well as the good organization and the kindness, warmth and efficiency of the Conference staff led by Mrs. Maria Teresa Tibaldi. Bologna was found to be a city rich in history and art. The city's cuisine was mentioned in several messages received by the Conference Organization. The 50 kg IGAC cake for the Conference dinner surely helped in this regard!

The IGAC '99 web page (www.fisbat.bo.cnr.it / IGAC99) will be kept active for some time: new information on publication of the proceedings, updates, and a picture gallery can be found there.

HO_x chemistry in the upper troposphere: Where do we stand?

Contributed by **Lyatt Jaeglé** (lyj@io.harvard.edu), *Harvard University, USA*

The central role of OH and HO_2 radicals (collectively known as HO_x) in driving tropospheric chemistry has long been recognized. OH oxidation of SO_2 in the upper troposphere initiates the nucleation of new particles, and HO_x radicals together with nitrogen oxides (NO_x) are key catalysts in the production of ozone, an effective greenhouse gas. Attention has recently focused on the upper troposphere due to the potential role of NO_x emissions from commercial aircraft in changing ozone and its climate forcing. Knowledge of the chemistry of HO_x is essential to assessing the effect of aircraft on ozone. Over the last five years direct atmospheric measurements of HO_x radicals and their critical controlling species have been conducted in the upper troposphere, providing the first tests of HO_x photochemistry in this region.

Initial surprises of upper tropospheric HO_x observations

The first measurements of HO_x radicals in the upper troposphere during the ASHOE/MAESA (1994), STRAT (1995-1996) and SUCCESS (1996) aircraft missions revealed a more photochemically active upper troposphere than had been anticipated [Folkins *et al*., 1997; Wennberg *et al*., 1998; Brune *et al*., 1998]. Observed HO_x levels were frequently 2-4 times higher than expected based on the commonly assumed primary source:

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \qquad (R1)$$
$$O(^1D) + H_2O \rightarrow OH + OH \qquad (R2)$$

By contrast, observations in the lower stratosphere had been generally reproduced well by models. To explain the elevated levels of HO_x in the upper troposphere, a number of new sources have been proposed. Acetone is ubiquitous in the troposphere and, at the low levels of water vapor in the upper troposphere, its photolysis can largely dominate (R2) as a source of HO_x [Singh *et al*., 1995; Arnold *et al*., 1997]. Inclusion of this source improved the predictions of models [McKeen *et al*., 1997; Brune *et al*., 1998], but in many cases observed HO_x levels were still much higher than expected. These cases were often associated with recent deep convection. How can deep convection affect upper tropospheric HO_x concentrations? Prather and Jacob [1997] found that convection turns over the upper troposphere at rates comparable to the photochemical processes controlling the abundance of HO_x. Thus, injection of air from the surface, carrying high levels of HO_x precursors, could be an additional HO_x source to the upper troposphere. Such precursors might include H_2O_2 [Chatfield and Crutzen, 1984], CH_3OOH [Prather and Jacob, 1997; Cohan *et al*., 1999], and aldehydes [Müller and Brasseur, 1999]. Photolysis of convected peroxides and CH_2O, together with acetone, seemed indeed to provide a strong enough source to account for the observed levels of HO_x [Jaeglé *et al*., 1997]. However, it was not possible to test the importance of these new sources directly because they were not measured during the initial three campaigns.

Recent observations of HO_x and its precursors during SONEX

The 1997 SONEX aircraft campaign over the North Atlantic provided the first measurements of HO_x concentrations concurrent with the ensemble of species thought to control HO_x production and loss: H_2O_2, CH_3OOH, CH_2O, O_3, H_2O, acetone and hydrocarbons. These observations allowed a detailed evaluation of our understanding of HO_x chemistry in the upper troposphere. Figure 1 shows a summary comparison between SONEX measurements and model calculations for HO_2, OH, and HO_2/OH.

The cycling between OH and HO_2 takes place on a time scale of a few seconds and is mainly controlled by CO+OH (R3) and HO_2+NO (R4). This cycle is very important because it also leads to the production of ozone:

$$CO + OH\ (+O_2) \rightarrow CO_2 + HO_2 \qquad (R3)$$
$$HO_2 + NO \rightarrow OH + NO_2 \qquad (R4)$$
$$NO_2 + h\nu\ (+O_2) \rightarrow NO + O_3 \qquad (R5)$$

As seen in Figure 1c, the HO_2/OH ratio is reproduced by model calculations to within the combined uncertainties of observations (±20%) and rate coefficients (±100%). Thus, the photochemical processes driving the cycling between OH and HO_2 appear to be well understood [Wennberg *et al*., 1998; Brune *et al*., 1998, 1999]. How well are the absolute values of OH and HO_2 reproduced by model calculations constrained with observations of HO_x precursors? Figure 1 illustrates that observed levels of HO_2 and OH are predicted to within about 40% (the reported accuracy of the HO_x observations). The median model-to-observed ratio for HO_2 is 1.12. The model captures 80% of the observed variance in HO_x, which is driven by the local concentration of NO_x and the strength of the primary HO_x sources [Jaeglé *et al*., 1999b].

Despite this overall good agreement, some systematic differences between observed and modeled HO_x as a function of NO have been noted and could reflect flaws in our understanding of the coupling between HO_x and NO_x chemistry involving HO_2NO_2 in particular [Brune *et al*., 1999; Faloona *et al*., 1999]. The observations shown in Figure 1 are for cloud-free, daytime conditions only. The

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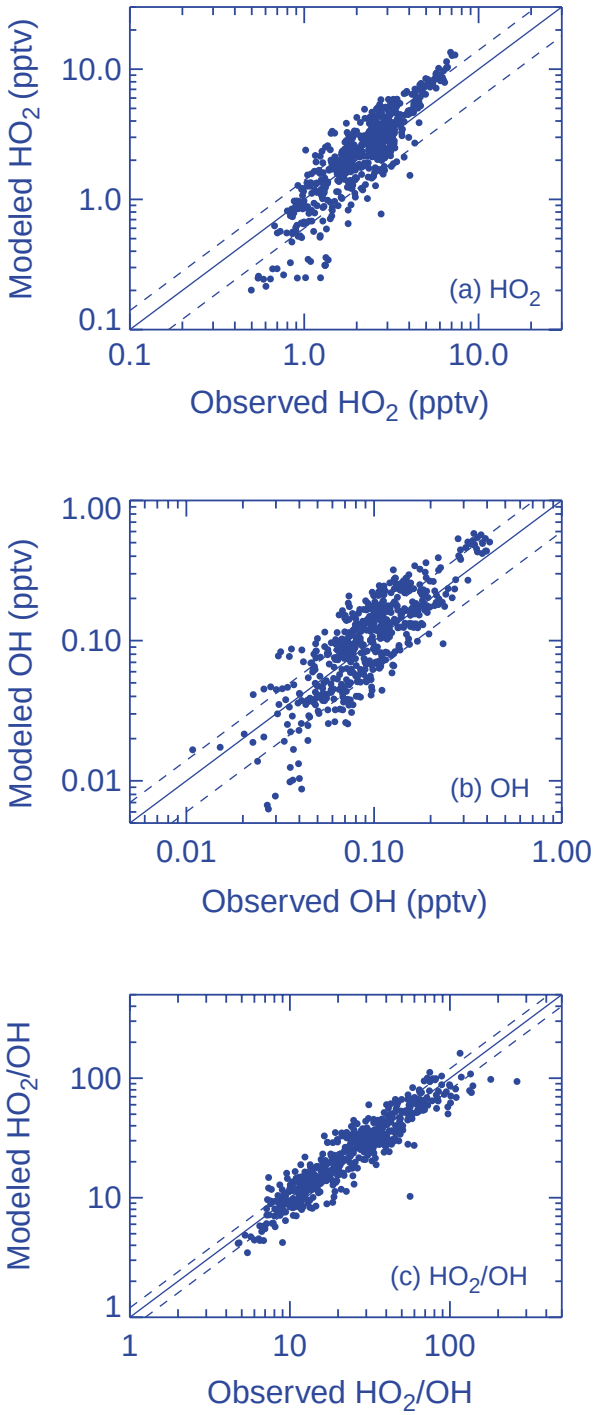

Figure 1. Comparisons between model predictions and observations for (a) HO_2, (b) OH, and (c) HO_2/OH in the upper troposphere (8-12 km altitude) during SONEX. Observations are for cloud-free, daytime conditions. The calculations were obtained with a diel steady state photochemical model constrained with local observations of H_2O_2, CH_3OOH, NO, O_3, H_2O, CO, CH_4, ethane, propane, acetone, temperature, pressure, aerosol surface area and actinic flux. The 1:1 line is indicated by the solid line and the dashed lines correspond to the instrumental accuracy. Adapted from Brune *et al.* [1999].

chemistry of HO_x at night and close to the terminator is not fully understood [Wennberg *et al.*, 1999; Jaeglé *et al.*, 1999b]. Model overestimates of HO_x inside cirrus clouds could be due to the rapid uptake of HO_2 on ice particles.

The primary sources of HO_x during SONEX were $O(^1D)+H_2O$ and acetone photolysis. The role of H_2O_2, CH_3OOH and CH_2O as net sources of HO_x was of much smaller importance compared to what had been inferred from previous campaigns. Although the concentrations of these HO_x precursors were enhanced in fresh convective outflows, the enhancements were driven primarily by the high levels of water vapor in these outflows. Most of the observations during SONEX took place at lower altitudes and warmer temperatures, such that water vapor levels were 3-10 times higher than during STRAT, SUCCESS, and ASHOE/MAESA, swamping out the effect of convected peroxides and aldehydes.

However, the concurrent observations of HO_x, H_2O_2, CH_3OOH and CH_2O allowed a constrained analysis of the photochemical interactions between HO_x and these species. In particular, observed H_2O_2 concentrations were reproduced by model calculations if heterogeneous conversion of HO_2 to H_2O_2 on aerosols was included [Jaeglé *et al.*, 1999b]. Observations of CH_3OOH were systematically underestimated by factors of 2 or more, possibly indicating poor knowledge of CH_3OOH reaction kinetics at cold temperatures. Observations of CH_2O were generally below the 50 pptv detection limit of the instrument, consistent with model results; however frequent occurrences of high values in the observations were not captured by the model. These high CH_2O values were associated with high methanol, so heterogeneous conversion of methanol to CH_2O on aerosols might provide an explanation [Singh *et al.*, 1999].

Sensitivity of HO_x and ozone production to changes in NO_x

The chemistry of HO_x and ozone production is tightly linked to the concentrations of NO_x: NO_x controls the cycling within HO_x, which leads to ozone production, and NO_x also regulates the loss of HO_x through reactions of OH with HO_2, HO_2NO_2 and NO_2. This results in the well known non-linear dependence of HO_x and ozone production on NO_x, which we can now test directly in the atmosphere with measurements of HO_x and NO_x species.

Figure 2a and Figure 2b show the variations of OH and HO_2 as a function of NO_x concentration during the SONEX mission. Photochemical model calculations for median background conditions, shown by the solid lines, illustrate the expected behavior of OH and HO_2 as a function of NO_x. In the model, OH increases with NO_x up to ~300 pptv NO_x due to the shift in the HO_2/OH ratio towards OH (reaction R4), and decreases with increasing NO_x at higher NO_x concentrations due to the loss of HO_x

promoted by NO_x. The concentration of HO_2 decreases with increasing NO_x as a result of the shift in the HO_2/OH ratio towards OH and thus a greater efficiency of HO_x sinks which depend on the OH concentrations.

These model dependencies of HO_x on NO_x are also generally found in the observations (Figures 2a and 2b). The scatter around the model lines can be often explained by variations in the magnitude of the local HO_x source [Jaeglé *et al.*, 1999a]. However, for high NO_x concentrations (>300 pptv), the model constrained with background conditions during SONEX underestimated observed HO_x by a factor of 2 or more. These high levels of NO_x were often associated with convection and lightning. Using the locally observed concentrations of HO_x precursors (H_2O, acetone, peroxides and CH_2O) for these points improves the agreement but still falls short of the observed levels of HO_x (see Figure 1). This discrepancy at high NO_x could be due to the presence of unmeasured HO_x precursors transported by convection, such as higher aldehydes, or it could indicate an incomplete understanding of the coupling between HO_x and NO_x chemistry at very high NO_x [Faloona *et al.*, 1999; Brune *et al.*, 1999].

Ozone production is initiated by OH oxidation of CO (R3), followed by reaction of the resulting HO_2 with NO (R4) and photolysis of NO_2 (R5). The rate-limiting step in this ozone production cycle is reaction of HO_2 with NO, such that the ozone production rate can be expressed as $P(O_3) \sim k_4[HO_2][NO]$. Concurrent observations of HO_2 and NO can thus lead to a direct determination of $P(O_3)$ in the upper troposphere (reaction of organic peroxy radicals RO_2 with NO generally contributes less than 15% of $P(O_3)$). As shown in Figure 2c, the expected dependence of $P(O_3)$ on NO_x is similar to that of OH: the model predicts that $P(O_3)$ should increase with increasing NO_x (NO_x-limited regime) up to a turnover point of ~300 pptv NO_x, beyond which further increases in NO_x cause $P(O_3)$ to decrease (NO_x-saturated regime). The bulk of the observations (NO_x<300 pptv) indeed shows a leveling off of the dependence of $P(O_3)$ on NO_x as NO_x increases above 70 pptv, in accordance with the expected behavior. However at the highest NO_x concentrations, $P(O_3)$ computed from observed HO_2 and NO continues to increase with increasing NO_x, suggesting a consistently NO_x-limited regime which is at odds with model results. This directly results from the model underestimates of HO_2 at high NO_x (Figure 2a).

Similarly to results from the SONEX mission, $P(O_3)$ versus NO_x relationships during ASHOE/MAESA, STRAT and SUCCESS also indicated a much greater prevalence of NO_x-limited conditions than expected from models. Part of this dependence could be due to the association of elevated NO_x with elevated HO_x precursors transported by convection. However, problems remain for very high NO_x. Are these problems due to missing HO_x sources, or due to flaws in our understanding of the chemistry? Determining the cause for this discrepancy is essential because it greatly affects the sensitivity of $P(O_3)$ to increasing NO_x. Current levels of NO_x (~50-100 pptv) place the upper troposphere in the NO_x-limited regime. Will future increases in NO_x due to anthropogenic activities lead to a leveling off of $P(O_3)$ in the NO_x-saturated regime as predicted by models, or will $P(O_3)$ continue to increase as suggested by observations? This issue clearly needs to be addressed, and calls for further studies of upper tropospheric chemistry.

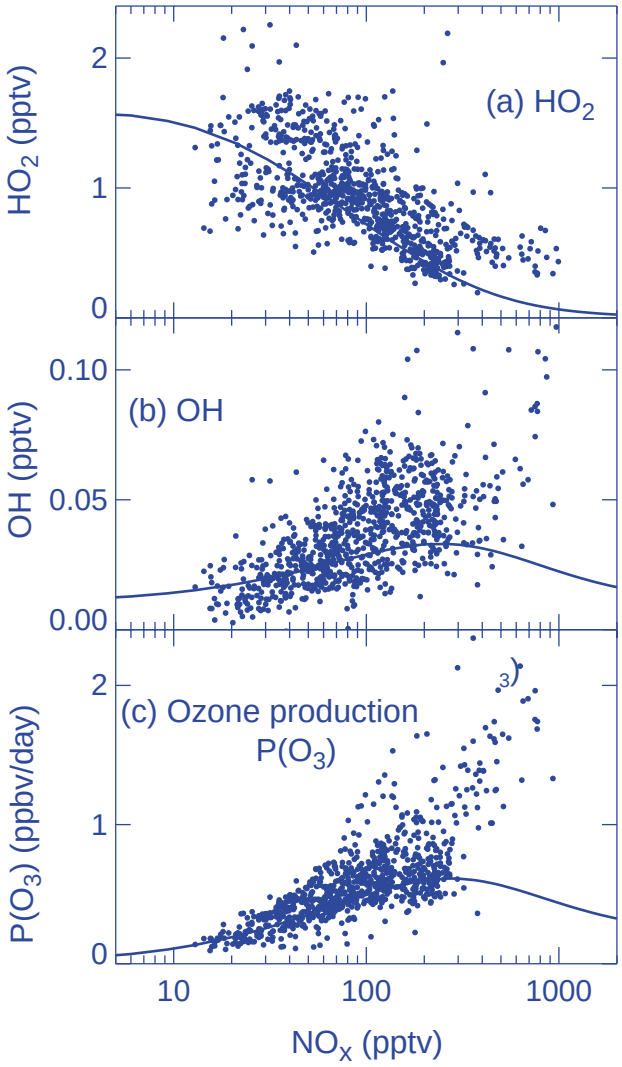

Figure 2. Observed (a) HO_2, (b) OH, and (c) ozone production rates $P(O_3)$ in SONEX (8-12 km altitude, 40°-60°N latitude) plotted as a function of the NO_x concentration (NO_x=NO+NO_2). The observed rates and concentrations are averaged over 24 hours to remove the influence of the diurnal cycle of solar radiation. The lines on the three panels correspond to model-calculated values for median upper tropospheric background conditions during SONEX. Adapted from Jaeglé *et al.* [1999a].

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Methyl bromide: An introduction to its use, its impacts, and its future

Contributed by **James H. Butler** (jbutler@cmdl.noaa.gov), *NOAA Climate Monitoring and Diagnostics Laboratory, USA*

Methyl bromide (CH_3Br) is an ozone-depleting trace gas in the atmosphere that for the past decade has been the focus of considerable scientific and political controversy. This controversy stems from the role of CH_3Br in stratospheric ozone depletion and its toxicity to humans, contrasted with its value as an agricultural fumigant. Although CH_3Br has been employed in a variety of applications, including fumigation of buildings, preservation of grains in silos, and treatment of fresh fruits, vegetables, or timber for export, its main use continues to be fumigation of soils (see article by Batchelor, this issue). Methyl bromide is particularly effective because it attacks a broad spectrum of pests, including weeds, nematodes, insects, fungi, bacteria, and some parasitic plants [Klein, 1996]. Because it penetrates the soil quickly, requires only a short period of exposure, and dissipates rapidly from the soil, it is ideal for pre-planting applications. Crop yield is considerably enhanced following such treatment and, unlike treatment with persistent pesticides, no organic residue is left in the soil to be concentrated through the food web. Much of the use of CH_3Br is for annual crops such as strawberries, melons, tobacco, flowers, and a variety of vegetables, but it is also effective in treating soils before planting fruit trees and grape vines.

Methyl bromide at high concentrations is toxic to humans. This has given rise to objections from farm workers and communities located near areas of its application. Efforts to tarp the soils and apply CH_3Br only during specific meteorological conditions have been made to reduce human exposure, but this is not always completely successful, nor is it always met with enthusiasm from nearby residents. Recent research suggests that employment of virtually impermeable film (VIF) tarps during application can reduce the emission of CH_3Br to the atmosphere to a few percent of that applied ([Yates *et al*., 1998]; see article by Yates *et al*., this issue). Deeper application into wetter soils can also reduce the flux of CH_3Br from the soil.

Despite this immediate health controversy, it is methyl bromide's role in depleting stratospheric ozone that has led to the planned, global phase-out of its anthropogenic production and use. Methyl bromide is responsible for over half of the bromine reaching the stratosphere [Schauffler *et al*., 1999], although not all of this is anthropogenic. Because stratospheric bromine is so efficient in depleting ozone (about 50 or 60 times that of chlorine on a per-atom basis), 10 pmol mol^{-1} (parts-per-trillion) of CH_3Br represents a chlorine equivalent on par with any one of the major CFC's at current atmospheric levels. However, unlike the CFCs and all other compounds being phased out by the Montreal Protocol and its amendments (e.g., UNEP, 1997), most CH_3Br in the atmosphere is emitted by natural processes and will continue to be emitted by these processes after fumigant emissions cease. The questions being addressed by the scientific community at this time are: (1) How much of the CH_3Br in the atmosphere is man-made? (2) What is the anticipated change in atmospheric mole fraction with change in emissions? (3) Where is CH_3Br in the atmosphere coming from? (4) Where is it going? and (5) How will natural fluxes be altered in the face of global change?

The most recent estimates of the global budget for CH_3Br cannot account for almost half of its sources ([Kurylo *et al*., 1999; Yvon-Lewis and Butler, 1997]; see article by Yvon-Lewis, this issue). Uncertainties on at least one of the budget terms, the soil sink, are large, but it is difficult to devise scenarios to balance the budget that do not require including additional, unidentified sources. Reaction of CH_3Br with tropospheric OH [Mellouki *et al*., 1992] and its irreversible loss to the ocean [Butler, 1994; Yvon-Lewis and Butler, 1997], two of the major loss terms, are reasonably well constrained. Recent studies have narrowed the calculated gap between sources and sinks, but a significant deficit of sources remains, amounting to about 30% of the identified sinks.

One of the difficulties in assessing natural, predominantly biological influences upon an atmospheric gas is that organisms or ecosystems can simultaneously consume or produce the gas (see article by Crill, this issue). They can do this much faster than the gas is exchanged with the atmosphere. This is clearly evident for CH_3Br, which is produced and degraded at fast rates in the oceans, produced and degraded by terrestrial plants, and perhaps produced and degraded in soils and sediments. Thus a measured net flux of the gas only tells part of the story. Although the net flux of a gas can be small, it may result from the near balance of two large, but opposite, gross fluxes, as evidenced by the exchange of CH_3Br (or CO_2, for that matter) between the atmosphere and ocean. The net flux also can be large and dominant, and thus approximate a gross flux to or from the atmosphere. The relative roles of these production and loss processes are at the core of the last question posed above: Just how might these production and loss processes be affected by some significant global change? The most obvious of possible global changes is, of course, temperature, but it also could be the amount, type and distribution of precipitation, or the dramatic reformation, replacement or loss of ecosystems. It is unlikely that any change, however widespread, will affect the rates of production and loss equally.

Methyl bromide's role in ozone depletion depends not only upon the amount of bromine it delivers to the stratosphere, but also upon the amount of chlorine present, as the removal of ozone by bromine involves the reaction of BrO with ClO. With plenty of chlorine available in the stratosphere in the future [Montzka *et al*., 1996; Montzka *et al*., 1999], increases or decreases in the total natural flux

of CH_3Br could still have a significant effect on stratospheric ozone or the timing of the recovery of the ozone hole. What is important now is to try to understand the cycling of CH_3Br in nature, how its fluxes might change in the future, and what effect this might have upon the atmosphere.

In this issue of IGAC*tivities*, articles are presented addressing the current status of our understanding of the behavior of CH_3Br in nature and the potential for its use or replacement as a fumigant in the future. Shari Yvon-Lewis of NOAA's Atlantic Oceanographic and Meteorological Laboratory summarizes the state of our knowledge on CH_3Br in the atmosphere and oceans. Patrick Crill of the University of New Hampshire discusses the effects of natural terrestrial systems upon atmospheric CH_3Br and the implications of some of the most recent findings in this field. Scott Yates of the USDA and the University of California at Riverside provides a synopsis of the fate of CH_3Br in soils following application and the factors controlling its emission. And Tom Batchelor, Co-Chair of the UNEP Methyl Bromide Technical Options Committee, gives us some insight into potential replacements for CH_3Br, their uses and limitations.

Editor's Note: *We gratefully acknowledge Jim Butler's help in organizing this group of articles on CH_3Br.*

Methyl bromide in the atmosphere and ocean

Contributed by **Shari Yvon-Lewis** (syvon@aoml.noaa.gov), *NOAA Atlantic Oceanographic and Meteorological Laboratory, USA*

Atmosphere

An understanding of the global distribution and temporal trends of atmospheric methyl bromide (CH_3Br) is necessary to place constraints on the magnitude and distribution of its sources and sinks. Although evidence suggests that the atmospheric burden of CH_3Br increased during the 1980s, its atmospheric mole fraction does not appear to have changed significantly during the past decade. Sources of CH_3Br include oceanic production, biomass burning, leaded fuel combustion, plant and marsh emissions, and fumigation of soils, durable goods, perishables, and structures. Sinks include photochemical decomposition in the atmosphere (reaction with hydroxyl radicals (OH) and photolysis at higher altitudes), loss to soils, chemical and biological degradation in the ocean, and uptake by green plants.

The ozone depletion potential (ODP) of CH_3Br is a function, in part, of its total atmospheric lifetime. The total atmospheric lifetime, τ, is determined by the reciprocal of the sum of the reciprocal partial atmospheric lifetimes with respect to each sink:

$$\frac{1}{\tau} = \frac{1}{\tau_{atm}} + \frac{1}{\tau_{soil}} + \frac{1}{\tau_{ocn}} + \left(\frac{1}{\tau_{plant}} ? \right) \qquad (1)$$

A substantial change in the ability of any one of these sinks to remove CH_3Br from the atmosphere can result in a change in the atmospheric lifetime and ODP for this trace gas. For example, a reduction in the global OH concentration would result in a longer partial lifetime, τ_{atm}, and a larger ODP. The effect of an increase in the sea-surface temperature would be more complicated. Oceanic chemical degradation rates would increase. Alone this would result in a reduction of the partial lifetime, τ_{ocn}, and subsequently the ODP. However, the effect that the increase in SST might have on the biological production and degradation of CH_3Br is not yet known. Global climate change could alter both the lifetime and ODP of this trace gas as well as other trace gases with similarly sensitive sources and sinks. There are studies currently underway that are beginning to examine the potential effect that global change may have on the lifetime and ODP of CH_3Br.

Distributions and trends

The number of field and monitoring programs that include CH_3Br has increased over the past few years. While the techniques and standards used by each investigator differ, recent intercalibrations combined with ambient measurements indicate that the global mean atmospheric mixing ratio for CH_3Br is between 9 and 10 pmol mol^{-1} [Kurylo *et al.*, 1999]. From a number of these field studies, the mean interhemispheric ratio (IHR) is currently estimated at 1.3 ± 0.1. This ratio appears to vary seasonally by about 0.2, driven mainly by variations in the Northern Hemisphere (NH) [Wingenter *et al.*, 1998]. The seasonal cycle observed in the high latitude NH appears consistent with OH seasonal variability, but is much larger than the seasonal cycle present in the SH (Figure1). This is not consistent with seasonality driven by OH oxidation. It strongly suggests that the variations of CH_3Br in the troposphere are modulated in good part by other seasonally varying sources and sinks in one or both hemispheres [Kurylo *et al.*, 1999].

The vertical distribution of CH_3Br has been studied both in the lower stratosphere and in the troposphere. Tropospheric levels of CH_3Br are typically found near the tropopause as well, although some profiles show a slightly decreased concentration of CH_3Br at the highest altitudes [Blake *et al.*, 1997; Schauffler *et al.*, 1998]. Once CH_3Br is in the stratosphere, its mixing ratios drop off rapidly with height, as a significant amount of reactive bromine is released [Lal *et al.*, 1994; Kourtidis *et al.*, 1998]. For some trace gases, vertical profiles in the troposphere

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may be used to put a lower limit on their lifetimes in the troposphere. A gas with a short atmospheric lifetime relative to the mixing time in the troposphere and having only surface sources should exhibit a tropospheric vertical profile that decreases with increasing altitude. However, once CH_3Br and other gases like it that have a relatively long lifetime with respect to gas phase reactions (1.7 y for CH_3Br) are released from the surface, they can become well mixed in the troposphere. There may be some near-surface gradients as a result of locally large surface sources or sinks, but this would depend strongly on local mixing and would not affect the calculated lifetime of this gas [Kurylo *et al.*, 1999].

Current monitoring networks did not start measuring CH_3Br regularly until just before the anthropogenic production rate was frozen by international agreement [UNEP, 1992]. The only long-term record of CH_3Br measurements before this period was reported by Khalil *et al.* [1993] and began in 1978 in the NH and in 1983 globally. The mean latitudinally-weighted, global growth rate calculated from these data was 0.15 ± 0.08 pmol mol^{-1} y^{-1} between 1983 and 1992. To obtain an idea of the earlier trends of CH_3Br in the atmosphere, Butler *et al.* [1999] measured CH_3Br in air that has been trapped in consolidated snow (firn) in Antarctica and Greenland. Although the Greenland data suggested unusual growth of CH_3Br in the firn air, which gives rise to questions about the integrity of an atmospheric imprint of this gas in the firn, results from Antarctica showed no signs of this activity. The Antarctic results, taken at face value, suggest that the CH_3Br growth rate increased from 0.01 pmol mol^{-1} y^{-1} in the early 1900s to 0.05-0.06 (±0.01) pmol mol^{-1} y^{-1} during the 1970s and 1980s. The increased growth rate during the 1970's coincides with increasing use of CH_3Br as an agricultural fumigant and is consistent with the SH measurements of Khalil *et al.* [1993] for that period.

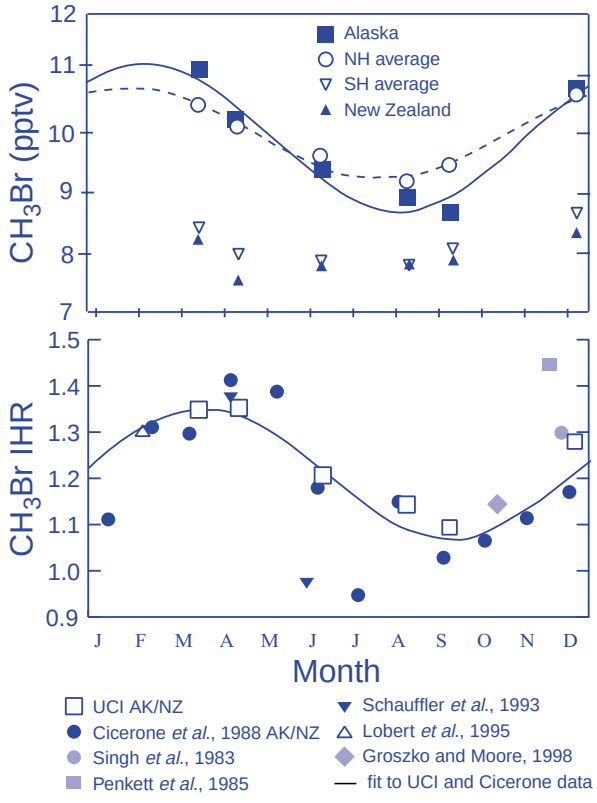

Figure 1. (a) Seasonality in CH_3Br mixing ratios in both the NH and SH; (b) Seasonality in IHR. Figure from Kurylo *et al.* [1999].

Ocean

The ocean acts as both a source and a sink for CH_3Br. The net flux of CH_3Br across the air-sea interface is controlled by a dynamic balance of *in situ* production and degradation as well as degradation during mixing out of the surface layer. Results from recent laboratory culture studies suggest that CH_3Br is produced by phytoplankton, although other organisms, such as zooplankton and bacteria cannot be ruled out as contributors [Tokarczyk and Moore, 1994; Moore *et al.*, 1995, 1996; Saemundsdóttir and Matrai, 1997]. Methyl bromide is degraded in seawater via hydrolysis and chloride substitution [Elliott and Rowland, 1993; Jeffers and Wolfe, 1996; King and Saltzman, 1997]. It has been shown that CH_3Br also undergoes biological degradation in tropical waters, which may be due to bacterial uptake [King and Saltzman, 1997] and that these rates are likely significant. Results from field studies, showing large undersaturations in polar and subpolar waters, also suggest a significant biological sink mechanism [Moore and Webb, 1996; Lobert *et al.*, 1997].

Oceanic uptake and emission

Recent laboratory studies have greatly improved the parameterizations for the chemical degradation rate constant [King and Saltzman, 1997; Jeffers and Wolfe, 1996], solubility [DeBruyn and Saltzman, 1997a], and diffusion coefficient [DeBruyn and Saltzman, 1997b] of CH_3Br. Using these results and a 2°x2° gridded global data set of physical properties of the ocean, Yvon and Butler [1996] calculated a τ_{ocn} of 2.7 y (2.4 – 6.5 y) for CH_3Br. This approach reduced the uncertainty in the Butler [1994] calculation of τ_{ocn} by including the seasonal and spatial variability of the ocean's physical properties. Nevertheless, significant uncertainties remain in the calculation of oceanic uptake and lifetime. The gas exchange coefficient, which is typically calculated from parameterizations defined by Liss and Merlivat [1986] or Wanninkhof [1992], imparts a factor of two uncertainty on the calculation of lifetime and uptake. Recent results indicate that the known chemical degradation mechanisms are not the only degradation mechanisms for CH_3Br in the oceans and make this calculation even more uncertain. Another degradation rate constant term must be included to account for this additional loss pathway. To date, King and Saltzman [1997] have reported the only direct measurement of this additional degradation rate. Moore and Webb [1996], Lobert *et al.* [1997], and Grosko and Moore [1998] reported indirect evidence for this additional degradation, where

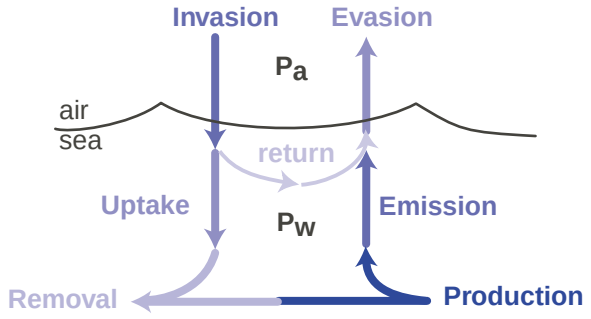

Figure 2. Schematic of the coupled ocean-atmosphere system, where P_a and P_w are the partial pressures of the species of interest in air and in the water. The net flux can be calculated as the difference between evasion and invasion, emission and uptake, or production and removal. The derivation and mathematical expressions for these terms are given in Butler and Rodriguez [1996]. The partial lifetime of atmospheric CH_3Br with respect to oceanic loss is calculated from uptake, which is an irreversible loss.

the observed saturation anomalies (deviations from air-sea equilibrium) could only be sustained with degradation rates substantially larger than the known chemical degradation rates. Yvon-Lewis and Butler [1997] estimated the magnitude and distribution of biological degradation from these data and recalculated a τ_{ocn} of 1.85 y (1.1 – 3.9 y), which now includes the additional loss.

A similar approach can be used to calculate the emission rate (Figure 2) of CH_3Br from the ocean to the atmosphere, where emission is defined as the fraction of CH_3Br produced in the ocean that reaches the atmosphere before being degraded in the water. Emission is distinct from evasion, as emission does not include the return of gas originating in the atmosphere (Figure 2). (This is similar to uptake and invasion.) While results from recent laboratory culture studies suggest that CH_3Br is produced, at least in part, by phytoplankton [Tokarczyk and Moore, 1994; Moore *et al.*, 1995, 1996; Saemundsdóttir and Matrai, 1997], the magnitude and distribution of gross production rates for CH_3Br are not known. Therefore, it has not been possible to calculate the emission rate directly. Currently, the emission rate must be calculated by difference between the net flux determined from the measured saturation anomaly and the uptake rate calculated using known oceanic degradation mechanisms (e.g., Lobert *et al.* 1995).

Observations of net flux

Results from a number of recent research cruises are used to determine the globally averaged net flux of CH_3Br across the air-sea interface. The net flux is calculated from the difference in the observed partial pressures of CH_3Br in air and dissolved in surface seawater and a calculated gas exchange coefficient. Not too long ago it was thought that the oceans were largely supersaturated in CH_3Br [Singh *et al.* 1983, Khalil *et al.* 1993]. This was noted in the 1994 Scientific Assessment of Ozone Depletion and it indicated that the oceans were a significant net source of CH_3Br to the atmosphere [Penkett *et al.*, 1995]. However, recent field studies in the Pacific [Lobert et al, 1995; Grosko and Moore, 1998], the Atlantic [Lobert *et al.*, 1996], the Labrador Sea [Moore and Webb, 1996; Grosko and Moore, 1998], and the Southern Ocean [Lobert *et al.*, 1997] have demonstrated that the oceans are a net sink for CH_3Br (Figure 3). The estimated global net flux of -21 Gg y^{-1} (-11 to -32 Gg y^{-1}) determined by Lobert *et al.* [1997] includes data from two cruises with long latitudinal transects in both hemispheres in the Atlantic and Pacific Oceans and one cruise in the Southern Ocean. Grosko and Moore [1998] calculated a global net flux of -10 Gg yr^{-1} (-3 to -13 Gg y^{-1}) from one long transect in the Pacific Ocean and a regional cruise in the Labrador

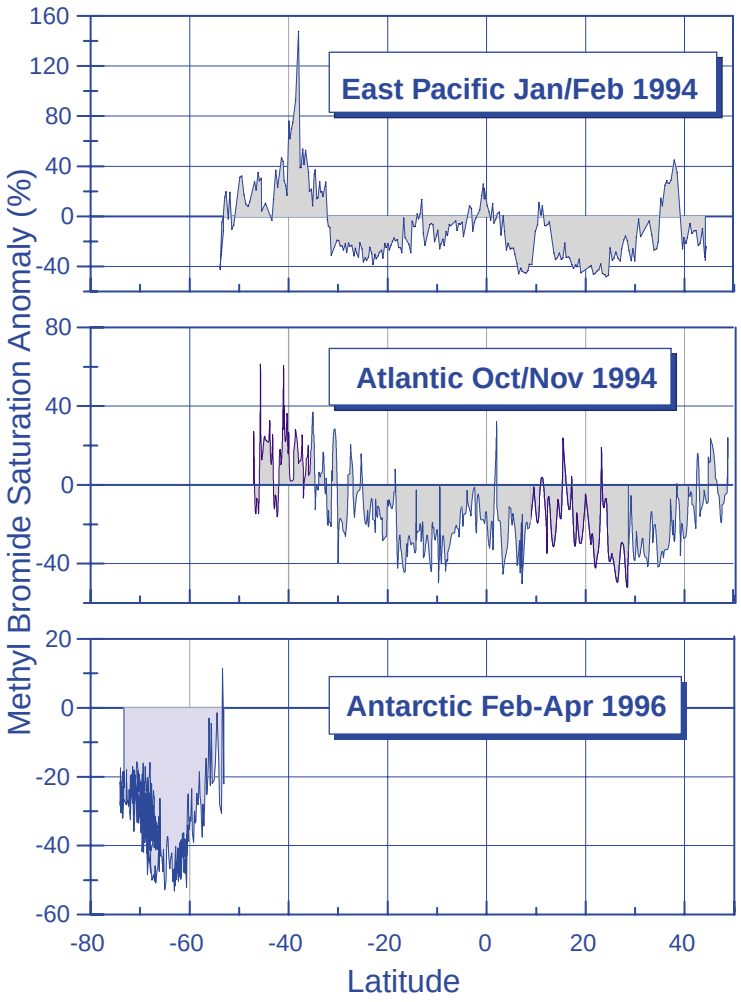

Figure 3. Distribution of the methyl bromide saturation anomaly from Lobert *et al.* [1995], Lobert *et al.* [1996], and Lobert *et al.* [1997].

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Sea. The Grosko and Moore [1998] studies were conducted at different times of year than that of Lobert *et al.* [1997], suggesting that seasonality may play a role in modulating the average global net flux. One recent study clearly demonstrated a seasonal cycle in dissolved CH_3Br in the shallow waters of the North Sea [Baker *et al.* 1998] and from the above studies there is weak evidence for seasonal cycling in temperate waters.

In attempts to derive the oceanic net flux of CH_3Br from differences in aquatic production and degradation, Anbar *et al.* [1996] and Pilinis *et al.* [1996] used different models whose results suggest that the high productivity in the high latitude polar waters would result in large supersaturations of CH_3Br in these regions. They predicted that polar and subpolar supersaturations were so large (200% - 500%) that the global net ocean-atmosphere flux left the oceans as a significant net source of CH_3Br to the atmosphere. To evaluate these predictions, measurements of the CH_3Br saturation anomaly (difference from equilibrium) were made in the Southern Ocean in early 1996, and showed a ~35% undersaturation virtually everywhere along the cruise track. This indicated that the polar oceans were a net sink, not a net source of CH_3Br [Lobert *et al.*, 1997]. Moore and Webb [1996] and Grosko and Moore [1998] obtained similar results for work in the Labrador Sea and northern Atlantic Ocean. The most recent Scientific Assessment on Ozone Depletion has adopted the -21 Gg y^{-1} from Lobert *et al.* [1997] as the current best estimate for the oceanic net flux of CH_3Br, but has expanded the uncertainty to include measurements of Groszko and Moore [1998]. This leaves a possible range of -3 to -32 Gg y^{-1} [Kurylo *et al.*, 1999].

Oceanic impact on atmospheric budget

A summary of the CH_3Br budget adopted by the most recent WMO Scientific Assessment for Ozone Depletion: [Kurylo *et al.*, 1999] is shown in Table 1. Since the assessment was finalized, additional research has generated emission estimates for some newly discovered, terrestrial sources of CH_3Br (see article by Patrick Crill, this issue). The results from some of these recent studies are also shown in Table 1. Gan *et al.* [1998] suggested that the global emission rate from the rapeseed plant alone is 7 Gg y^{-1}. From a study of salt marshes, Rhew *et al.* [1999] estimated that 10% (~14 Gg y^{-1}) of the total CH_3Br global emissions emanated from that source. Varner *et al.* [1999b], measuring the flux of CH_3Br from a fen and a bog in New Hampshire, put the global emission rate from wetlands at 4.6 Gg y^{-1}. An additional small source flux has been observed from rice fields, 1.5 Gg y^{-1} [Redecker *et al.*, 1999]. The emission of CH_3Br from the fungal decomposition of woody litter has been calculated at 1.7 Gg y^{-1} using a model and assuming that the CH_3Br production parallels methyl chloride production [Lee-Taylor and Holland, 1999].

Oceanic uptake of CH_3Br is currently estimated at 77 Gg y^{-1} [Kurylo *et al.*, 1999; Yvon-Lewis and Butler, 1997].

Table 1. Atmospheric CH_3Br budget adapted from *Kurylo et al.* [1999] and references therein. Italicized items are from work that was published after the WMO report was finalized. Numbers in parentheses represent the range of uncertainty for the best estimate shown.

Source Type	**Emissions (Gg y^{-1})**
Oceans	56 (5-130)[i]
Fumigation - soils	26.5 (16-48)
Fumigation - durables	6.6 (4.8-8.4)
Fumigation - perishables	5.7 (5.4-6.0)
Fumigation - structures	2 (2-2)
Gasoline	5 (0-10)
Biomass Burning	20 (10-40)
Wetlands	*4.6[b] (?)*
Salt marshes	*14[c] (7-29)*
Plants - rapeseed	*6.6[d] (4.8-8.4))*
Rice Fields	*1.5[e] (0.5-2.5)*
Fungus	*1.7[f] (0.5-5.2)*
Total =	**151[g] (56-290)**
Sink Type	**Uptake (Gg y^{-1})**
Oceans	77 (37-133)[i]
OH and hν	86 (65-107)
Soils	*46.8[a] (32-154)*
Plants	[h]
Total =	**210[g] (134-394)**

[a]Revised total soil uptake including cultivated soil uptake from *Varner et al.* [1999a]; [b]*Varner et al.* [1999b]; [c]*Rhew et al.* [1999]; [d]*Gan et al.* [1998] – net flux; [e]*Redecker et al.* [1999]; [f]*Lee-Taylor and Holland* [1999]; [g]Totals are rounded to the nearest integer; [h]Global estimate for plants not yet available; [i]The ranges in the oceanic source and sink terms must conserve the accepted range in the net flux, –3 to –32 Gg y^{-1}. Therefore, the lower limit in uptake, 37 Gg y^{-1} added to the upper limit for the net flux, –32 Gg y^{-1}, generates the lower limit in emission, 5 Gg y^{-1}.

This is comparable to the atmospheric degradation rate due to reaction with hydroxyl radicals and photolysis (86 Gg y^{-1}). Combined with losses to soils the total uptake of CH_3Br by sinks with at least partially known global distributions becomes 210 Gg y^{-1}. To maintain the net sink of 21 Gg y^{-1}, the estimated oceanic emission of CH_3Br must be 56 Gg y^{-1}. This leaves only 151 Gg y^{-1} in total emissions of CH_3Br to the atmosphere (Table 1). The remaining imbalance in the budget for CH_3Br is a 59 Gg y^{-1} missing source or sources—smaller than that given in the 1998 Scientific Assessment but still large enough to be of concern. Since the oceanic net flux could be at most 18 Gg y^{-1} too large, it is unlikely that the missing source will be found in oceanic fluxes. However, the ocean does constitute about one third of the budget and we do not know yet how the ocean will respond to global change in temperature, radiation or precipitation. Solutions to these questions can only come from studies of *in situ* production and degradation and their dependencies upon temperature, light, nutrients and other variables that regulate biological processes in the sea.

Natural terrestrial sources and sinks of tropospheric methyl bromide

Contributed by **Patrick Crill (**patrick.crill@unh.edu*), University of New Hampshire, USA*

Methyl bromide (CH_3Br) is an anthropogenically influenced trace gas that plays a central role in the Earth's stratospheric ozone balance. However, its environmental biogeochemistry is not well understood. Even though estimates of the mean tropospheric mixing ratio now agree within 10%, the atmospheric budget remains out of balance. Identified sinks outweigh known sources. Recent field observations have revealed hitherto unrecognized sinks and sources. Deposition of tropospheric CH_3Br to aerobic soils, perhaps a ubiquitous process, has added another sink. Now we are coming to realize that some of this imbalance may be resolved with recently discovered terrestrial sources of CH_3Br from salt marshes and flooded peatlands that could significantly impact its global budget. We are at a very early stage of this exciting research. Information is still lacking about the regional distribution, temporal and spatial variability, and magnitude of these newly recognized sources. Further research is required if we are to understand how flooded or altered soils might affect the ambient mixing ratios of CH_3Br and other methyl halides.

Introduction

The degree to which CH_3Br released in the lower atmosphere migrates to the stratosphere and releases Br to catalyze ozone destruction is directly proportional to its tropospheric lifetime [Solomon *et al.*, 1992; Mellouki *et al.*, 1992; Kurylo and Rodriguez, 1999]. Its lifetime is influenced by the rate at which CH_3Br reacts with hydroxyl radicals in the troposphere, the rate at which it is absorbed into surface waters, and the rate at which it is taken up into and destroyed in soil and / or on vegetation surfaces. The first loss term (reaction with hydroxyl radical) is reasonably well known [Mellouki *et al.*, 1992]. The second (oceanic uptake) is estimated from CH_3Br solubility, diffusivity, and surface exchange coefficient [Butler, 1994]. There are few data to allow an estimate of the third term (soil consumption). It had been observed that CH_3Br could be consumed in agricultural soils and this consumption was linked to ammonium fertilizer applications [e.g., Ou *et al.*, 1994]. It was also demonstrated that anaerobic soils when exposed to high levels could also consume CH_3Br [Oremland *et al.*, 1994]. However it was only recently demonstrated by the work of Shorter *et al.* [1995] that a wide variety of aerobic, drained, near-surface upland soils consume CH_3Br at near-ambient tropospheric mixing ratios. This observation has been subsequently corroborated by others [e.g., Serça *et al.*, 1998]; it appears to be a ubiquitous process of aerobic terrestrial soils.

The discovery of a hitherto unrecognized sink had two effects. One, it put the tropospheric budget further out of balance than it had been previously and, two, it lowered the ozone depletion potential from 0.6 to 0.4 [Kurylo and Rodriguez, 1999]. In terms of the balance between sources and sinks, either the tropospheric lifetime of CH_3Br had to be seriously overestimated (unlikely) and / or there had to be previously unidentified sources.

The soil sink of tropospheric CH_3Br

The principal sinks of atmospheric CH_3Br include reaction with OH [Mellouki *et al.*, 1992], irreversible loss to the ocean [Butler, 1994; Yvon and Butler, 1996], uptake by soils [Shorter *et al.*, 1995; Serça *et al.*, 1998], and possibly uptake by green plants [Jeffers *et al.*, 1998]. The sinks total approximately 205 Gg / yr [Kurylo and Rodrigues, 1999; Yvon-Lewis and Butler, 1997; see article by Yvon-Lewis in this issue for the most recent modifications], with the earliest reports of the soil sink contributing between 20% (42 ± 32 Gg y^{-1}, [Shorter *et al.*, 1995]) and 45% (94 ± 54 Gg y^{-1}, [Serça *et al.*, 1998]) of the total.

The Shorter *et al.* [1995] report was the first attempt to estimate the global uptake of ambient CH_3Br by soils. The research involved measuring the uptake of CH_3Br by selected soils from a New Hampshire forest, cornfield, and grassy field, as well as soils from Costa Rican tropical forest and Canadian boreal forest. Consumption into surface soils from enclosed headspace [chamber fluxes] was also observed. In the direct chamber measurements the loss rate of CH_3Br was greater than the loss of an inert tracer (SF_6) [Shorter *et al.*, 1995, Serça *et al.*, 1998] indicating an active consumption process. The rate of chamber-measured influx was consistent with flux rates extrapolated from soil incubation techniques. The use of a soil incubation assay for consumption allowed broad surveys to be carried out relatively quickly. Since the Shorter *et al.* [1995] paper, more than 230 soil samples have been collected from over 90 sampling locations across the United States, Alaska, Canada, Costa Rica, Brazil, Germany, China, Finland and Siberia. The soils were collected at agricultural, forest, meadow, pasture and desert locations, representing most of the major soil classification groupings. Consumption of CH_3Br could be measured in all the soil samples (see Table 1).

The temperate zone soils had the most rapid uptake of CH_3Br while the northern and tropical zones were consistently less active by about 10%. Surface soils were on average approximately 50% more active than deeper soils. In a few isolated cases deeper agricultural soils were more active. Similar rates of uptake of ambient CH_3Br were observed with direct chamber measurements of drained upland forest and agricultural soils in New Hampshire [Varner and Crill, unpublished data]. In addition Serça *et al.* [1998] reported bog microcosms to consume 2.1 + / - 0.9 Gg y^{-1}. However, direct chamber flux measurements indicate natural wetlands are net sources of CH_3Br rather than net sinks (see below).

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Table 1. Rates of uptake of CH_3Br by soils from different biomes.

Biome	Area x 10^{12} m^2	Active Season Days	Flux nmol m^{-2} d^{-1}	Total Uptake x 10^9 g y^{-1}
Tropical Forest and Savanna	22.5	365	8.3 ± 0.19	6.3 - 6.6[1]
Temperate Forest and Shrubland	20.0	240	47 ± 26	9.6 - 34[1]
Temperate Grassland	9.0	240	47 ± 16	6.5 - 13[1]
Boreal Forest	12.0	180	8.3 ± 0.21	1.6 - 1.7[1]
Cultivated Land	19.0	240	17.3 ± 0.15	6.8 - 8.1[2]
				26 - 95[3]
Bog, swamp, marshland	2.9	240	37 ± 14	1.5 - 3.3[3]
TOTAL				**32 -154**

[1]Shorter *et al.*, 1994; [2]Varner *et al.*, 1999a; [3]Serça *et al.*, 1998

Green plant material from a wide variety of species has also been shown in laboratory incubations of tissue under ppmv levels to be capable of consuming CH_3Br [Jeffers and Wolfe, 1997; Jeffers *et al.*, 1998]. Even though the authors point out that their observations are consistent with an enzymatic degradation, it is still uncertain how this fits into the atmospheric budget or whether this mechanism is operative under ambient (part-per-trillion by volume) mixing ratios. The role of plants in the consumption (and production) of atmospheric CH_3Br remains an exciting avenue of investigation.

The use of methyl halides by bacteria has been studied (but not in great detail) for more than 20 years. In the case of CH_3Br, more studies have concentrated on aerobic consumption because of fears of release of CH_3Br from soils during agricultural fumigation practices [Yates *et al.*, 1996a,b; Miller *et al.*, 1997]. Methyl halides can be consumed by whole cells and cell extracts of methanotrophic bacteria [Oremland *et al.*, 1994, Goodwin *et al.*, 1998]. Nitrifying bacteria also consume methyl halides via ammonia monooxygenase [Rasche *et al.*, 1990], and additions of ammonia fertilizers stimulate consumption by agricultural soils [Ou *et al.*, 1997].

Methyl halides can also be consumed microbially in anaerobic environments. CH_3Br can be utilized through a nucleophilic substitution with sulfide, which produces methylated S gases [Oremland *et al.*, 1994b].

The above studies were performed with mixing ratios or concentrations of substrate that were orders of magnitude larger than ambient levels. Since then, techniques have been developed that allow us to measure the process of CH_3Br consumption at near-ambient levels. We have learned the following from these studies [cf., Hines *et al.*, 1998]:

- *Consumption in aerobic soils is biologically mediated.* The temperature response of the activity—specifically, declining activity above 30°C—is consistent with biological processes. Autoclaving stops consumption altogether.
- *Consumption is bacterial*. Consumption is sensitive to antibiotics specific to bacteria but not sensitive to inhibitors that affect higher organisms.
- *Rates of consumption appear to be sensitive to soil moisture and/or soil organic matter (SOM) content*. Drier soils and those poor in organic content demonstrate slower rates. SOM and soil moisture are not independent variables, so it is difficult to distinguish the effect of either.
- *The activity is aerobic*. Flooding soil samples with nitrogen slows or stops the activity.
- *The depth distribution of the activity in soils is different from that of methane oxidation*. Unlike methane oxidation, where the activity is greatest a few centimeters deep in the soil just at the base of the surface organic layer, CH_3Br consumption activity is always greatest at the surface except in the driest agricultural soils.

Non-anthropogenic terrestrial sources of tropospheric CH_3Br

The few estimates of global sources of CH_3Br per annum are listed by Yvon-Lewis and Butler [1997] and in the latest Scientific Assessment of Ozone Depletion [Kurylo and Rodrigues, 1999; see also article by Yvon-Lewis in this issue.] The only number known with any certainty is the annual production by the CH_3Br industry of 66 Gg. Of that amount, 20-80% is thought to make its way into the troposphere [Yagi *et al.*, 1995]. The oceanic source of 56 Gg y^{-1} is exceeded by its sink of 77 Gg y^{-1}, leaving a small net flux from the atmosphere to the ocean. Expanding the work of Harper *et al.* [1986], Lee and Holland [1999] suggest that the ability of *Phellinus* spp. fungi to methylate halogens could result in a potential source of 0.5 to 5.2 Gg y^{-1} to the global atmosphere from forest soils.

Biomass burning is another important source of tropospheric methyl halides [Manö and Andreae, 1994, Blake *et al.*, 1996]. Biomass burning may inject into the troposphere an amount of CH_3Br that is similar in magnitude to oceanic and industrial sources. The uncertainty in the estimates is such that burning could contribute about 20% of the total source.

As noted above, the global budget of CH_3Br has been significantly out of balance with known sinks greater than identified sources by over 80 Gg y^{-1}. Recently, this number has been reduced to 60 Gg y^{-1}, owing to the discovery of specific plant sources. Within the past two years, the field observations of three graduate students, Robert Rhew of Scripps Institution of Oceanography (UC San Diego), Claudia Dimmer of University of Bristol, UK, and Ruth Varner at the University of New Hampshire, have revealed potentially important new sources of CH_3Br (and other methylated halogens) from salt marshes and freshwater wetlands. Also, Kelly Redecker at UC-Irvine has been working to characterize the emissions of CH_3Br from the anthropogenic wetlands of rice agriculture.

Laboratory incubations of small amounts of material collected in the field have not identified peats or other organic rich soils to be sources of CH_3Br. This is in part due to the small sample sizes and the attendant analytical difficulties. Direct field measurements use large chambers or boxes (often temperature controlled and mixed with fans) to isolate an atmosphere over a soil surface, and changes in the mixing ratios of CH_3Br are measured by sequentially sampling the enclosed headspace. A chemically and biologically inert tracer (SF_6 or a CFC) is sometimes used to measure the dilution and the diffusive and advective loss rates of the gas from the chamber.

Dimmer *et al.* [1999] and Varner *et al.* [1999b] have measured effluxes directly in Irish peatlands and in New Hampshire wetlands, respectively; extrapolation yields net annual global emissions of CH_3Br of about 5.0 and 4.6 Gg. The extrapolated fluxes from rice fields are significantly less, at 1.5 Gg [Redecker *et al.*, 1998]. Rhew *et al.* [1999] have observed substantially higher emissions from coastal salt marshes that extrapolate globally to 14 Gg y^{-1}. As they point out, this would mean that 0.1% of the global surface area could produce roughly 10% of the total flux. If 60 Gg y^{-1} are from fumigation losses and leaded gasoline burning and all of the biomass burning is considered non-anthropogenic, then the natural emission is 80 Gg y^{-1} and the contribution of salt marshes would be closer to 18% of the total.

New sources of atmospheric CH_3Br have been discovered and the relative magnitudes of those sources are just beginning to be quantified. We need to understand both the spatial and temporal variability in the emissions across a landscape and why the variability is so great. The accumulation and flux of methyl halides in wetlands must be controlled by both production and consumption processes, and these processes are probably controlled by biogeochemical conditions.

Plants, specifically those from the Brassicaceae family, have been shown to produce CH_3Br when grown in soils with elevated bromide concentrations [Gan *et al.*,1998]. Leaf disks from a number of different plants of different species and different families will produce methyl halogens when floated in solutions with elevated halide concentrations [Saini *et al.*, 1995]. Gan *et al.* suggest that one crop alone (rapeseed) could be contributing a net of 7 Gg y^{-1} to the atmospheric budget. Saini *et al.* [1995] point to the likely involvement of a non-specific methyl transferase. This would also imply a correlation between CH_3Br production and that of other halogenated methanes, such as methyl chloride, which has been observed in the flux studies [Rhew *et al.*, 1999; Varner *et al.*, 1999b]. Rhew *et al.* [1999] also noticed a correlation between green plant density and emission implicating plants in the production and / or transport of CH_3Br from salt marsh soils to the atmosphere.

There has been considerable progress recently in quantifying and understanding the variability of CH_3Br exchange with the atmosphere. Our beginnings remind us of how much remains to be done to address these important issues. Tasks include the following:

- Determine the rate and ubiquity of CH_3Br (and other halogenated methanes when possible) exchange from direct measurement surveys across aerobic soil types from different biomes, along trophic gradients of freshwater wetlands, and across salinity gradients of coastal salt marshes.

- Determine quantitatively the controls and the biological dynamics of formation and consumption of CH_3Br (and other halogenated methanes when possible) with laboratory studies and field measurement programs designed to resolve spatial variability with specific biome types.

- Determine the magnitude and the seasonality of exchange rates of CH_3Br at a number of field sites by frequent direct measurements of soil exchange.

- Develop techniques to resolve quantitatively the simultaneous processes of consumption and production (the gross fluxes) of methyl bromide from terrestrial systems, by use of isotopes or other novel approaches. This understanding is needed to obtain an accurate estimate of the partial atmospheric lifetime with respect to these sinks, and to evaluate or predict the effects of global change upon the emission of CH_3Br and, ultimately, its atmospheric burden.

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Controlling agricultural emissions of methyl bromide

Contributed by **Scott R. Yates** (syates@ussl.ars.usda.gov), **Dong Wang**, **Sharon K. Papiernik** *and* **Jay Gan**, *U.S. Dept. of Agriculture, Agricultural Research Service, USA*

Over the last 40-50 years methyl bromide (CH_3Br) has been used throughout the world to sterilize soils in preparation for planting various high-cash-value fruit and vegetable crops. Highly toxic, CH_3Br is very effective in controlling a variety of soil-borne pests, such as nematodes, weeds and fungi. CH_3Br has been an important component of agricultural systems in the U.S. and its phase-out is expected to cause financial hardship to agricultural producers. Recent economic assessments estimate that more than $1.5 billion in annual lost production would occur in the United States alone [NAPIAP, 1993; Ferguson and Padula, 1994].

In most commercial operations, CH_3Br is applied from a tractor pulling two or more metal shanks that cut into the soil. CH_3Br is injected into the soil at approximately 25 cm depth from nozzles on the backside of each shank. Simultaneously, the tractor lays down a 3.5 m wide sheet of 0.025 mm thick high-density polyethylene (HDPE) plastic film; burying one side and gluing the other side to the previous plastic sheet. This creates a series of panels down the field and a continuous cover over the field. Large amounts of CH_3Br are applied at rates ranging from 200 to 400 kg / ha.

Emission of CH_3Br into the atmosphere is affected to a large degree by the properties of the soil, ambient environmental conditions, application methods, and properties of the plastic film used to seal the surface. Recent research has shown that the traditional HDPE film is largely ineffective in containing CH_3Br in soil. This can be seen from Figure 1, where the fraction of CH_3Br lost to the atmosphere is presented as affected by various fumigation practices (e.g., shallow vs. deep injection, cover vs. no cover, HDPE vs. Hytibar, dry soil vs. sealing the soil surface with water).

This figure includes all recent experiments on CH_3Br emissions into the atmosphere [Yagi *et al.*, 1993, 1995; Majewski *et al.*, 1995; Yates *et al.*, 1996, 1997; Williams *et al.*, 1997; Wang *et al.*, 1997]. It is clear that HDPE's effectiveness in controlling emissions is similar to that of bare soil, deep injection or applying water to seal the soil surface. The use of a virtually impermeable film (VIF) such as Hytibar, however, shows a dramatic reduction in the emission rate.

Hytibar is many times less permeable than HDPE, as shown by the film's mass transfer coefficient (Table 1). The mass transfer coefficient is a property of a film that characterizes the ease with which a chemical passes through the film. For standard HDPE, the mass transfer coefficient is 0.35 cm h^{-1} while that for Hytibar is almost three orders of magnitude lower.

If the film plays an integral role in controlling the emission process, one would expect that the ratio of the observed emissions from a field covered with HDPE to one covered with VIF would be similar to the ratio of the permeability of HDPE to VIF. For example, the ratio of the film permeability (HDPE / Hytibar) has been estimated to be from 200 [Wang *et al.*, 1998] to 900 (Table 1). These values were obtained in an ideal system where there is no degradation and the film remains in ideal condition. In the field, however, the film is subjected to a harsh environment and one would expect the field-scale permeability to be affected by stretching, tears, holes and the seams between plastic sheets. Therefore, the effective permeability would be less than this ideal case. In a recent experiment using Hytibar conducted in the field, the ratio of the total emissions from plots covered with HDPE to those covered with Hytibar was approximately 33 [Yates *et al.*, 1998]. This result suggests that total emissions can be reduced by an order of magnitude by using VIF.

The main disadvantage of using VIFs alone is the need to keep the soil covered for several weeks to avoid the release of fu-

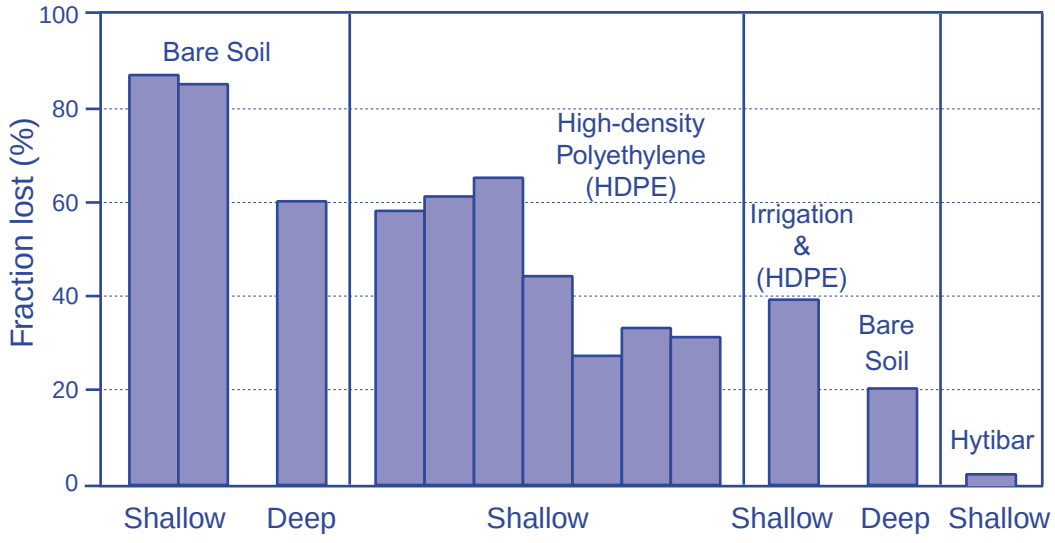

Figure 1. Comparison of total emission loss as affected by various fumigation practices. Shallow (25-30cm) and deep (50-70cm) indicate the injection depth.

migant when the tarp is removed. Soil degradation is highly variable and depends primarily on the soil water content and soil organic matter content. However, CH_3Br can be degraded in soil by hydrolysis, with a half life of approximately 50 d, or by reaction with nucleophilic functional groups (e.g., $–NH_2$, –NH, –SH, –OH) in soil organic matter or soil amendments. The rate of nucleophilic substitution is highly variable and depends on the quantity and type of functional groups available in soils. In loamy soils with greater than 1% organic matter, observed degradation half-lives range from 4 to 21 days [Arvieu, 1983; Gan *et al.*, 1998a].

Table 1. Mass transfer coefficients (cm h^{-1}) for CH_3Br and chloropicrin diffusing through four plastics at 20°C. The data were obtained using static permeability cells [Papiernik *et al.*, 1999]. Film permeability (cm^2 h^{-1}) can be obtained by multiplying the mass transfer coefficient by the film thickness.

Fumigant	1-mi HDPE	4-mil black HDPE	2-mil silver mirrored mylar	1-mil Hytibar
Methyl bromide	0.35	0.097	0¶	0.00038§
Chloropicrin	0.57	0.15	0¶	na

§ - preliminary value.

¶ - not measurable after 40 days.

The addition of soil amendments (e.g., organic matter or thiosulfate materials) can enhance the degradation of CH_3Br. Recent research has demonstrated that significant reductions in emissions of CH_3Br and other soil fumigants can be obtained by simply adding organic material or a thiosulfate fertilizer to the soil surface [Gan *et al.*, 1998a,b]. Shown in Figure 2 is the fraction of fumigant lost from soil after the soil has been amended with either organic material or ammonium thiosulfate.

The addition of organic material can help reduce CH_3Br emission by as much as 25%. Spraying a thiosulfate amendment onto the soil surface after fumigation can reduce emissions by an order of magnitude, provided a sufficient quantity of thiosulfate is applied. Ammonium thiosulfate is a commonly used agricultural fertilizer and would add only a small cost to soil fumigation. In addition, a fertilizer amendment might be needed anyway to help add nutrients for the growing season.

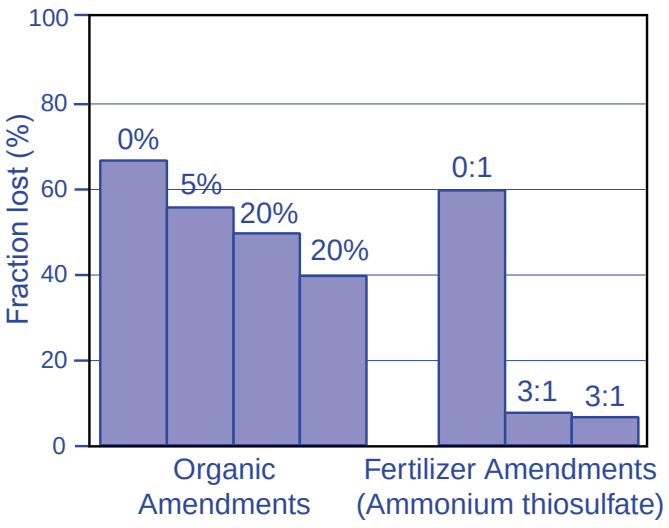

Figure 2. Effect of soil amendments on the fraction of fumigant lost from soil columns after addition of organic material or increasing ratios of ammonium thiosulfate.

Therefore, CH_3Br emissions can be significantly reduced by improving containment, or enhancing soil degradation, or both. Since various transport processes also affect the total degradation in soil, CH_3Br emissions can be managed, provided the chemical remains in the soil for a sufficient amount of time. Enhancing soil degradation by adding nucleophilic material may provide added benefit to the soil (e.g., nutrients or soil conditioners) and could increase the degradation rate so that VIF would not have to remain on the soil surface for excessively long periods. If market competition reduces the price of VIF, the fumigation cost should not increase appreciably. Also, since VIFs maintain higher fumigant concentrations for longer times, the fumigation cost may even be reduced due to a lower application rate of CH_3Br needed for pathogen control.

As the CH_3Br phase-out date approaches, some questions remain whether restricting CH_3Br use will have a significant effect on stratospheric ozone levels [Honaganahalli and Seiber, 1997]. Further, it appears that methodology exists that would enable CH_3Br emissions from fumigated soils to be reduced by at least one order of magnitude. This would reduce the global CH_3Br contribution from agricultural use to less than 1% [Yates *et al.*, 1998] of the worldwide sources.

The question that seems to have been overlooked in deriving current regulations is whether any of the replacement chemicals will be more harmful to the environment as a whole than CH_3Br, and if so, what steps can be taken to continue its use but eliminate the negative environmental impacts. If the issue is mainly to keep CH_3Br out of the atmosphere, then approaches other than banning use of the chemical may be equally suitable. In fact, providing incentives to develop technology that minimizes negative characteristics before they become environmental or public health problems is certainly a desirable overall approach to any environmental regulation. As scientists we must continue to find methods to protect the environment. In the case of CH_3Br, considering alternatives to a ban on its production and use might minimize negative effects to the economy or food supply as well.

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Alternatives for the ozone depleting chemical, methyl bromide

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Introduction

Methyl bromide (CH_3Br) is a fumigant that was first listed as an Ozone Depleting Substance (ODS) under the 1992 Montreal Protocol, an international environmental agreement that aims to eliminate chemicals that reduce the ozone layer. Methyl bromide is a versatile chemical with a wide range of applications. For more than 40 years it has been used commercially to control pests such as fungi, bacteria, soil-borne viruses, insects, mites, nematodes and rodents. CH_3Br has sufficient phytotoxicity to control many weeds and seeds in soils. Used mostly for soil fumigation, a moderate amount is also used for disinfestation of durable and perishable commodities and a minor amount is used for disinfestation of buildings, ships and aircraft. Its action is usually sufficiently fast and it airs rapidly enough from treated systems to cause relatively little disruption to commerce or crop production.

Ozone depletion

Methyl bromide is a significant ozone depleter with a 0.4 Ozone Depletion Potential (ODP), according to the most recent Scientific Assessment on Ozone Depletion [Kurylo *et al*., 1999]. This means that, on a per molecule basis, its effectiveness in depleting ozone is about four times that of methyl choroform and 40% that of CFC-11, two chemicals banned in 1996. Thus, the bromine in CH_3Br, known to deplete 40-50 times more ozone than chlorine (atom for atom), makes CH_3Br one of the more hazardous substances for the ozone layer listed under the Protocol, despite its low atmospheric concentration.

In the international schedule to phase out production of CH_3Br, governments under the Protocol agreed that developed countries would cut CH_3Br consumption by 25% in 1999, 50% in 2001, 70% in 2003, with phase out by 2005. Developing countries need to reduce their consumption by 20% in 2005 and phase out by 2015. CH_3Br used for quarantine and pre-shipment (QPS) treatments is exempt from these controls, as the governments under the Protocol considered that CH_3Br was strategically useful for protecting countries against unwanted pests in imported agricultural foods. The volume of CH_3Br consumed for this purpose is relatively small. Similarly, CH_3Br used for feedstock in industrial processes is also exempt, as most of it is consumed in chemical reaction.

Despite CH_3Br being a useful pest management agent in specific instances, its listing under the Protocol necessitates ultimately that its production must cease.

Consumption

Of the 1996 global production of methyl bromide of 71,425 tons, approximately 2,759 tons (3.9%) was used as a feedstock for chemical synthesis with the remaining 68,666 tons produced for fumigation. Based on official data, the 1996 global consumption for fumigation (including that used for quarantine treatments) was estimated as 66,750 tons, with approximately 76% of this used as a treatment to control soil pests, weeds and diseases immediately prior to planting a crop; 15% for fumigation of durable commodities (such as walnuts, rice and grain) and structures (such as flour mills and food processing facilities); and 9% for perishable commodities (such as apples and leafy vegetables).

There has been consistent evidence in recent years showing that the Montreal Protocol system is working. Scientists are reporting for the first time a consistent downward trend since 1994 in effective chlorine loading in the lower atmosphere [Montzka *et al*., 1999; Montzka *et al*., 1996]. As the upper atmosphere lags behind by about 6 years, it is predicted that a similar trend will be recorded there next year.

However, the stratosphere is most vulnerable to ozone depletion today and will remain so for the next couple of decades [Hofmann *et al*., 1999]. There is no evidence of replenished levels of ozone and this is not expected for another 20-30 years. For these reasons, countries are constantly reminded not to be complacent and to make every endeavor to continue to phase out ozone-depleting chemicals.

Development of alternatives to CH_3Br

One of the challenges of the last decade has been the ongoing need to develop and implement alternatives to CH_3Br for all its diverse uses. Research institutes and agencies in both developed and developing countries are finding that there is no one-shot replacement for CH_3Br and that combinations of practices or treatments will often be required. This results in farmers and pest control operators having to learn new ways of controlling pests and, unlike most chemical control methods, these new ways are knowledge intensive.

A report detailing alternatives available or being developed to substitute for CH_3Br was recently submitted to the United Nations Environment Programme (UNEP) for the governments under the Montreal Protocol [UNEP, 1998]. The report was written by UNEP's Methyl Bromide Technical Options Committee (MBTOC), which currently consists of 35 experts—12 from developing countries and 23 from developed countries. (This report is available on http://www.teap.org, a website that reports on alternatives for a number of ozone depleting substances including CH_3Br.)

The report assesses alternatives available in four categories of use and discusses opportunities for capturing and recycling this fumigant. The categories are treatments for fumigating the soil before planting a crop, for quarantine, for durable commodities, and for food processing facilities.

Soil treatments

Soil fumigation with CH_3Br is the single largest use category, accounting for about 76% of global use. Methyl bromide is used as a pre-plant soil fumigant in locations where a broad complex of soil-borne pests limits economic production of crops and particularly in situations where the same crops are grown repeatedly on the same land. Methyl bromide has been successfully used under a variety of cropping systems. The major current categories of use include vegetables, fruits, ornamentals, tobacco and some nursery crops.

Significant progress has been made in the past four years identifying alternatives to CH_3Br for soil fumigation. In spite of the widespread use of CH_3Br as a soil fumigant, the MBTOC did not identify a single crop that could not be produced successfully without the use of this fumigant. However, increased investment in research and technology transfer would be necessary to fully implement alternative pest management systems worldwide.

Integrated pest management (IPM) strategies, which combine various pest management methods (non-chemical and / or chemical), were considered the best alternative to CH_3Br, as they are likely to be the most sustainable and environmentally benign. IPM programs have one or more of the following key elements based on incorporating as many biological control methods as possible:

- Cultural practices such as crop rotation, soil-less culture, organic amendments, biofumigation, planting time, water management and flooding, mulching, cover crops and sanitation
- Biological control such as plant growth promoting rhizobacteria, resistant plant varieties and grafting of annual and perennial crops
- Physical methods such as soil solarization and steam treatments
- Strategic applications of selective pesticides

Quarantine treatments

Methyl bromide is typically applied to perishable commodities as a quarantine treatment to prevent pests from becoming established in an area where they are not currently present. Perishable commodities include fresh fruit and vegetables, cut flowers, ornamental plants, fresh root crops, and bulbs. About 9% of global CH_3Br consumption is used for disinfestation of perishable commodities, with about half used for disinfestation of fruit for quarantine purposes.

The MBTOC identified at least thirteen different categories of alternative treatments (e.g., heat, cold, irradiation) that are approved by regulatory agencies in one or more countries for disinfestation of perishable commodities, but only for very specific applications. Only a small proportion of commodities in commercial trade are treated in the export country using these alternatives, as most countries have specific requirements for proving the efficacy of any treatments for each commodity-pest combination. Post-entry alternative treatments used by the importing country are particularly problematic because many alternatives have neither been approved for treating a specific product on arrival, nor would they be easy to implement. To solve this problem, a range of alternatives is urgently needed to cope with the large and varied volume of produce entering via multiple air and seaports. Such treatments would need to be able to treat perishable commodities quickly in order to avoid congestion at air and seaports.

In the future, if CH_3Br for quarantine treatments is not permitted and no alternatives are available, infested consignments may be prohibited until satisfactory 'on-arrival' treatments are developed and approved, or the consignments may be re-shipped or destroyed. Alternatively, import of consignments considered high risk for pest infestation may be prohibited until an alternative treatment has been implemented in the exporting country to reduce pest contamination to a level acceptable to the importing country.

The MBTOC identified a range of alternatives for perishable products that were either in use or under development. These included non-chemical treatments that kill pests by exposure to changes in temperature and / or atmospheric conditions; high energy processes such as irradiation and microwaves; or physical removal using air or water jets. A combination of treatments may be required to kill pests if they are tolerant to single exposure treatments.

Commercialization of these replacements for CH_3Br will depend on a number of considerations that include proven treatment efficacy, commodity tolerance, equipment design and commercial availability, cost competitiveness, regulatory approval, logistical capability, availability and agreement on the scientific research required for regulatory approval, and technology adoption. As there are many aspects to complete for any new quarantine treatment, the time from conception to implementation can vary from 2 to 15 years.

Durable commodities and food processing facilities

Currently, CH_3Br is primarily used to disinfest grain stacked in bags; to disinfest food processing facilities such as mills; to treat durable commodities such as cocoa, grain, certain dried fruit and nuts at the time of export and post-entry; and a variety of quarantine applications, notably treatment of logs.

It is estimated that approximately 12% of the global consumption of CH_3Br is used for the disinfestation of durable commodities and about 3% for structures. Some of the CH_3Br uses for durables, wood products and structures fall within the QPS exemption.

A variety of alternatives to CH_3Br exists for disinfestation of durable commodities and structures. The princi-

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pal ones are phosphine (PH_3), heat, cold and contact pesticides for durable commodities; sulfuryl fluoride, chemical wood preservatives and heat for wood products; and sulfuryl fluoride and heat for food processing facilities. The choice of appropriate alternatives depends on the commodity or structure to be treated, the situation in which the treatment is required, the accepted level of risk, the speed of action required and the cost.

Emissions reduction

Emissions from fumigation operations occur through leakage and permeation during treatment (inadvertent emissions) and from venting at the end of a treatment (intentional emissions). Estimates of the proportion of CH_3Br used that is released into the atmosphere vary widely because of differences in usage patterns, the condition and nature of fumigated materials, the gas-tightness of enclosures, and local environmental conditions. Also, some CH_3Br may react during use, so it is incorrect to equate production with emissions as at least part of CH_3Br applied is converted in use to non-volatile materials**.**

Under current usage patterns, the proportions of applied CH_3Br eventually emitted to the atmosphere globally are estimated by the MBTOC to be: 32–87% of applied dosage for soil, 85–95% for perishable commodities, 69–79% for durable commodities and 90–95% for structural treatments. These figures correspond to a range of 43–87% overall emission from agricultural and related uses, with a best estimate of overall emissions of 73% or 50,240 tons (based on 1996 production data).

There has been some limited implementation of recovery and recycling for CH_3Br, mainly in North America. A plant has recently been installed at an airport in Texas to recover CH_3Br from fumigation facilities. The recovered CH_3Br is transported to production facilities where the bromine is removed with heat. Recovery and recycling systems are generally complex and expensive to install compared with the cost of the fumigation facility itself. Some systems would also have high running costs associated with energy requirements and many would require a level of technical competence not normally found at fumigation facilities. For these reasons, there are few examples of recovery and recycle in current commercial use.

Methyl bromide for quarantine and pre-shipment treatments

The MBTOC reported that consumption of CH_3Br for quarantine and pre-shipment treatment (QPS) has increased to about 22% of global fumigant use for both developed and developing countries. A pre-shipment treatment is one that is used mainly to kill non-quarantine pests in products such as grain, typically within 14 days of shipment. The quantity of CH_3Br used for QPS has increased owing to increased import and export trade throughout the world.

Many countries are now considering that the exemption for QPS is not in the best interests of the ozone layer. There also is limited development of alternatives for CH_3Br used in QPS, as funding agencies are focusing on near-term solutions to pest problems that must be controlled with limited volumes of CH_3Br. In contrast, CH_3Br for QPS currently has no volume restrictions and therefore the exemption under the Protocol acts as a disincentive for promoting expenditure on research.

Representatives of governments under the Montreal Protocol are currently meeting in Beijing, China to consider a range of further measures for all ozone depleting substances, including CH_3Br. One proposal under consideration is more strict use of CH_3Br for QPS treatments, a freeze in consumption at some time in the future, and official data reporting of the quantities of CH_3Br used in this area. If parties accept a freeze on consumption as a form of control, funds will be made available under the Protocol to finance the development and implementation of alternatives to QPS in developing countries. This is a difficult decision for representatives to consider. Accepting limits on the availability for QPS at some time in the future may result in less being available for fumigation of food crops imported by countries with strict pest control measures. On the other hand, limits on availability will result in funds being deployed for developing alternatives. Only one thing is for sure—the representatives will decide only by consensus on any new measures under the Protocol.

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