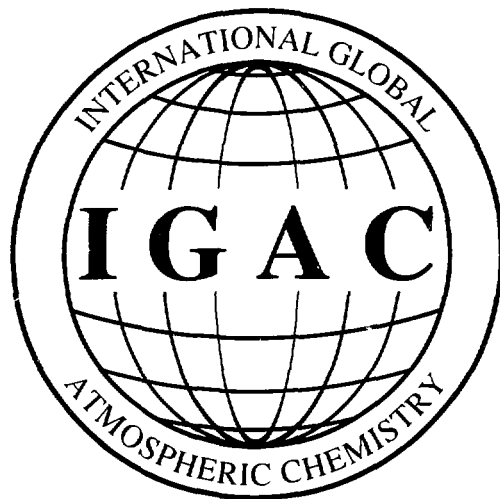


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**BOOK OF ABSTRACTS**

**THE 1<sup>ST</sup> IGAC SCIENTIFIC CONFERENCE:**  
**GLOBAL ATMOSPHERIC-BIOSPHERIC CHEMISTRY**



**April 18 - April 22, 1993**  
**Eilat, Israel**

*The 37th Conference in the*  
**OHOLE Conference Series**



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# Global Atmospheric -Biospheric Chemistry: The First IGAC Scientific Conference

April 18 – April 22, 1993  
Eilat, Israel

## INTRODUCTION

Welcome to Eilat! This conference will review and present new results in the area of global atmospheric chemistry and its interactions with the biosphere. Early scientific achievements of the International Global Atmospheric Chemistry Project (IGAC), a core project of the International Geosphere-Biosphere Program (IGBP) will be highlighted.

The invited papers of this conference will be published in a Conference Proceedings Volume in the Oholo Conference Series (Plenum Publishing Corp., NY), which should be available in November, 1993. Conference participants may order the volume at a reduced price of \$37.50 per copy, if ordered during the conference. After the conference, the volume can be ordered from the IGAC Core Project Office at the cost of \$50 per copy.

A special issue of the Journal of Geophysical Research will be devoted to this conference. All contributed oral and poster papers are eligible for submission. The special issue should be published in approximately May of 1994. Submissions to this special issue must be received by the IGAC Core Project Office no later than August 1, 1993. To submit a paper, send 5 copies of the manuscript, along with names, complete addresses, and telephone numbers of 5 potential referees to the IGAC Core Project Office, MIT Room 24-409, Cambridge, MA 02139, USA. For more information, contact the Project Officer, Dr. Alex Pszenny, at tel: 617-253-9887, fax: 617-253-9886.

## ORGANIZING COMMITTEE

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Dr. Pamela A. Matson, NASA-Ames Research Center, USA  
Prof. Henning Rodhe, Stockholm University, Sweden  
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The International Global Atmospheric Chemistry Program would like to thank the following for their support of the First IGAC Scientific Conference:

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## FOREWORD

Some of the following abstracts have been edited slightly to achieve consistency throughout the book. Every effort was made to preserve the information contained therein. The number (or letter) following the author name(s) is the paper's reference number (or letter), which is used in the program schedule on the following page. The papers are grouped by IGAC Activity foci. Please check the conference schedule posted at the meeting site for any last minute changes to the program.

	Saturday 17 April	Sunday 18 April	Monday 19 April	Tuesday 20 April	Wednesday 21 April	Thursday 22 April
7:30-8:30	Breakfast for Council	Breakfast for Council	Breakfast	Breakfast	Breakfast	Breakfast
8:30-9:30	IGAC Council* Meeting Begins	Day 2 of IGAC Council Meeting	NARE: A NARE: 9, 5	BATGE: D BATGE: 30, 31	HESS: H HESS: 55, 114	GEIA: 41, 45 GEIA: 88, 91
9:30-10:30	↑ ↓	↑ ↓	NARE: 2, 3 MAGE: B	BATGE: 33, 34 DEBITS: 36, 35	TRAGEX: I TRAGEX: 58, 66	GEIA: 99, 95 GEIA: 100; GIM: 93
10:30-11:00	Break for Council	Break for Council	Break	Break	Break	Break
11:00-12:00	↑ ↓	↑ ↓	MAGE: 14, 19 MAGE: 12, 16	RICE: F RICE: 47, 48	TRAGEX: 71, 109 MILOX: 56, 68	GIM: 96, 105 GIM: 118; FUND: 106
12:00-13:00	↑ ↓	↑ ↓	MAGE: 1 MAC: L, 4	RICE: 49, 51 PAC: G	MILOX: 69, 65 GLOCARB: 101, 17	Summary and Panel Discussion
13:00-14:30	Lunch for Council	Lunch for Council	Lunch	Lunch	Lunch	Adjourn
14:30-15:30	↑ ↓	Registration and Check-in Begins	APARE: C APARE: 20,21		GLOCHEM: J GLOCHEM: 77, 78	Activity Committee Meetings  (To be arranged by each Activity Convener)
15:30-16:30	↑ ↓	↑ ↓	APARE: 22, 23 APARE: 24, 25		GLOCHEM: 81, 86 GLOCHEM: 83, 85	
16:30-17:00	Break for Council	Break for Council	Break	Excursion Time	Break	
17:00-18:00	↑ ↓	↑ ↓	BIBEX: E BIBEX: 37, 38		GEIA: K Poster Presentations: TRAGEX: 59, 60, 61, 62, 63, 64, 67, 72, 121, 124; HESS: 52, 53, 119; MILOX: 70, 73, 74; FUND: 107, 108, 111	
18:00-19:00		IGAC Council Meeting Adjourns	BIBEX: 39, 40 BIBEX: 42, 44			
19:00-20:00	Dinner for Council	Dinner	Dinner	Dinner	Dinner	Invited papers (referenced as A-L) are 30 minutes each, including time for questions and discussion. Contributed papers (numbered from 1-123) are 15 minutes each. Paper reference numbers and letters are given on the following papers.
20:30-22:00	* The IGAC Council consists of the 17 members of the Scientific Steering Committee plus the Convener(s) of each of the 23 Activities.	Overview Lecture;  Welcoming Reception and Party	Poster Presentations: NARE: 6, 7, 8, 10, 11; MAGE: 13, 15; MAC: 18, 104; APARE: 27; BIBEX: 43, 120; GLOCHEM: 76, 79, 80, 84	Poster Presentations: BATGE: 29, 32; RICE: 46, 50; PAC: 117; GLOCARB: 102, 103; GEIA: 90, 97, 98; GIM: 92, 94, 122, 123; FUND: 110, 115, 116	Farewell Party	

## OVERVIEW

*Global Atmospheric-Biospheric Chemistry*

R. Prinn

The global atmosphere is a chemically complex system with significant chemical interactions both internally and with the oceans, land, and living organisms. Its composition is observed to be changing today and there is also evidence for major changes over the last 160,000 years contained in ice cores. Much of the key atmospheric chemistry occurs in either the troposphere or the stratosphere and influences the global environment through its maintenance of the ozone layer and significant levels of radiatively active gases and particles. Methane, a very important greenhouse gas, has major natural biological and anthropogenic sources and is destroyed largely by reaction with the hydroxyl radical in the troposphere. Both its sources and sink are strongly influenced by human activity. Nitrous oxide has a similar range of sources. Through its decomposition it plays a controlling function in the ozone layer and it is also a significant greenhouse gas. The chlorofluorocarbons (CFCs) are purely anthropogenic and play a similar controlling role in the ozone layer. However, the potency of both nitrous oxide and the CFCs as greenhouse gases is offset partially by the ozone they destroy. Ozone, a key chemical and protective ultraviolet shield, has a complex chemistry influenced by many other trace species and is also an important greenhouse gas. Nitric oxide, nitrogen dioxide, hydrocarbons heavier than methane, and carbon monoxide, while not very important directly as greenhouse gases, play a key role through their influence on the ozone, hydroxyl radical, and methane concentrations. Carbon dioxide, the most important greenhouse substance after water vapor and clouds, has major oceanic and terrestrial net sinks and anthropogenic net sources. The precise magnitude of the oceanic sink and even the fundamental processes involved in the terrestrial sink have yet to be resolved. Gaseous sulfur compounds, both natural and anthropogenic, are efficiently oxidized to particulate sulfates which can be very important contributors to the albedo, offsetting somewhat the influence of the greenhouse gases.

It is important to recognize the many complex interactions among the atmospheric, oceanic, terrestrial, and biological processes controlling atmospheric chemistry. Among other things, these link changes in industrial activity, climate, and land use to changes in atmospheric composition in ways not realistically described by single numbers such as "potentials" for ozone depletion or warming. The International Global Atmospheric Chemistry (IGAC) Project is underway and dedicated to understanding this complex system through a combination of observations, theory, and laboratory and modelling studies.

## NARE: North Atlantic Regional Experiment

*Atmospheric Chemistry and Composition of Air Over the North Atlantic Ocean*

S. Penkett, F. Fehsenfeld, J. Prospero (invited) A

The North Atlantic Regional Experiment (NARE) activity of IGAC seeks to study chemical processing and transport over the North Atlantic Ocean of pollutants emitted from the surrounding continents. It has various components with research activities based on measurements of aerosol composition, and ozone and its precursors.

The results obtained on the chemical composition of aerosols over the past several years clearly show that the entire North Atlantic atmosphere is heavily impacted by anthropogenic sources. For example, mean aerosol  $\text{NO}_3^-$  concentrations are 5 - 17 times higher than those measured in the remote South Pacific;  $\text{nss-SO}_4^{2-}$  values are 2 - 7 times higher. High concentrations of aerosols (and some gases) can be clearly related to the transport of pollutants from continental sources. The measured concentrations of sulphate aerosols equal or exceed those used in recent calculations that suggest that anthropogenic aerosols could have a significant cooling effect on climate in the northern hemisphere (Langner and Rodhe, 1991; Charlson et al., 1992). Nonetheless, at some locations at various times of year, natural sources do play an important role in the cycles of a number of important aerosol, gas and precipitation species.

Ozone has both natural and anthropogenic sources in the troposphere. The primary natural source is injection from the stratosphere. The anthropogenic source is photochemical production from precursors emitted by industrial and transportation combustion sources. Observations of ozone in the free troposphere at an altitude of 3 km over the North Atlantic show a marked seasonal oscillation, with a maximum of about 55 ppbv in late spring (May - June) and a minimum of about 35 ppbv in winter (December - January). Measurements show that this same seasonal pattern is exhibited by the hydrocarbon chemical precursors of ozone. These results suggest that the increase in ozone between January and May are in part due to increased production from photochemical processes within the troposphere. A further feature of interest, which comes from close examination of the Atlantic free tropospheric hydrocarbon data, is that the distribution of hydrocarbons, particularly with respect to the ratio of the normal to the isomer of pentane, hexane, heptane and octane, can be interpreted in terms of an efficient  $\text{NO}_3$  chemistry preferentially removing the iso isomer during winter months.

Measurements also provided the basis for estimating the amount of  $\text{O}_3$  that is produced photochemically from anthropogenic pollution in North America and transported to the North Atlantic. To evaluate the significance of this transport,  $\text{O}_3$  and carbon monoxide (CO) levels were measured during 1991 and 1992 at sites on the Atlantic coast of Canada. A strong positive summertime correlation between CO and  $\text{O}_3$  was attributed to photochemical production of  $\text{O}_3$  from anthropogenic emissions. In contrast, during the winter when  $\text{O}_3$  is titrated by NO and other anthropogenic emissions, CO and  $\text{O}_3$  were anti-correlated. The measured relations between the concentrations of  $\text{O}_3$  and CO provide the basis to an estimate of  $\text{O}_3$  exported from North America: approximately 100 billion moles of  $\text{O}_3$  per summer. This amount is greater than that reaching the lower troposphere in this region from the stratosphere, the primary natural source of ozone. This conclusion supports the contention that ozone derived from anthropogenic pollution has a hemisphere-wide effect at northern temperature latitudes.

**Retrieval of the Desert Aerosol Optical Thickness over the Tropical Northeastern Atlantic from Satellite and Ground-Based Data**  
**F. Guillard, I. Chiappello, F. Dulac, G. Bergametti, D. Tanre, O. Silva, J. Lima (oral) #9**

The long-range transport of desert aerosols has an impact on the physics and chemistry of the marine atmosphere and on biogeochemical cycles in seawater. The best potential to monitor the large-scale transport of desert dust particles lies with meteorological satellites. Nevertheless, the atmospheric dust load determined from satellite data through radiative transfer modelling must first be validated with pertinent ground observations.

Since December 1991 a land-based atmospheric station has been operated in the tropical northeastern Atlantic off the coast of Senegal at Sal, one of the Cape Verde Islands. This station continuously measures elemental concentrations in atmospheric particulate matter from daily filtrations; tracers are used to determine the relative contributions to solar extinction of the various aerosol types (e.g., desert dust, sea-salt, non-sea-salt water soluble particles). In one approach, the total atmospheric aerosol optical thickness is inferred by combining the concentration of each aerosol type, their respective extinction cross-sections, and the aerosol dust layer depth deduced from radiosounding data. In another approach, the atmospheric aerosol optical thickness is determined by analysing coincident data from Meteostat satellite. The atmospheric aerosol optical thicknesses deduced from these two methods are compared with values obtained from sunphotometer measurements of solar extinction also performed at Sal Island. Finally, the relative merits of these different methods are discussed.

**Naturally Occurring Continental Materials in the Atmosphere over the North Atlantic Ocean**

**R. Arimoto, R. Duce, B. Ray, J. Cullen, W. Graustein, K. Turekian (oral) #5**

The long-range transport of mineral dust produced from the weathering of the earth's crust is the major source for numerous trace elements, including Al, Fe, Sc, the rare earths, etc., in the marine atmosphere. Radon, also emitted from the continents, undergoes radioactive decay through a series of short-lived daughters to produce  $^{210}\text{Pb}$  that rapidly attaches to the ambient aerosol. As part of the Atmosphere-Ocean Chemistry Experiment (AEROCE), we have determined the concentration of aluminum, which is representative of mineral aerosol, and  $^{210}\text{Pb}$  in daily aerosol particle samples from four sites in the North Atlantic: Bermuda, Barbados, Ireland, and Tenerife. In this paper we compare and contrast the behavior of these two continentally-derived substances.

Mineral dust, which originates primarily from the Sahara, exhibits highly variable concentrations, and the atmospheric dust concentrations are characterized by pronounced seasonal cycles with maximum concentrations occurring in the summer.  $^{210}\text{Pb}$  also exhibits considerable variability with time, but its seasonal cycle is substantially damped relative to that of mineral dust. More important, the seasonal cycles of dust and  $^{210}\text{Pb}$  are not synchronous even though peaks in the two substances are often coincident. Further, the concentrations of the two substances at each of the sites are uncorrelated when dust loads are low. However, air masses containing high dust concentrations generally also have high  $^{210}\text{Pb}$ . This relationship may be explained by the fact that dust particles are only produced in arid and semi-arid lands while radon sources are more uniformly distributed over the continents.

**Trace Element Sources, Scavenging and Deposition in the Western North Atlantic Troposphere**

**A. Véron, T. Church, R. Arimoto, G. Cutter (oral) #2**

Trace elements (Al, Fe, Mn, Ni, Cu, Zn, Se, Sb) have been analyzed in precipitation and aerosol samples collected in Bermuda (1988 - 1990) as part of the AEROCE program (Atmosphere-Ocean Chemistry Experiment). The scavenging efficiency of trace metal-containing air masses by precipitation has been estimated using the so-called "Scavenging Ratios" (SR) which are calculated from paired aerosol-precipitation events. The Scavenging Ratios have been sorted according to air mass sources determined by three dimensional isentropic air mass trajectories provided by AEROCE meteorologists, and by lead isotope signatures. A confident choice of the best trajectory is made only after careful analysis of many trajectories surrounding the precipitation event.

Average SR values calculated within the Trade Easterlies are generally 0.2 to 2 times lower than those associated with North American Temperate Westerlies. This difference is even more pronounced for crustal elements (Al, Fe, Mn). According to the isentropic trajectories, 70 to 90% of these elements deposited to Bermuda originate from the Trade Easterlies.

There are many physical and chemical processes which determine the scavenging ratio. These include: (1) trace element introduction and removal both in the scavenging air masses and in the boundary layer during long range transport; (2) relative humidity and air mass mixing during scavenging; and (3) the chemical nature or solubility of competitive nucleating particles. These processes will be discussed and delineated according to the observed scavenging ratios. However, without further data or experiments, the resolution or ranking of the importance of such processes for scavenging ratios is limited.

The relative contribution of dry and wet deposition to Bermuda has been calculated for each metal. Dry deposition accounts for at least 50% of the crustal element (Al, Fe, Mn) deposition while it generally represents less than 15% for the metalloids Sb and Se. The dry deposition contribution for Ni and Zn shows significant seasonal variations ranging from greater than 70% during summer to less than 20% during winter.

These results suggest significantly different impacts of the easterly and westerly meteorological regimes on the chemical climatology which controls trace element transport and deposition to the western North Atlantic. This should be considered when evaluating the budgets of trace elements in the North Atlantic troposphere and surface ocean waters.

**Oceanic and Anthropogenic Contributions to Nonsea-Salt Sulfate in the Marine Boundary Layer over the North Atlantic Ocean**  
**D. Savoie, R. Arimoto, J. Prospero, R. Duce, W. Graustein, K. Turekian, J. Galloway, W. Keene (oral) #3**

As a part of the Atmosphere/Ocean Chemistry Program (AEROCE), daily aerosol samples are collected in the marine boundary layer at Barbados, West Indies (13.17°N, 59.43°W), Bermuda (32.27°N, 64.87°W), and Mace Head, Ireland (53.32°N, 9.85°W). In this report, we use multiple variable regression analyses with methanesulfonate (MSA) and either Sb or NO<sub>3</sub> as the independent variables to assess the relative contributions of the marine biogenic and anthropogenic sources to the total nss SO<sub>4</sub><sup>2-</sup> concentrations at the three North Atlantic sites. The marine biogenic nss SO<sub>4</sub><sup>2-</sup>/MSA ratios derived from these analyses are further verified by examining the ratios in samples for which the <sup>210</sup>Pb concentrations, an indicator of continental air, were very low. The upper limit is set at 0.1 mBq m<sup>-3</sup>, the maximum concentration that was measured at American Samoa during the Sea/Air Exchange Program (SEAREX). At Bermuda and Barbados, the marine nss SO<sub>4</sub><sup>2-</sup>/MSA ratios (19.6 ± 2.1 and 18.8 ± 2.2) are consistent throughout the year and comparable to those at American Samoa in the tropical South Pacific (18.1 ± 0.9). At Mace Head, this ratio is about 3.01 (± 0.53). An analysis of the residuals and an assessment of the root mean square deviations indicates that the ratio at Mace Head can also be reasonably applied throughout the year. However, there is enough uncertainty during the winter that we can not rule out a significant increase (to about 20) during periods with very low concentrations of both MSA and NO<sub>3</sub>. In general, the ratios are rather robust and appear to be independent of the concentrations of natural and/or anthropogenic continental material. At Bermuda, where North American sources are expected to dominate, the continental nss SO<sub>4</sub><sup>2-</sup>/Sb ratio (28,600 ± 1200) is about twice those at the other two sites (11,000 – 18,000) where European and African sources are believed to be most important. Estimates based on these ratios indicate that, on an annual basis, the contributions from anthropogenic sources account for about 50% of the total nss SO<sub>4</sub><sup>2-</sup> in aerosols at Barbados, 70% at Bermuda, and 85–90% at Mace Head. If the same biogenic nss SO<sub>4</sub><sup>2-</sup>/MSA ratios are applicable to rainwater, then the relative contributions in precipitation at Barbados and Bermuda are comparable to those in the aerosols. The estimates at Barbados are particularly notable because the results from various global transport/chemistry models indicate that the marine source should overwhelmingly dominate at that location. Moreover, recent model estimates of the biogenic nss SO<sub>4</sub><sup>2-</sup> component appear to be factors of 3 to 5 too low in the region of Bermuda.

#### *The Results of Atmospheric Marine Monitoring in the North Atlantic*

V. Medinets, A. Ryaboshapko (poster) #6

The results of aerosol composition and trace gas concentration observations in the North Atlantic surface atmosphere during 1981 – 1991 carried out on board the weather ships will be shown and discussed. Measurements of SO<sub>2</sub>, NO<sub>x</sub> concentrations, aerosol ionic composition (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, Cl<sup>-</sup>) and Radon-222 were carried out. The most complete series of observations was obtained for the ocean station "C" (52°45'N, 35°40'W) and for the Newfoundland Energy-Active Zone (NEAZO). Background concentrations are estimated for all the species measured in the atmosphere over the ocean. It is shown that even over the remote areas of the ocean anthropogenic impact accounts for 20 to 60%.

On the basis of the meteorological analysis the conclusion is made that the chemical compound and Radon-222 concentration levels in the North Atlantic surface atmosphere are primarily the result of air mass transport from the continental regions of the North America.

Mean values of sulfur and nitrogen compounds' atmospheric precipitation at the ocean surface are calculated. Prospects of radioactive tracer use for estimation of the parameters of long-range transport of anthropogenic emissions from continents to the ocean are discussed.

#### *Air Mass Sources and Temporal Variations in Trace Metal Transport and Wet Deposition from the North Atlantic Troposphere*

T. Church, A. Véron, J. Scudlark (poster) #7

Trace metals (Al, Mn, Fe, Ni, Cu, Zn, Cd, Pb) have been analyzed in precipitation continuously collected on a daily basis at Bermuda (1988 – 1991) and Ireland (1990 – 1991) as part of the AEROCE program. Our objectives are to document the continental sources, tropospheric transport and wet deposition of the crustal and anthropogenic metals from the atmosphere to the North Atlantic Ocean. The continuous collections allow us to evaluate the impact of seasonal and interannual variations on these processes.

Annual weighted average concentrations at Bermuda do not vary significantly from 1988 to 1991, except for Zn and to a lesser extent Pb and Cd. Comparison of this data set with the 1983 – 1985 WATOX record at Bermuda suggests a substantial decrease in anthropogenic trace metal concentrations (Cd, Pb, Zn, Ni); crustal element concentrations do not show any significant variation except for a peak in 1985 due to a larger input of dust from the Trade Easterlies.

Precipitation events have been sorted according to three dimensional isentropic air mass trajectories provided by AEROCE meteorologists. The major meteorological regimes include the Trade Easterlies, the North American Westerlies and the Boreal European Easterlies, the North American Westerlies and the boreal European Easterlies. Here, over the western North Atlantic, average weighted concentrations of crustal elements in precipitation appear 2 to 6 times higher in air masses associated with the Trade Easterlies than those with the North American Westerlies due to the impact of crustal dust from Africa. However, at Ireland in the eastern North Atlantic, the strong anthropogenic sources of trace metals originating from northern Europe and North America tend to minimize the contribution of the crustal material. Average trace metal concentrations measured in the North American Westerlies at Bermuda and Ireland are well correlated. Considering this observation, the export and tropospheric transport of trace metals associated with the North American Westerlies is evaluated using the long term data set from Lewes (DE), Bermuda and Ireland. Budget calculations suggest that 20 to 40% of the trace metals exported from North America are deposited in western Atlantic coastal areas, with the little deposition (20% or less) over remote marine regions. According to meteorological sectoring, the Trade Easterlies generally represent 60 to 80% of the crustal material deposited by precipitation to the western North Atlantic and account for 20 to 40% of the anthropogenic trace metal input.

***Regional and Seasonal Changes of Nitrogen and Phosphorus Input from the Atmosphere into the Baltic Sea***

**L. Falkowska (poster) #8**

The Baltic Sea is a semi-enclosed body of brackish water surrounded by nine moderately densely populated states of north-eastern Europe, and separated from the North Sea by shallow and narrow Danish straits. It is strongly eutrophied especially in the coastal zone of its southern part. Analysis of long-term results of studies on the content of nitrogen and phosphorus compounds in rains, aerosols and air showed that the atmosphere appears to be a rich source of these substances.

The input of nitrogen compounds from the atmosphere was comparable to the input by rivers. Significant regional differences in the amounts of nitrogen and phosphorus in wet and dry deposition between coastal zone and the open sea have been found. The coastal zone received ca. 4 kg/km<sup>2</sup> of phosphorus and ca. 500 kg/km<sup>2</sup> of nitrogen annually, whereas the open sea received about 4 times less phosphorus and about 10 times less nitrogen. Dry deposition contributes much more annual input than wet deposition.

Multifold increase of concentrations of nitrous dioxide and ammonia in the air and nitrogen compounds in aerosols have been determined in the coastal zone in winter time. Ammonia and nitrogen dioxide constituted about 50% of the total nitrogen introduced to the open sea and about 65% of the total nitrogen introduced to the coastal zone. The input of nitrogen and phosphorus compounds from the atmosphere is of great significance for the nutrient balance of the Baltic Sea.

***Long-Range Transport of Sulfur and Nitrogen Compounds from the North American Continent into the Atlantic Atmosphere***

**V. Medinets, A. Ryaboshapko (poster) #10**

The research and calculations have shown that about 6.5 million tons (Mt) of sulfur and 3.6 Mt of nitrogen are received by the North Atlantic as the result of long-range atmospheric transport annually in the form of the aerosol and gas admixtures. Maximum intensity of transport was observed during Autumn - Winter period and comprised about 70% of the total annual flow. The largest contributions to the total nitrogen and sulfur flow (more than 50%) are transported in the zone of 40 - 50°N where the main sources of emission are situated. The results of the research into the excess sulfate in the aerosol and atmospheric precipitation give evidence of a major contribution from continental sources to the total sulfate content in the atmosphere over the North Atlantic.

***Surface Measurements of Aerosol Black Carbon at Wrangel Island***

**A. Polissar, V. Kapustin, A. Hansen (poster) #11**

In winter and spring, the Arctic troposphere is filled with large concentrations of a number of pollutants (the "Arctic Haze") including optically-absorbing aerosol elemental carbon. If this carbon is deposited to the ice surface, its accumulation over the winter season may cause a significant reduction in the surface albedo.

From 1989 to 1992 aerosol samples were collected on quartz fiber filters at Wrangel Island in the eastern Russian Arctic. The samples were analyzed by an optical transmission method to determine the concentrations of aerosol elemental (or "black") carbon, with results ranging approximately from 1 to 500 nanograms per standard cubic meter. The results show that the highest concentrations are found in the winter and spring seasons, and the lowest concentrations in the summer.

These results are compared with the ongoing, continuous measurements at the NOAA/CMDL/GMCC monitoring station at Barrow, Alaska. Meteorological trajectories frequently connect directly from Barrow to Wrangel, giving us the possibility to estimate the loss of aerosol to the surface by deposition. This deposition of optically-absorbing material to the high-albedo ice surface may lead to a change in the solar radiation balance, premature thawing, and possible implication for climate change.

**MAGE: Marine Aerosol and Gas Exchange**

***Marine Aerosol and Gas Exchange and Global Atmospheric Effects***

**B.J. Huebert (invited) B**

It is becoming clear that the global climate system is controlled by numerous links between the biosphere and the atmosphere. The objective of IGAC's Marine Aerosol and Gas Exchange: Atmospheric Chemistry and Climate (MAGE) activity is to quantify those links through interdisciplinary multinational research on air/sea exchange and its biological controls and impacts. We seek to bring together scientists from a variety of disciplines to study the interfaces between them. Wherever possible, we encourage collaborative work between marine scientists who look up at the interface from the water column and atmospheric chemists, whose work in the atmosphere has frequently treated the ocean's surface as a featureless source or sink.

Several problems require this interdisciplinary approach. Marine biological productivity in some areas is controlled by the supply of nutrients from the atmosphere. In certain nitrogen-rich regions, for instance, the supply of iron from atmospheric aerosols may limit productivity. In other areas, the wet and dry deposition of atmospheric nitrate and ammonium may be a significant source of fixed nitrogen to biological communities. MAGE helped to organize an international group of scientists who studied the effect of atmospheric iron on biological productivity, phytoplankton speciation, and DMS production as a part of the Equatorial Pacific JGOFS experiment in the spring of 1992. A second MAGE/JGOFS cruise studied the fluxes of biogenic gases through the air/sea interface in the same region.

To quantitate the impact of marine biota on atmospheric aerosols, cloud properties, and climate, one must precisely measure (and then parametrize for use in models) the emission of trace gases from the ocean's surface. MAGE is seeking to develop new strategies for measuring some of these elusive fluxes. During the Atlantic Stratocumulus Transition Experiment (ASTEX) in June of 1992, MAGE organized scientists from 5 countries to study air/sea fluxes, their biological forcing, and their

atmospheric effects. Three aircraft, two ships, two islands, and a dozen constant-density balloons were used to test a Lagrangian strategy for studying two airmasses. By repeatedly sampling the same air, we hope to reduce the perennial problem of deconvoluting transport and chemistry so that we can clearly understand processes and fluxes. In this way we will improve our understanding of the marine nitrogen budget (including both ammonia emissions and nitrate deposition), as well as the climatically-important sulfur cycle and DMS emissions.

***Atmospheric Aerosol Input and Open Ocean Productivity: The FeLINE Program in the Equatorial Pacific***

**N. Tindale, R. Duce, A. Hanson, D. Kester, J. Martin, K. Coale, K. Johnson, P. Liss (oral) #14**

Recent work has shown that for areas of open ocean surface waters that contain excess levels of nutrients, particularly nitrate, the input of iron can affect phytoplankton productivity. Areas of high nutrient, low chlorophyll, in the Pacific include the Gulf of Alaska, the Southern Ocean and the Equatorial Pacific. Indirect evidence suggests that the primary source of iron to these regions is via atmospheric input. As part of an ONR funded study, we have been looking at the role of iron in productivity in the Equatorial Pacific region. This multi-group program has included two cruises to the Equator (0, 114°W), one in mid-1990 (FeLINE-I) and the IGAC/MAGE FeLINE-II cruise in March - April 1992 aboard the R/V *Wecoma*. Aerosol concentrations in this region are extremely low, especially south of the ITCZ in the Southern Hemisphere. Shipboard incubation experiments (iron enrichment experiments) during the FeLINE cruises showed that the addition of aerosol leachate increased productivity in surface water samples collected from this region. During the FeLINE-II cruise we were fortunate enough to follow and sample an individual rain event while in the study region and were able to record the input of the rain water into the surface layer through the peroxide and iron signals and the depression in surface salinity. An enrichment experiment using the freshly collected rain water also showed an increase in the productivity.

***Airborne Ammonium and Nitrate Concentrations over the Ocean around Southeast Asia***

**H. Kreilien, P. Schäfer, A. Ibram, J. Constantin, G. Gravenhorst (oral) #19**

The airborne concentrations of gaseous ammonia and nitric acid and particulate bound ammonium and nitrate were measured over the Indian Ocean, in the vicinity of Indonesian Islands, in the South China Sea and the Tropical West Pacific by the filter method. The filter method was tested in an international comparison with other methods for  $\text{NH}_3/\text{NH}_4$  at a Mediterranean station and achieved very good results. The gaseous nitric acid concentrations seem to be much smaller than the particulate nitrate phase at the sea surface in contrast to the middle atmosphere. The concentration of airborne nitrogen compounds increased remarkably under continental influence and decreased towards remote regions. The concentrations are interpreted in relation to oceanic fluxes and compared with situations in other oceanic areas.

***Evidence of Inorganic Chlorine Gases other than Hydrogen Chloride in Marine Surface Air***

**A. Pszenny, W. Keene, D. Jacob, S. Fan, J. Maben, M. Zetwo, M. Springer-Young, J. Galloway (oral) #12**

We report the first measurements of inorganic chlorine gases in the marine atmosphere using a new tandem must chamber method. Surface air was sampled in late January, 1992, at Virginia Key, Florida. After passing through an inertial preseparator to remove coarse aerosol and a teflon prefilter to remove fine aerosol, the chlorine gases were collected with an acidic mist chamber ( $\text{HCl}^*$ , including  $\text{HCl}$ ,  $\text{ClNO}_3$ ,  $\text{ClNO}_2$ , and  $\text{NOCl}$ ), followed by an alkaline mist chamber ( $\text{Cl}_2^*$ , including  $\text{Cl}_2$  and any  $\text{HOCl}$  not trapped in the acidic mist chamber).  $\text{HOCl}$  does not contribute to  $\text{HCl}^*$ . Concentrations of  $\text{HCl}^*$  were in the range 144 to 268 pptv and concentrations of  $\text{Cl}_2^*$  were in the range < 26 to 254 pptv as  $\text{Cl}$ . Concentrations of  $\text{Cl}_2^*$  increased during the night, and decreased after sunrise as  $\text{HCl}^*$  concentrations increased by similar amounts. The measurements suggest an unknown source of either  $\text{HOCl}$  or  $\text{Cl}_2$  to the marine atmosphere. Photochemical model calculations indicate that photolysis of the observed  $\text{Cl}_2^*$  would yield a chlorine atom ( $\text{Cl}^*$ ) concentration of order  $10^4 - 10^5 \text{ cm}^{-3}$ . Oxidation by  $\text{Cl}^*$  would then represent a significant sink for alkanes and dimethylsulfide (DMS) in the marine boundary layer. The cycling of  $\text{Cl}^*$  would provide either a source (high  $\text{NO}_x$ ) or a sink (low  $\text{NO}_x$ ) for  $\text{O}_3$ .

***The Oceanic Source of Methyl Chloride***

**V. Tait, R. Moore, R. Tokarczyk (oral) #16**

A cruise during April - June, 1991, in the north-west Atlantic produced further evidence that the ocean is a source of methyl chloride to the atmosphere. Higher concentrations were observed within the surface layer above the seasonal thermocline. Assuming a boundary layer mixing ratio of 1 ppbv (based on a review of available literature), the average saturation was 180% (range 84 - 265). Near surface maxima, with saturations in some cases exceeding 300%, were a feature common to many of the vertical profiles. Using the method of Liss and Slater (1974), a flux of  $1.3 \times 10^{11} \text{ g CH}_3\text{Cl}$  might be expected from the mid-to-high latitude North Atlantic during the spring-summer months. Assuming this region is representative of all mid-to-high latitude oceans during spring and summer, this estimate can be extrapolated over these ocean areas to give a flux of  $9.1 \times 10^{11} \text{ g}$  for the 6 month spring-summer period. The magnitude of ocean to atmosphere transfer may have been overestimated in previous studies.

Despite the diversity of oceanic regions sampled, methyl chloride showed a notable degree of uniformity. No strong coastal signal was evident in the distribution, suggesting that coastal macroalgae are not an important source of methyl chloride in the region of study. The role of phytoplankton in oceanic methyl chloride production is still unclear. There were only a limited number of stations at which both methyl chloride and bulk phytoplankton biomass (as chlorophyll-a) were measured. However, from these data, any correlation between the two is likely not a strong one. Indirect mechanisms of methyl chloride production through reaction of biologically produced precursors are considered, with particular emphasis on methyl iodide and dimethylsulphoniopropionate.



**Measurements of Aerosol Black Carbon over the North Atlantic****A. Polissar (oral) #1**

Aerosol samples were collected on quartz fiber filters from July to September, 1990, aboard the research ship "Professor Viese" in the North, Greenland and Norway seas. The samples were analyzed by an optical transmission technique to determine the concentrations of aerosol elemental carbon, giving results ranging from 0.5 to 545 nanograms per standard cubic meter.

From synoptic maps for the 1000 and 500 hPa levels, we obtained 3-day and 5-day backward trajectories. The results show that the highest concentrations were found in the Norway and Greenland Sea locations with transport from Great Britain, while the lowest concentrations were measured in the Greenland sea area with transport from the Arctic. The mean concentrations in these two cases were 143 and 6 ng/m<sup>3</sup>, respectively. It was more frequent for meteorological transport to be from the south-west, from the North American continent, with a mean aerosol elemental carbon concentration of 24 ng/m<sup>3</sup>. When sampling on the North Sea, high concentrations of elemental carbon were observed when trajectories brought aerosol from Great Britain and the European continent to the ship's location.

We conclude that the concentrations of anthropogenic aerosol measured at remote locations are influenced to the highest degree by the meteorological situation.

**The Atmospheric Input of Trace Metals to the Oceans Aerosol Dissolution Studies****L. Spokes, T. Jickells, B. Lim (poster) #13**

The atmosphere has now been recognised as a major source of both trace metals and nutrients to the oceans. To understand the effects of these atmospheric inputs of trace metals on the ocean system requires a knowledge of the form in which the metal is deposited. Since in most ocean areas wet deposition (precipitation — rain, snow, etc.) exceeds the dry deposition of aerosols (Duce, et al., 1991) it is of particular importance to understand how elements are (1) distributed between their dissolved and particulate phases in precipitation and (2) whether this phase distribution changes upon deposition to seawater.

The pH of rainwater, controlled by a balance between the concentrations of acid species (predominantly H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> of anthropogenic origin) and neutralising agents (mineral dust of natural origin and NH<sub>3</sub> of natural and/or anthropogenic origin), has been shown to be a major control on the solubility of metals. For many trace metals, however this relationship is not a simple one, and it appears that the history of the parent aerosol in the atmosphere also plays an important role in governing the solubility of metals within precipitation.

Before aerosol particles are removed in precipitation they are subjected to repeated wetting and drying cycles during cloud formation and evaporation. As a result of SO<sub>2</sub> and NO<sub>x</sub> oxidation the cloud pH values can be extremely low and thus the final pH of the rain may not reflect the pH conditions to which the aerosol is exposed to in the atmosphere. Laboratory studies are being conducted which aim to mimic this cloud cycling behaviour and assess the solubility of a range of metals during repeated cycling through varying pH values.

The results suggest that, particularly for the crustal elements, metal solubility is a strong function of pH. Highest solubilities are seen in the low pH environments, indicative of clouds, with reduced solubilities seen at higher pH. The results also show a marked increase in the solubility of many metals at high pH after a period at low pH compared to their solubilities initially at the high pH value. It appears therefore that dissolution processes are not truly reversible and that the phase distribution of metals in rainwater may depend on the cycling of aerosols in the atmosphere before removal in precipitation.

**Photochemical Production of Methyl Iodide in Seawater****R. Moore (poster) #15**

It has been proposed that methyl iodide is the major contributor to the flux of iodine from the ocean to the atmosphere, but to date the sources of the compound in the ocean are largely unknown, an exception being the production by some species of coastal macrophytes. In this paper, observations are described of methyl iodide production in seawater that has been irradiated using either natural sunlight or an artificial light source having a spectral output and intensity that approximates closely to sunlight at sea level. The water samples are filtered, removing particles down to a size of ca. 0.5 microns, to prevent interference from plankton or bacteria. The process reported here is therefore non-biological except in so far as the necessary organic precursor of the photochemical reaction has a biological source. Before irradiation the samples are thoroughly purged to remove existing volatile components. It is found that the rate of methyl iodide production is critically dependent on the purge gas; oxygen-free water yielding a much higher rate than oxygenated water. Experiments are in progress to elucidate the mechanism of this process and to determine whether it can contribute significantly to the methyl iodide flux from ocean to atmosphere.

**MAC: Multiphase Atmospheric Chemistry****Multiphase Atmospheric Chemistry: Implications for Climate****R. Charlson, J. Lelieveld, P. Crutzen (invited) L**

While it has been known for over a century that atmospheric aerosol particles are an important factor governing the interaction of solar radiation with the earth, both through direct influences on solar radiation and indirectly as cloud condensation nuclei, the large degree of variability in both aerosol composition and concentration precluded all but crude global appraisals of the actual forcing (W/m<sup>2</sup>). The advent of global chemical reaction/transport/removal models has made it possible to estimate the direct climatic forcing for sulfate aerosol and for condensed organic materials from biomass

combustion. Thus the study of multiphase atmospheric chemistry has made possible a species-by-species and mechanism-by-mechanism approach to assessing these physical effects. Examination of the generalized heat balance equation for the earth suggests that there must be numerous other important aerosol species and several more mechanisms by which climate is affected. To date, the assessment of effects by anthropogenic sulfate and smoke from biomass combustion indicates that these aerosols cause a climatic forcing that, when averaged over the Northern Hemisphere, is comparable in magnitude but opposite in sign to the "greenhouse" forcing by  $\text{CO}_2$ ,  $\text{CH}_4$ , CFCs, etc. Three steps are involved in these coupled chemical/radiative transfer models; description of the geographical, time and height dependent aerosol formation process, description of the microphysical properties as functions of the source processes of species characteristics, and coupling of these to geographically dependent radiative transfer calculations. We first present a description of the main aerosol production mechanisms and resultant physical properties. Subsequently we address the direct and indirect (CCN-cloud albedo) radiative forcings, leaving open the important questions of influence of aerosol particles on cloud amount and cloud-droplet longevity. We will emphasize the importance of the open scientific questions, concluding that it is not yet possible to fully quantify climate forcing by anthropogenic natural aerosols.

#### *Dimethylsulfide, Sulfur Dioxide, Aerosol and Condensation Nuclei over the Tropical North Atlantic Ocean*

J. Putaud, B. Nguyen, S. Belviso, N. Mihalopoulos, P. Buat-Menard (oral) #4

Dimethylsulfide in surface seawater and in the atmosphere were simultaneously sampled during the oceanic cruises EUMELI 3 and SOFIA/ASTEX in the Eastern Tropical North Atlantic Ocean and the Azores area in September - October 1991 and June 1992 respectively.

Large variations in DMS oceanic flux occurred (range 1 - 40  $\mu\text{mol m}^{-2}\text{d}^{-1}$ ), resulting from variations in wind speed and in DMS concentration in surface seawater due to changes in DMSP and phytoplankton biomass. Atmospheric DMS concentrations (range 1 - 65  $\text{nmol m}^{-3}$ ) generally covaried with DMS flux. During EUMELI 3,  $\text{SO}_2$  and aerosol were sampled using the West-Gaeke method and a 6-stage cascade impactor respectively.  $\text{SO}_2$ , MSA, and  $\text{H}_2\text{SO}_4$  ranged from < 0.02 to 5, 0.05 to 0.8, and 1 to 60  $\text{nmol m}^{-3}$ , respectively, with about 50% of sulfur aerosol being in particles < 0.6  $\mu\text{m}$ . Variations of main DMS oxidation products ( $\text{SO}_2$ , MSA,  $\text{H}_2\text{SO}_4$ ) were not always directly related with local DMS flux or atmospheric concentrations. Condensation nuclei (CN) concentrations ranged from 150 to 1600  $\text{cm}^{-3}$ . There is a good correlation ( $R = 0.82$ ,  $n = 21$ ) between daily average DMS and CN concentrations. However, sulfur aerosol concentrations cannot be clearly related with CN. This could indicate that DMS oxidation products are mainly in very small particles (< 0.1  $\mu\text{m}$ ) which can be numerous without representing an important mass fraction, even in the < 0.6  $\mu\text{m}$  range. Contributions of other sources to the concentrations of  $\text{H}_2\text{SO}_4$  and CN will be discussed from  $^{222}\text{Rn}$  monitoring and cation concentrations in aerosol.

#### *Aqueous Oxidation of Dimethylsulfide by Ozone and its Atmospheric Implications*

Y. Lee, X. Zhou (poster) #18

In order to understand and predict the budgets and distributions of ozone ( $\text{O}_3$ ) and dimethylsulfide (DMS) in the marine atmosphere, the chemical properties, including aqueous reactions in clouds and surface water, influencing the lifetimes of these species must be known. We determined the kinetics of aqueous-phase reaction of  $\text{O}_3$  and DMS in the laboratory using a gas-liquid reactor in conjunction with a photometric  $\text{O}_3$  detector and a flame photometric sulfur detector. The reaction stoichiometry was found to be 1:1, consistent with  $\text{O}_3 + (\text{CH}_3)_2\text{S} \rightarrow (\text{CH}_3)_2\text{SO} + \text{O}_2$ , and the second-order aqueous rate coefficient was determined to be  $5 \times 10^8 (\pm 40\%) \text{ M}^{-1}\text{s}^{-1}$  at  $15.0 \pm 0.2^\circ\text{C}$ . The implications of this rapid aqueous  $\text{O}_3$ -DMS reaction include: (1) the gas-phase rate constant of in-cloud  $\text{O}_3$ -DMS reaction (at 30 ppb of  $\text{O}_3$  and 1  $\text{gm m}^{-3}$  liquid water concentration),  $\sim 0.02 \text{ hr}^{-1}$ , is comparable to that of the homogeneous OH-DMS reaction at  $[\text{OH}] = 2 \times 10^6 \text{ molec cm}^{-3}$  and represents an important removal process for DMS that may not lead to new particle formation, (2) the deposition of atmospheric  $\text{O}_3$  to the ocean surface could be enhanced by this aqueous  $\text{O}_3$ -DMS reaction at the highest surface DMS concentration observed, i.e.,  $\sim 40 \text{ nM}$ , and (3) the sea to air flux of DMS is most likely not affected by this aqueous  $\text{O}_3$ -DMS reactions at  $\text{O}_3$  concentrations typical of marine atmosphere.

#### *DMS Emissions from Contrasting Trophic Regimes in the Tropical Northeastern Atlantic Ocean and their Relation with Condensation Nuclei Formation*

S. Belviso, J. Putaud, M. Corn, B. Nguyen, P. Buat-Menard (poster) #104

During the third and fourth EUMELI (France-JGOFS) cruises (September - October 1991, May - June 1992, respectively) in the tropical northeastern Atlantic Ocean, changes in dimethyl sulfide (DMS) levels in the upper ocean were examined along an ecological continuum where the intensity of the phytoplankton biomass varied at least by a 1 to 100 ratio. This ratio range is representative of the global ocean.

In upper ocean waters 1500 km off the Mauritanian coast, under conditions of low nitrate (< 0.01  $\mu\text{M}$ ) concentrations, low phytoplankton biomass (chlorophyll a < 0.2  $\mu\text{g/l}$ ) and low primary productivity (< 5  $\text{mg C m}^{-3}\text{d}^{-1}$ ), DMS levels were not significantly different from levels in eutrophic waters of the active upwelling band off Mauritania under conditions of high nitrate (10 nM) and chlorophyll a (6  $\mu\text{g/l}$ ) concentrations, and high primary productivity (150  $\text{mg C m}^{-3}\text{d}^{-1}$ ). In mesotrophic waters, under intermediate levels of nitrate, chlorophyll a and primary productivity, DMS levels were 2 - 3 times higher than in oligotrophic or eutrophic regimes. The variability in DMS in the tropical northeastern Atlantic Ocean thus appears to be unrelated to meso-scale distribution of upper ocean phytoplankton biomass. The high DMS levels observed in the mesotrophic regime more likely reflect the specificity of the food chain in this marine environment.

As an attempt to investigate the role of DMS in atmospheric condensation nuclei (CN) production over this oceanic area, atmospheric concentrations of DMS and CN number concentration were measured during the third EUMELI cruise. Although DMS and CN were positively correlated ( $R = 0.82$ ,  $n = 21$ ,  $p < 0.001$ ), CN population could however be strongly

influenced by continental inputs less than 500 km downwind of Africa. This implies that direct evidences of relationship between DMS and cloud condensation nuclei (CCN) may be obtained only over remote marine areas.

### **APARE: East Asian / North Pacific Regional Experiment (PEM-West and PEACOMPOT)**

#### *Atmospheric Chemistry of the East-Asian Northwest Pacific Region*

H. Akimoto, S. Liu, D. Davis (Invited) C

The East Asian Continental Rim Region is characterized by high and rapidly growing anthropogenic emissions of  $\text{NO}_x$ ,  $\text{SO}_2$ , hydrocarbons, and other air pollutants due to its high and growing population density and, in some regions, intensive industrial development. Emissions of  $\text{NO}_x$  and  $\text{SO}_2$  from the East Asian region have been growing at a rate of ca. 4% per year in the last decade, which is in marked contrast to the trends in Western Europe and North America where those emissions have been stabilized or started to decline after 1980. The main focus of the IGAC/APARE is to understand the strengthening human impact on the chemical processes occurring in the atmosphere of the East-Asian Northwest Pacific ocean. Scientists from Pacific Rim countries (China, Taiwan, Hong Kong, Japan, South Korea and Russia) as well as the United States and Australia joined to steer the IGAC/APARE activity.

The first intensive APARE field study was completed in September - October, 1991, by the cooperative leadership of the U.S. National Aeronautics and Space Administration (NASA) and the Japanese National Institute of Environmental Studies (NIES). NASA's initiative, named PEM-West (Pacific Exploratory Mission), consisted of airborne measurements using the NASA DC-8 and ground-based studies. The DC-8 flew across the Pacific ocean and intensive data flights were conducted from operational bases established in Japan, Hong Kong and Guam. Data were obtained over a wide range of selected geographical area and meteorological conditions. NIES organized a study called PEACOMPOT (Perturbation by East Asian Continental Air Mass to the Pacific Oceanic Troposphere) which consisted of airborne measurements using a CESSNA-404 and ground-based studies. The CESSNA-404 sampled the air in the selected area of East China Sea, Yellow Sea and Japan Sea. Ground stations were situated on the eastern coast of China, and in Japan, Korea, Taiwan and Hawaii, as well as on several remote Pacific islands, and scientists from involved countries joined the study.

The PEM-West measurements provided an extensive characterization of air masses over the western North Pacific Ocean including clean oceanic air, continental outflow, stratospheric air, equatorial marine air and Southern Hemispherical marine air. The major greenhouse gases, ozone and its precursors, sulfur species, and continental and marine aerosols were measured, and the airborne remote lidar system has provided a two-dimensional mapping of the atmospheric ozone and aerosol distributions along the entire flight tracks. A unique result was obtained for the transport of trace gases in a major typhoon. The PEACOMPOT measurements characterized the air masses near the continental rim of East Asia.

#### *Reactive Nitrogen and Ozone Relationships over the Western Pacific Based on the 1991 PEM-West Expedition*

H. Singh, D. Herith, L. Salas, J. Bradshaw, S. Sandholm, D. Davis, Y. Kondo, R. Talbot, G. Gregory, G. Sachse, E. Browell, D. Blake, F. Rowland, R. Newell, J. Merrill, S. Liu (oral) #20

Reactive nitrogen plays a central role in the chemistry of the atmosphere and controls key processes such as the formation of ozone, acids, and OH radicals. Measurements of important reactive nitrogen species ( $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HNO}_3$ , PAN, PPN,  $\text{NO}_3^+$ ,  $\text{NO}_y$ ),  $\text{C}_1$  to  $\text{C}_6$  hydrocarbons,  $\text{O}_3$ , chemical tracers ( $\text{C}_2\text{Cl}_4$ , CO) and important meteorological parameters were made in the troposphere over western Pacific (0 - 65°N) during the PEM-West deployment (September - October 1991) throughout 0 to 12 km altitudes. The expedition sampled continental outflows from the Pacific rim countries, pristine background air associated with easterly trajectories, stratospheric intrusions ( $\text{O}_3 > 250$  ppb), and plumes impacted by fires and processed by hurricanes (Mireille). Ozone poor regions of the equatorial Pacific ( $\text{O}_3 < 10$  ppb) were also sampled and comprehensive data obtained for the first time. Some of the cleanest air to be found anywhere in the northern hemisphere was encountered.

These data are analyzed to quantitatively describe the distribution of and relationships between measured odd nitrogen species and ozone. Meteorological and chemical tracers are used as appropriate. An analysis of the reactive nitrogen loading is performed to estimate the magnitude of the continental outflow. Pristine background concentrations of key photochemical species (reactive nitrogen, ozone, CO and select hydrocarbons) associated with easterly trajectories are defined and contrasted with the composition of recently perturbed air masses. Measurements over the western Pacific are compared with other regions of the globe. The remarkable similarity between  $\text{NO}_x$  levels at widely different geographical locations around the globe is noted and reasons for these explored. Model and experimental data are compared to show major shortcomings in our present knowledge of photochemical theory.

#### *Characterization of Air Mass Plumes from Distant Sources over the Western Pacific During PEM-West*

F. Rowland, D. Blake, E. Browell, G. Sachse, J. Bradshaw, S. Sandholm, D. Davis, G. Gregory, B. Anderson, D. Thornton, A. Bandy, S. Liu, H. Singh, K. Kelly, B. Heikes, J. Merrill, M. Shipham, S. Bachmeier, R. Talbot, J. Dibb, R. Newell, Y. Kondo (oral) #21

The first PEM-West (Pacific Exploratory Mission-West) field campaign was conducted in September/October 1991 in conjunction with the IGAC/APARE program. A comprehensive set of measurements of gases and aerosols was recorded from the NASA DC-8 aircraft using both in situ and remote sensing apparatuses. Data were recorded on a series of flights around the northern Pacific from San Jose to Anchorage to Tokyo/Hong Kong with many additional flights in the western Pacific. The recording of high-precision data for numerous man-made halocarbon compounds such as  $\text{CCl}_2\text{F}_2$ ,  $\text{CCl}_4$ ,  $\text{CH}_3\text{CCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CCl}_2=\text{CCl}_2$ ,  $\text{CCl}_2\text{FCCl}_2$  provides multivariate identification of similarity or differences in air mass composition. The

short-lived (~6 months)  $\text{CCl}_2=\text{CCl}_2$  is an especially effective signature for major urban pollution.

While many of the air masses were reasonably well-mixed, numerous plumes of various size were encountered which had carried distinctive chemical signatures for long distances from the likely sources. The plumes encountered over the Celebes Sea from biomass burning in Borneo showed elevated levels of  $\text{CO}$ ,  $\text{CO}_2$ , and many hydrocarbons, as well as traces of methyl halides. Because the atmospheric lifetimes of some of the hydrocarbons are quite short, estimates of chemical reactivity in the plumes are possible.

This paper describes the detailed chemical composition of several of these specific plume encounters, and attempts to identify both the source regions and the nature of the processes responsible for the trace gas signatures. The excess trace concentrations in fresh city plumes (e.g., Tokyo, Hong Kong) provide estimates of the relative emissions of various compounds in each. Tropospheric fly-by flights sample the regional emission compositions for Japan and Taiwan. Stratospheric air has its own composition characteristics with evidence of specific stratospheric loss processes.

***Influence of Relative Air Mass Age on the Chemical Composition of the Troposphere over the Western Pacific During PEM-West***

J. Bradshaw, J. Merrill, D. Blake, B. Heikes, B. Talbot, J. Dibb, D. Thornton, R. Newell, E. Browell, G. Gregory, B. Anderson, G. Sachse, H. Singh, S. Sandholm, M. Shipham, S. Bachmeier, A. Bandy, F. Rowland, K. Kelly, S. Liu, Y. Kondo (oral) #22

During September/October 1991, NASA conducted the Pacific Exploratory Mission-West (PEM-West) field measurement campaign in conjunction with IGAC's APARE program. A major scientific objective of PEM-West and APARE is an investigation of the tropospheric trace gas distributions, sources, and photochemical state over the western Pacific, and an assessment of the degree to which the troposphere over this region is impacted by anthropogenic influences. To address these scientific issues, a comprehensive set of in situ and remotely sensed measurements of gases and aerosols were made from NASA's DC-8 aircraft within the tropospheric column overlying the middle/lower northern latitudes of the western Pacific.

During PEM-West, aged Pacific air masses were frequently sampled over the western Pacific in conjunction with a general pattern of easterly airflow. Chemical signatures found within these air masses support air mass back-trajectory analyses that indicate these air masses had not been recently influenced by continental sources. Within these particular air masses, boundary layer mixing ratios of trace gases with moderate tropospheric lifetimes were generally smaller within the marine boundary layer (<1 km) where, for example, mixing ratios of carbon monoxide averaged ~70 ppbv, ozone ~15 ppbv, ethane ~350 pptv, and ethyne ~25 pptv. Aged free tropospheric western Pacific air was often found to have modestly enhanced mixing ratios of these compounds with mixing ratios of carbon monoxide averaging ~75 ppbv, ozone ~25 ppbv, ethane ~450 pptv, and ethyne ~40 pptv. More reactive compounds were found to have a similar tendency within these air masses, with  $\text{NO}_x$  mixing ratios averaging ~25 pptv within the free troposphere.

This paper describes the detailed chemical characteristics of these well defined, aged Pacific air masses. This analysis will include a comparison of the chemical characteristics of these air masses relative to their age based upon both air-mass trajectories and non-methane hydrocarbon ratios (as a surrogate age indicator). A comparison will also be made to several Asian outflow air masses that had been recently influenced by continental sources.

***Influence of Stratospheric Intrusions on the Chemical Composition of the Troposphere over the Western Pacific During PEM-West***

E. Browell, A. Bandy, D. Blake, J. Bradshaw, C. Butler, D. Davis, J. Dibb, M. Fenn, W. Grant, G. Gregory, B. Heikes, K. Kelly, Y. Kondo, S. Liu, J. Merrill, R. Newell, F. Rowland, G. Sachse, S. Sandholm, F. Sakamaki, M. Shipham, H. Singh, R. Talbot, D. Thornton, Z-X. Wu (oral) #23

The NASA Pacific Exploratory Mission-West (PEM-West) was conducted during September - October 1991 to investigate the sources and sinks of tropospheric gases and aerosols over the western Pacific during the period when air in the lower troposphere has the least influence from continental sources. Remote and in situ measurements of gases and aerosols were made from the NASA DC-8 aircraft during flights conducted primarily from bases in Japan, Hong Kong, and Guam. An airborne lidar provided vertical measurements of ozone ( $\text{O}_3$ ) and aerosol profiles from near the surface to above the tropopause along the flight track, and a comprehensive set of in situ measurements were made on the aircraft for determining chemical and meteorological characteristics of the sampled air.

During the PEM-West, the airflow in the lower troposphere was generally easterly, and without recent continental influences. This air typically had low aerosol loading and low  $\text{O}_3$  ( $\leq 40$  ppb). In the middle to upper troposphere the air flow was mostly westerly, and the background  $\text{O}_3$  was generally less than ~55 ppb. On 60% of the PEM-West flights,  $\text{O}_3$  was observed to exceed these levels in regions that were determined to be associated with stratospheric intrusions. In these cases, the stratospheric air was also found to have enhanced aerosol loading due to the eruption of Mt. Pinatubo in June 1991. In strong intrusions,  $\text{O}_3$  was observed to exceed 250 ppb with dew point levels below  $-70^\circ\text{C}$ . The sulfur dioxide and sulfate concentrations were very elevated in these intrusions, with observed levels exceeding 500 ppt and 400 ppt, respectively. These levels were about five times higher than was observed in the background tropospheric air. In addition, the nitric acid levels of  $\geq 200$  ppb in the intrusions were more than twice the background level. In the stratospheric air, beryllium-7 was  $\geq 3900$   $\text{fc}/\text{m}^3$  compared to background levels of  $\leq 500$   $\text{fc}/\text{m}^3$ . The lowest levels of carbon monoxide ( $\leq 50$  ppb) and methane ( $\leq 1670$  ppb) were observed in the stratospheric air, while their typical tropospheric background levels were in the range of 75 to 85 ppb and 1705 to 1730 ppb, respectively. Also, nitrous oxide and hydrocarbon levels all decreased on entering the intrusions.

PEM-West provided the first opportunity for detailed characterization of the stratospheric air that was being transported into the troposphere at mid and low latitudes over the Pacific. Airborne lidar measurements of  $\text{O}_3$  and aerosol distributions showed the vertical scale of these intrusion events, and the meteorological analysis of potential vorticity fields

provided information on their areal extent. This paper describes the chemical composition, spatial extent, and influence of stratosphere-troposphere exchange on the troposphere over the western Pacific during PEM-West.

***Atmospheric Trace Constituents Measured in Typhoon Mireille from the NASA DC-8 During PEM-West: Possible Explanations***

R. Newell, Z.-X. Wu, Y. Zhu, W. Hu, A. Bandy, D. Thornton, D. Blake, F. Rowland, W. Brockett, L. DeGreef, D. Lewis, E. Monitz, D. McCormick, E. Browell, G. Gregory, G. Sachse, M. Shipham, S. Bachmeier, D. Davis, S. Liu, K. Kelly, J. Merrill, H. Singh (oral) #24

Mireille was first mentioned as an organized area of cloudiness on 13 September 1991 at about 12°N, 172°E. This area drifted to the WNW and was classified as a typhoon (wind speed > 65 kt) on 16 September at 15°N, 157°E. The typhoon then moved westwards and turned to the north-west at 15°N, 135°E on 21 September, with wind speeds reaching 130 kt the following day. It continued to move NW to 25°N, 126°E when it recurved on 26 September, its winds having weakened to 115 kt. A large area of ocean was disturbed by intense wave activity, and venting of gases like DMS was therefore encouraged. The high velocities attained were associated with an even larger area of inflow in the free atmosphere, and divergent wind computations showed that material from mainland China was easily entrained. The NASA DC-8 sampled Mireille from Tokyo on September 27 heading first SSW, descending to the boundary layer to sample air at 300m, returning to higher altitude on a WNW heading to penetrate the eye at ~11 km from the SW, and heading NE out of the eye in the outflow direction after spending over 30 minutes in the eye region. Following this a section perpendicular to the flow in the upper troposphere was explored before returning to Tokyo. Maps were drawn for an altitude of 11.3 km of wind velocity, temperature, water vapor, ozone, and other trace gases in the eye region. They show much fine structure with a center of subsidence but no typical stratospheric ozone values. In fact, while ozone in the boundary layer was 10 – 15 ppbv, maximum mixing ratio in the eye was only about 50 ppbv. DMS was high in the eye being about 70% of the value found in the boundary layer to the SW of the eye. Hydrocarbons and carbon monoxide were high in the eye and in the outflow and were higher in the upper troposphere than in the boundary layer. Rotational and irrotational wind components have been drawn up and used to assess the area over which material was entrained into the central region. Mass fluxes were computed to show the entrainment in the lower layers and the detrainment in the upper layers as a function of time. It appears that material was scavenged from the sea surface layer as well as the lower troposphere over a wide area. Quantitative values of these fluxes will be presented.

***Measurement of Atmospheric Trace Constituents over the Pacific Rim Region of East Asia During PEACOMPOT***

H. Akimoto, S. Hatakeyama, K. Murano, H. Bandow, A. Shimizu, H. Mukai, M. Nishikawa, F. Sakamaki, T. Mizoguchi, M. Yamato, S. Tanaka, H. Tsuruta, I. Watanabe, D. Jaffe, X.-Y. Tang, D. Blake, S. Rowland, J. Merrill (oral) #25

The PEACOMPOT (Perturbation by East Asian Air Mass to Pacific Oceanic Troposphere) field campaign was conducted in October 1991 under the IGAC/APARE program. Aircraft observations of gases and aerosols were made using a CESSNA-404 flying over the East China Sea, Yellow Sea and Japan Sea at the altitude of 0.5 – 3 km. Important reactive species such as O<sub>3</sub>, NO<sub>x</sub>, SO<sub>2</sub>, CO, C<sub>3</sub>-C<sub>5</sub> hydrocarbons and aldehydes were measured, as well as nitrates and sulfates. During the flight over the East China Sea, air masses with westerly airflow which traveled from the continent were sampled. The air masses were characterized by higher concentrations of ozone and NO<sub>x</sub> in a boundary layer continental air mass. On the contrary, during the flight over Japan Sea, northeasterly airflow prevailed due to the approach of a typhoon to the southern coast of the main island of Japan. Apparently, the air mass sampled in a boundary layer is photochemically inactive and the ozone concentration (< 45 ppb) in the lower level is lower than in the upper layer.

Ground sampling of air was simultaneously conducted at remote sites at Oki, Tsushima and Okinawa Islands. In particular, intensive simultaneous measurements of O<sub>3</sub>, CO, NO<sub>y</sub>/NO, SO<sub>2</sub> and aerosols were made at Oki station. Air masses sampled in traveling high pressure frequently show high concentrations of CO and NO<sub>y</sub> (up to 263 and 4.0 ppb, respectively) which are mostly associated with wind directions of SW-W. The "cleanest" air masses come from NNE-NE traveling over the Japan Sea. These contain O<sub>3</sub>, CO and NO<sub>y</sub> typically at levels of ca. 38, 100 and 0.23 ppb, respectively. Okinawa was found to be frequently under "polluted" continental air which contains levels of O<sub>3</sub> and SO<sub>2</sub> as high as at Tsushima, which is located much closer to Korea and Japan.

***Chemistry of Aerosol Particles over Asia and the North Pacific***

R. Arimoto, Y. Gao, X. Zhang, Z. An, M. Zhou, R. Duce, J. Prospero, D. Savoie (poster) #27

Aerosol particles from several sites in Asia and from a cruise in the East China sea have been analyzed for selected trace elements and ionic species. Trace element concentrations were determined using instrumental neutron activation analysis and proton induced x-ray emission. Ion chromatography was used for the determination of nitrate, sulfate and methanesulfonate.

Mineral dust concentrations over Asia, which are based on Al, are three to four orders of magnitude higher than those over the central North Pacific. The atmospheric dust flux to the loess plateau is up to 100 times higher than that of the Yellow Sea, which in turn is among the highest of any coastal region yet studied. Mass-particle size distributions show that the dust particles between 2 and 20 μm in diameter dominate the mass of particulate material in the atmosphere over the loess plateau, but anomalously enriched elements are also evident even during dust storms. Higher mass-median diameters for mineral particles occur during dust storms, and model-derived dry deposition velocities for dust particles are 5 to 10 cm/s during dusty periods. Nevertheless, the annual dust flux over central Asia is mainly attributable to non-dust storm conditions.

Vanadium concentrations over Asia are generally low compared with those over North America, and this reflects the low usage of fuel oil in Asia. In contrast, the selenium concentrations at the Asian sites are high, suggesting a pervasive

influence of emissions resulting from coal combustion. These trace element results are supported by the high concentrations of non-seasalt (nss) sulfate and the high mss sulfate/nitrate ratios in aerosol particles from Asia.

### **BIBEX: Biomass Burning Experiment: Impact on the Atmosphere and Biosphere**

#### *Atmospheric Impacts from Biomass Burning*

**M.O. Andreae (invited) E**

Biomass burning is now recognized as a major source of important trace gases, including CO<sub>2</sub>, NO<sub>2</sub>, CO and CH<sub>4</sub>, and of aerosol particles. It takes on many forms: the burning of forested areas for land clearing, the extensive burning of grasslands and savannas to sustain grazing lands, the burning of harvest debris, and the use of biomass fuel for heating.

The emissions from biomass burning represent a large perturbation to global atmospheric chemistry, especially in the tropics. Here, satellite observations have shown high levels of O<sub>3</sub> and CO over vast areas of Africa and South America and over the tropical Atlantic and Indian Ocean. Recent studies have linked this phenomenon to biomass burning plumes, and demonstrate that pyrogenic emissions affect regional ozone concentrations and the oxidative characteristics of the tropical atmosphere. The particulates affect regional global radiation budgets by their light-scattering effects and their influence on cloud microphysical processes.

Fire also has both short- and long-term effects on trace gas emissions from affected ecosystems which, for instance in the case of CO<sub>2</sub> and N<sub>2</sub>O, may be more significant than their immediate release during the fire. Fire also alters the long-term dynamics of the cycling and storage of elements within terrestrial ecosystems, thereby altering their significance as sources or sinks of various trace gases. Finally, deposition of compounds produced by biomass burning on pristine tropical ecosystems may affect their composition and dynamics.

The importance of biomass burning is well recognized in IGAC, and one of the initial IGAC activities "Biomass Burning Experiment: Impact on the Atmosphere and Biosphere (BIBEX)" is focused on this phenomenon. It is aimed at quantifying the extent of the temporal and spatial distribution, dynamics, species emissions, and atmospheric consequences of biomass burning.

The first large, coordinated program being conducted under IGAC/BIBEX is the Southern Tropical Atlantic Regional Experiment (STARE), an aircraft and ground-based measurement program to investigate the sources of trace gases, their atmospheric transport, and the chemical processes in the atmosphere which lead to elevated levels of ozone, CO, and other trace gases over the southern tropical Atlantic Ocean. During August - October 1992, the first STARE field campaign took place successfully. Ca. 160 researchers from 14 nations participated in the field experiments, using eight aircraft and numerous ground-based measurement systems. Some measurement sites have remained in operation in order to investigate the seasonal and longer-term trends in the distribution of pyrogenic emissions and ecosystem behavior. High levels of O<sub>3</sub>, CO, NO<sub>x</sub>, and other trace gases, as well as aerosol particles were found in the entire region from South America to southern Africa, and could be related to forest and savanna fires on the two continents. Initial results will be presented at the meeting, together with a discussion of plans for future BIBEX experiments.

#### *Ground Based Monitoring Network of Aerosol Emissions from Biomass Burning in Brazil*

**B. Holben, T. Eck, E. Vermote, A. Setzer, J. Reagan, Y. Kaufman, D. Tanré, I. Slutsker (oral) #37**

Satellite platforms have provided a methodology for regional and global remote sensing of aerosols. New systems will significantly improve that capability during the EOS era, however the voluminous 20 year record of satellite data has produced only regional snapshots of aerosol loading and has not yielded a data base of the optical properties of those aerosols which are fundamental to our understanding of their influence on climate change. The prospect of fully understanding the properties of the aerosols with respect to climate change is small without validation and augmentation by ancillary ground based observations.

Sun photometry has been demonstrated to be an effective tool for ground based measurements of aerosol optical properties from fire emissions. Newer technology has expanded routine sun photometer measurements to spectral observations of solar aureole and almucantar allowing retrievals of size distributions, scattering phase function, and refractive index. A series of such observations have been made in Brazil's Amazon basin from a network of six simultaneously recording instruments deployed in September 1992. The instruments were located in areas removed from local aerosol sources such that sites are representative of regional aerosol conditions. The overall network was designed to cover the counter-clockwise tropospheric circulation of the Amazon basin.

We will discuss spectral measurements of sun, aureole and sky data for retrieval of aerosol optical thickness, particle size distribution and scattering phase function. Early results from the network clearly show the aerosol optical thickness to vary regionally and temporally. However, the wavelength exponent remained relatively constant compared to earlier data taken before the influence of stratospheric sulfate aerosols from the Mt. Pinatubo eruption.

#### *Biomass Burning as Source of Greenhouse and Sulfur Gases in Southeast Asia*

**B. Nguyen, J. Goldammer, J. Putaud, N. Mihalopoulos, S. Lancelin, B. Bonsang, C. Doan (oral) #38**

Biomass burning during the dry season in tropical South-East Asia produces large amounts of greenhouse gases (CO<sub>2</sub>, CH<sub>4</sub>) and carbonyl sulfide (OCS). These gases have a potential impact on the radiative balance of the troposphere. In order to study fluxes of these gases from biomass burning, field experiments have been conducted in the Central Highlands of Vietnam during the dry season (March 1992). Concentrations of CO<sub>2</sub>, CH<sub>4</sub>, CO, and OCS from the fires of rice straw, pine

and Dipterocarp savanna ranged from 3100 to 15000 ppmv, 5 to 56 ppmv, 28<sup>0</sup> to 1700 ppmv, 4 to 70 ppbv respectively. A significant correlation has been observed between OCS and CO concentrations indicating an OCS production during the smoldering combustion. The results obtained from field experiments in Vietnam allow us to estimate a mean COS/CO<sub>2</sub> and a COS emission from biomass burning in South-East Asia.

#### ***Trace Gas Emissions from Biomass Burning in Tropical Australian Savannas***

**D. Hurst, D. Griffith, G. Cook (oral) #39**

During the 1991 and 1992 dry seasons (April – October) we have collected and analysed over 100 samples of smoke from savanna fires at the Kapalga Research Station in Kakadu National Park, Northern Territory, Australia (12°S, 132°E). Samples were collected mainly from a light aircraft flying at 50 – 700 m above the fires, but also from the ground. They were analysed for CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, NMHCs, NO, NO<sub>x</sub>, NH<sub>3</sub>, N<sub>2</sub>O, CH<sub>2</sub>O, CH<sub>3</sub>CHO, HCN, CH<sub>3</sub>CN, SO<sub>2</sub>, OCS, CS<sub>2</sub> and a number of other species using gas-phase FTIR, matrix-isolation FTIR, chemiluminescence and gas chromatographic techniques. In addition we have made detailed analyses of the loading and elemental composition of both the pre-fire fuel and the post-fire ash and non-combusted material.

We will present data including measured emission ratios of the trace gases relative to emitted CO<sub>2</sub> and CO, emission factors of each gas relative to the elemental composition of the fuel, an overview of how each volatilised element (C, N and S) is distributed among the various trace gases, and estimates of the Australian savanna fire contribution to global budgets of important trace gases. In general, the data indicate efficient combustion with low CO:CO<sub>2</sub> emission ratios (< 10%) in these fires, which are predominantly of grass and other light fuels. NO<sub>x</sub> and NH<sub>3</sub> are the main emitted nitrogen species observed and are of comparable magnitude. All measured nitrogen species account for less than half the fuel nitrogen, consistent with previous laboratory studies.

#### ***SAFARI 92: Airborne Measurements of Trace Gases Emitted by Southern African Veld Fires***

**G. Harris, T. Zenker, F. Wienhold, U. Parchatka, M. Welling (oral) #40**

For the September/October 1992 Southern Africa Fire Atmosphere Research Initiative (SAFARI 92) campaign we installed a wide range of trace gas measurement equipment aboard a locally chartered DC-3 Jetprop aircraft in order to study the near and far field distributions of trace gases emitted from savanna fires throughout Southern Africa.

Two tunable diode laser spectrometers aboard measured NO<sub>2</sub>, HCHO, CH<sub>4</sub> and N<sub>2</sub>O with one minute time resolution and CO with one second time resolution. NO and NO<sub>y</sub> were measured using a chemiluminescence instrument and a gold-CO converter which was mounted externally to the cabin. CO<sub>2</sub> and O<sub>3</sub> (two methods) were measured using commercial instruments and pressurized whole air grab samples were obtained for GC analysis of NMHC, CH<sub>3</sub>Cl, etc. A forward looking video camera, a GPS system and a Rosemont (P, T, RH) probe were also installed.

Flights took place over South Africa, Swaziland, Botswana, Zimbabwe, Zambia and Namibia and measurements were made in the immediate vicinity of active fires and throughout the boundary layer between the surface and 12000 feet pressure altitude. We report the data in preliminary form, show calculated emission ratios for the measured trace gases relative to CO or CO<sub>2</sub> and discuss the implications of the emissions for oxidant formation on a subcontinental scale.

#### ***Airborne Measurements of Aerosol Emission Characteristics and Regional Distribution of Aerosols from Biomass Burning in Southern Africa During STARE/SAFARI 92***

**M.O. Andreae, T. Andreae, W. Elbert, F. Wienhold, T. Zenker (oral) #42**

The first coordinated field campaign of STARE/SAFARI (a component of IGBP/IGAC) took place in southern Africa during August – October 1992. Its objective was an investigation of the impact of biomass burning on the atmosphere over southern Africa and the surrounding oceans. We conducted research flights using an instrumented DC-3 aircraft in southern Africa during September – October 1992. The study region covered northern South Africa and Namibia, Botswana, Zimbabwe, Zambia, Swaziland and southeastern Angola. The aircraft was equipped with a PMS PCASP-100X laser-optical aerosol probe, from which aerosol spectra in the size range 0.10 – 3.0 μm diameter were obtained at a time resolution of 2 – 10 sec. The black carbon content of the aerosol was determined with a reflectance aethalometer. For the determination of aerosol chemical composition, we collected aerosol on quartz glass filters and on stacked filter units, consisting of a Nuclepore prefilter for particles larger than ca. 1 μm and a Teflon second filter for the submicron fraction. The filters were analyzed for soluble ionic components and for organic carbon.

We determined the emission ratios for aerosols (relative to CO<sub>2</sub> and CO as reference species) from fires in savanna, forest, and agricultural ecosystems by airborne sampling of fire plumes close to prescribed and incidental fires. We investigated the regional and large-scale distribution of pyrogenic aerosols on two survey missions of four and five days duration through the entire study area, and on several shorter flights. In spite of an intensive drought, which had reduced the biomass available for burning in 1992, we found high levels of aerosols throughout southern Africa, particularly during the first survey (24 – 28 September 1992). During this period, the airmasses sampled along the flight track had been exposed to smoke from numerous fires in tropical southern Africa. Our results suggest that pyrogenic emissions had a pronounced influence on the chemical and optical properties of the troposphere in southern Africa during the study period.

#### ***Effect of Smoke Particles on Cloud Microphysics and Reflectance in the Amazon***

**Y. Kaufman, R. Fraser, M. Lawrence (oral) #44**

NOAA-AVHRR images taken over the Brazilian Amazon basin during the biomass burning season of 1987 were used to study the effect of smoke particles on the properties of low cumulus and stratocumulus clouds. Smoke particles are

hygroscopic and interact with clouds, affecting their microphysics and radiative properties. The reflectance at a wavelength of 0.64  $\mu\text{m}$  and the drop size, derived from the cloud reflectance at 3.75  $\mu\text{m}$ , were studied for thousands of clouds. The opacity of the smoke layer adjacent to each cloud was also monitored simultaneously and used as a measure of the smoke particles loading. Since the effect of smoke particles on the cloud radiative properties depends on the cloud thickness, the cloud pixels were separated based on the cloud top temperature. Using this process we can observe separately the effect of smoke on thin clouds (high cloud top temperature) and thick clouds (lower temperature). The presence of dense smoke reduces the drop size of continental clouds in the tropics from 15  $\mu\text{m}$  to 9  $\mu\text{m}$ . Results show that smoke does not change the reflectance (at 0.64  $\mu\text{m}$ ) of clouds for reflectance of 0.5 and darkens clouds for reflectance of 0.6 to 0.7. Preliminary results for clouds with lower reflectance (0.3–0.4) show an increase in the reflectance from 0.35 to 0.42 with a moderate increase in the smoke loading and a decrease of the reflectance with heavy loading. Observations of these characteristics of clouds in the tropics is necessary in order to understand the effects of smoke particles on climate.

#### **Remote Sensing of Biomass Burning in the Amazon**

Y. Kaufman, B. Holben, D. Tanre, D. Ward (poster) #43

Satellite remote sensing, e.g., from the NOAA-AVHRR, is able to sense several important components of biomass burning in the Amazon and their effect on the atmosphere, on the radiation field and on climate. The visible channel (0.64  $\mu\text{m}$ ) is useful to sense the mass of the emitted smoke that later can be converted into the mass of the emitted trace gases. The 3.75  $\mu\text{m}$  channel is used to detect fires. The application of the remote sensing techniques requires knowledge of the relation between trace gas emission and the emission of particulates, and the average smoke aerosol particle size. These parameters were measured in the BASE field experiments. Application of the remote sensing techniques and the results from the field experiments to the 1987 biomass burning season, showed that the emission of smoke particulates and trace gases is larger than what would have been expected from land use computations. The Moderate Resolution Imaging Sensor (MODIS), scheduled to be launched in 1998 on the Earth Observing System will enhance smoke measurements significantly by applying additional channels. The 3.75  $\mu\text{m}$  channel, used to detect fires will not saturate on the MODIS system (as it does on the AVHRR), thus enabling remote sensing of the fire temperature, in order to distinguish between difference fire phases (smoldering and strong and moderate flaming).

For an operational application of these techniques, more systematic measurements of all the components of biomass burning and of atmospheric radiation field are required. In the "Smoke Cloud and Radiation" – SCAR experiment, planned for 1994, aircraft scanning radiometers will be used to measure the radiation field across the solar and IR spectrum simultaneously with rigorous measurements of the properties and concentration of trace gases, aerosol particles and clouds. Combination of such field studies with satellite analysis should enable an estimate of the climatic effects of biomass burning.

#### **Interdisciplinary Research Projects for Developing a Global Fire Science**

J. Goldammer (poster) #120

Despite increasing scientific interest given to the role of fire in ecosystem dynamics, biogeochemical cycles and atmospheric processes, it is necessary to state that (1) although vegetation fires and other plant biomass burning constitute an old and important natural and anthropogenic environmental factor, we have much less knowledge about extent and consequences on the global environment than about the consequences of fossil fuel burning, (2) attempts in establishing a global fire synthesis or in developing a global fire science have not yet been successful, (3) the development of such a global synthesis would require multi- and interdisciplinary research approaches, and (4) the rapidly increasing size of the Earth's human population and its accelerated use of fire require enhanced research efforts immediately to close these gaps.

The development of a "Global Fire Ecology" as a "Science of the Biosphere" must overcome traditional disciplinary fragmentation of science. More than ever before such a new science requires a continuous process of communication and cooperation between the participating fields. A strong multi- and interdisciplinary stimulation was provided by the Dahlem Workshop "Fire in the Environment: The Ecological, Atmospheric and Climatic Importance of Vegetation Fires" (March 1992). The results of that workshop had considerable influence on the conceptual design of the first intercontinental fire experiment SAFARI (Southern African Fire-Atmosphere Research Initiative, 1991 – 1994), in conjunction with TRACE-A (Transport and Atmospheric Chemistry Near the Equator – Atlantic) under the umbrella of the IGAC/BIBEX Southern Tropical Atlantic Regional Experiment (STARE).

The upcoming research projects and field campaigns are focusing on the regional fire ecology of boreal Eurasia (FIRESKAN – Fire Research Campaign Asia-North, 1993-95) and tropical Southeast Asia (SEAFIRE – South East Asian Fire Experiment, ca. 1996-97). The historical role of vegetation fires and other plant biomass burning will be investigated in an international fire history project "Historical Dimension of Natural and Anthropogenic Fire" (ca. 1993-96) and evaluated by a Dahlem-type Workshop (ca. 1996).

#### **BATGE: Biosphere-Atmosphere Trace Gas Exchange in the Tropics: Influence of Land-Use Change**

##### **Terrestrial Biosphere-Atmosphere Interactions and Land-Use Change in the Tropics**

M. Keller, P. Matson (Invited) D

Tropical soils and vegetation represent globally significant sources of a range of atmospheric gases, including  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{CH}_4$ , and volatile organic compounds. Conversion of tropical forests to agriculture and other uses, and intensification of agricultural practices in both forest and savanna areas are occurring very rapidly; yet the impacts of these



land-use practices on biogeochemical cycles, trace gas emissions, and atmospheric chemistry are not well understood. We present early results of BATGE studies that evaluate the importance of tropical land-use change on fluxes of a number of gases.

Soils are important sources and sinks for trace gases, especially for oxides of nitrogen. On-going studies in Brazil, Costa Rica, Puerto Rico, and Mexico suggest that conversion of forest to pasture results in elevated soil emissions of nitrogen oxides in the first decade or less after clearing, but that older pastures, unless intensively managed, have lower fluxes than forest. Forest conversion to pasture also diminishes the soil sink strength for methane; in some cases the direction of the flux is reversed and pasture soils become methane sources. Likewise, results from a number of tropical regions suggest that agricultural sites recently converted from native vegetation have elevated fluxes of nitrogen and carbon gases, but that high emissions of nitrogen oxides and reduced uptake of methane in older agricultural systems are maintained only with intensive management and fertilizer use. Moreover, the magnitude of flux in response to fertilization depends on soil type and management considerations such as crop type, fertilizer type, application rate, and application methods. The great spatial and temporal variability in trace gas responses to tropical agricultural practices complicates estimates of their importance at regional and global scales.

Few attempts have been made to study vegetation sources and sinks for trace gases in the tropics. It is clear that tropical vegetation can produce large quantities of volatile organic compounds. Forests may be strong sinks for oxidants and odd-nitrogen compounds. Changes in the species composition and structure of vegetation will almost certainly change these system properties; but our ability to predict the magnitude of these changes is severely hampered by dearth of relevant data.

#### *Simulation of Nitric Oxide Emission from Tropical Savanna Soils Using an Empirical Model*

A. Rondón, H. Rodhe, C. Johansson, E. Sanhueza, L. Cardenas (oral) #30

Measurements carried out in the Venezuelan savanna have shown that the rate of emission of NO from soils is mainly dependent on soil moisture and N-nutrient content, and to a lesser extent on soil temperature. Based on experimental observations and theoretical considerations we have defined a model to simulate the emission rate of NO from the soil ( $E_{NO}$ ) as a function of soil moisture (M), soil surface temperature (T) and soil nitrate content (N), as follows:

$$E_{NO} = f(M, T, N) = \alpha M \exp(-M/M^*) T \exp(T/T^*) N^\delta$$

where  $\alpha$  is a proportionality coefficient and  $M^*$  the optimum soil moisture, which is dependent on the physical characteristics of the upper layer of the soil and on the type of microbiological processes (e.g., nitrification or denitrification) that dominate the production of NO.  $T^*$  is the optimum soil surface temperature, probably dependent on the response function NO production-temperature for the dominant nitrifiers or denitrifiers in the soil. The parameter  $\delta$  ( $0 < \delta < 1$ ) characterizes the dependence on N.

The equation presented above is linearized and the parameters  $\alpha$ ,  $M^*$ ,  $T^*$  and  $\delta$  are calculated by adjusting the experimental data by a multilinear regression technique. The potential of using this model to calculate the NO emission over large areas will be discussed.

#### *Effect of Plowing on Trace Gas Fluxes from Tropical Savannah Soils*

E. Sanhueza (oral) #31

Increased conversion of natural savannah ecosystems to agricultural soils is occurring in the tropics, likely contributing to the change in the chemical composition of the atmosphere. In the savannah region of Venezuela, plots of native grassland soil were cultivated and the effect on  $CO_2$ , CO,  $CH_4$ ,  $N_2O$  and NO fluxes were evaluated. Here, the initial effect of plowing is presented.

The measurements did not show any notable change in  $CO_2$ ,  $CH_4$  or  $N_2O$  fluxes, suggesting that these gases have "long soil-lifetimes" and that their emissions to the atmosphere originate from a "deep" layer of soil, and also that in the short term, plowing does not significantly alter the activity that produces trace gases in soils. On the other hand, a significant change in CO and NO fluxes was produced, indicating that the transport of these gases within the soil plays an important role in determining their net flux to the atmosphere. For CO, non-perturbed soil switches from being a net source to being a net sink after plowing, suggesting that decompacted soils promote CO consumption by microbiological processes in deeper soil layers. In the case of NO, the plowing leads to a dramatic increase (5 times) of the emissions, likely due to an enhancement of the escape rate to the atmosphere of the NO biogenically produced in the soil.

In conclusion, it appears in the short term that plowing of savannah soil does not significantly alter the bacteria activity that produces trace gases in the soil, but significantly increases the transport processes within the soil and changes the soil-atmosphere flux of gases with "short soil-lifetimes" (i.e., NO, CO) in a notable way.

#### *Microbial Consumption of Atmospheric $CH_4$ , CO and NO in Soil*

R. Conrad, M. Bender (oral) #33

Microbial  $CH_4$  oxidation in soils is a potential sink for atmospheric  $CH_4$ . Therefore, we measured profiles of  $CH_4$  oxidation activity in the soil column and determined the kinetics of  $CH_4$  oxidation in soil and in methanotrophic soil bacteria. We also investigated the potential interaction of methanotrophic bacteria, nitrifying bacteria and carboxydophilic bacteria during consumption of atmospheric  $CH_4$ , CO and NO in soil.

Vertical profiles of  $CH_4$  mixing ratios, of  $CH_4$  oxidation activities and of numbers of methanotrophic bacteria showed that  $CH_4$  oxidation mainly occurred in subsurface layers of the soil. This is in contrast to oxidation of CO and NO which were generally located in the topmost soil layers.

$CH_4$  oxidation followed Michaelis-Menten kinetics with maximum oxidation rates ( $V_{max}$ ) of about 10 - 60 ng  $CH_4$  h<sup>-1</sup> g<sup>-1</sup> soil dry weight and half saturation constants ( $K_m$ ) of about 30 - 45 ppmv. Atmospheric  $CH_4$  mixing ratios were oxidized by

pseudo first-order kinetics down to a threshold of about 0.2 – 0.3 ppmv CH<sub>4</sub>. CH<sub>4</sub> was oxidized even below this threshold, but at a much lower rate. This result shows that oxidation of atmospheric CH<sub>4</sub> in the soil column is not a simple first-order reaction and emphasizes the need for careful interpretation of kinetic data with respect to field conditions.

The kinetics of CH<sub>4</sub> oxidation became even more complex when the soils were preincubated under high CH<sub>4</sub> concentrations (20% CH<sub>4</sub> in air). This treatment resulted in an additional CH<sub>4</sub> oxidation kinetic which was superimposed on the kinetic that was typical for the untreated fresh soil. The additional kinetic showed about 20 – 400 fold increased values for  $V_{max}$ ,  $K_m$  and threshold, and obviously was due to the growth of a methanotrophic bacterial population which was adapted to high CH<sub>4</sub> mixing ratios. The responsible methanotrophic bacteria apparently were those which are known from culture collections, while the bacteria responsible for the oxidation of atmospheric CH<sub>4</sub> mixing ratios are still unknown.

The increase of the methanotrophic population in soil not only resulted in increased rates of CH<sub>4</sub> oxidation, but also of consumption of atmospheric CO and NO. An increase of the nitrifying population, on the other hand, stimulated ammonium oxidation and CO consumption, but only to a small extent the consumption of CH<sub>4</sub> or NO. An increase of the carboxydrotrophic population stimulated the consumption of high CO mixing ratios but only to a small extent that of atmospheric CO and NO. These results indicate a significant potential of different metabolic groups of bacteria to cometabolize atmospheric trace compounds other than those to which they are adapted.

***Emissions of Nitrogen Oxides from Soils of the Equatorial Rain Forest: Emission Mechanisms and Influence on Atmospheric Chemistry within the Forest and the Boundary Layer***

R.A. Delmas, D. Serca, J. Lacaux, J. Lacombe, A. Lopez, C. Bouka-Biona, L. Labroue (oral) #34

Emissions of nitric oxide from soils of the equatorial rain forest were measured in the Dimonika Natural Park (4°30'S, 12°30'E) in the Mayombe Forest in Congo. Three research campaigns were carried out in June and July 1991 and in February 1992. Fluxes were measured by dynamic chamber techniques, chosen after laboratory experiments, using a Scintrex LMA3 chemiluminescence instrument. NO fluxes measured on natural soils are between 5 and  $17 \times 10^9$  molecules/cm<sup>2</sup>/s; they are of the same order of magnitude as those observed in similar tropical forest media. Soil treatment experiments show that, basically, nitric oxide is produced by auto-decomposition of HNO<sub>2</sub> in these acidic soils (pH 4) (chemodenitrification). Nitrous acid comes from autotrophic nitrification all year, and also from biological denitrification, evidenced by N<sub>2</sub>O emissions, during the rainy season. The regulation of NO release from soils is linked to ammonia production from litter mineralization or to direct NH<sub>4</sub> input by throughfall.

During the campaigns vertical profiles of NO, NO<sub>2</sub> and O<sub>3</sub> concentrations were measured between ground level and the top of the canopy. Micrometeorological parameters were measured by means of a metallic tower; the vertical diffusion coefficient ( $k_z$ ) was estimated by a method based on the determination of the thermic amplitude at two different levels under the canopy. In spite of significant emissions from soils, the concentration of NO within the forest remains very low (<100 pptv). NO is converted very quickly into NO<sub>2</sub> by reaction with O<sub>3</sub>. This is shown by experimental profiles and confirmed by numerical simulation with a Lagrangian photochemical model in which the vertical diffusivity is represented by  $k_z$  profiles. The model shows that biogenic emission of nitric oxide from the forest has a weak influence on photochemical ozone formation in the boundary layer (0 – 1200 m) and cannot explain the NO<sub>2</sub> concentrations observed at the top of the canopy. The influence of remote savannah fires is quite probable and, as almost everywhere in tropical Africa, regulates the atmospheric photochemistry even in this forested region.

***Effects of Soil Moisture, Temperature, and Nitrogen on NO Emissions from Acidic Tropical Savannah Soils***

L. Cardenas, A. Rondon, C. Johansson, E. Sanhueza (poster) #29

Soil NO fluxes were measured over a wide range of soil moisture, soil N-nutrients and soil temperature during the wet and the dry season at a Venezuelan savannah site. Emissions were measured using an enclosed chamber technique and NO was detected with a chemiluminescence analyzer.

Maximum NO emissions (~12 ng N m<sup>-2</sup> s<sup>-1</sup>) were observed at soil gravimetric moisture between 10% and 18%. Deviation from this optimum range produced a decrease in the NO flux; very low emissions (<2 ng N m<sup>-2</sup> s<sup>-1</sup>) were recorded at low (<2%) and high (>25%) soil humidities. This indicates that both NO production in the soil and its transport inside the soil play important roles in NO emission to the atmosphere. Under most conditions no temperature effect was observed. Fertilization experiments suggest that denitrification is the main process that produces NO in these acidic soils; at low and moderate soil moistures a significant relationship was observed between the soil nitrate and the NO fluxes. In low (natural) soil-nitrate and similar soil moisture conditions, NO emissions were larger during the dry season in comparisons to the rainy season; it is likely that the compaction of soils during the rainy season explains this constraint.

***CO Fluxes from Natural and Cultivated Tropical Savannah Soils***

E. Sanhueza, L. Donoso, D. Scharffe, P. Crutzen (poster) #32

As part of a comprehensive study on tropical land use change and its effect on atmospheric trace gas fluxes, here we report the CO fluxes recorded at a natural grassland site and the changes produced when this ecosystem is managed ("natural" grass) or cultivated with corn, sorghum and pasture. The field site is located in the central part of the savannah climatic region of Venezuela (Guarico state, 8°53'N; 67°19'W). Fluxes were measured in the dark using the enclosed chamber technique. CO was analyzed with a reduction-gas-detector (Trace Analytical) in combination with a molecular sieve 5A column for CO separation.

At all sites CO fluxes exhibited a strong diurnal variation, with net emission during daytime and consumption or no fluxed during nighttime. In unplowed soils, no differences were observed between dry and rainy season, suggesting that soil

moisture plays a minor role in controlling the CO fluxes. A large disparity was observed between unplowed and plowed grassland soils. Plowed soil showed a much smaller emission during daytime and a larger consumption at night. The 24-hour integrated fluxes indicated that the non-perturbed grassland switched from being a net source of CO ( $16 \text{ ng m}^{-2} \text{ s}^{-1}$ ) to being a net sink ( $-5.3 \text{ ng m}^{-2} \text{ s}^{-1}$ ) after plowing. It is likely that in decompacted soils, CO consumption by microbiological processes in deeper soil layers was promoted. As the rainy season progressed the plowed soil gradually compacted and CO fluxes changed back, and after three months the fluxes from plowed and the original unplowed soils were equal. Even though the various cultivated fields (corn, sorghum and pasture) received differing inorganic fertilization treatments, no significant differences in the CO fluxes resulted. Measurements during the dry season suggested that "degrading dry (dead) vegetation" produced CO under dark conditions.

To conclude, in tropical savannah soils CO fluxes are not significantly affected by soil moisture and inorganic nutrients, but are largely controlled by temperature and the physical structure of the soil. Plowed soils emit less CO to the atmosphere than "natural" soils.

## DEBITS: Deposition of Biogeochemically Important Trace-Gas Species

### *Chemical Composition of Precipitation at Two Background Locations in Thailand*

L. Granat, K. Suksomsankh, S. Simachaya, M. Tabucanon, H. Rodhe (oral) #36

As part of a joint Thai-Swedish collaborative effort within the framework of the IGAC/DEBITS/CAAP project, precipitation chemistry measurements were started in Thailand at two sites with the objective of obtaining regionally representative samples and investigating the importance under tropical conditions of different sampling equipment and different sampling times. One wet-only and several bulk collectors are used at each site with one-day and two-week sampling periods. Chemical changes in the samples are minimized by adding a preservative and are evaluated by comparing field and laboratory pH. Good agreement was obtained with preserved samples. Comparison with wet-only and bulk collectors, nearby as well as at some distance (several hundred meters), showed no significant difference for chloride, sulfate and nitrate, while the calcium concentration was about 20% higher in the bulk collectors.

The concentration of most components varies considerably from day to day. The correlation between the two sites is low. The correlation between individual components (ammonium/sulfate, nitrate/sulfate and sulfate/calcium) at the western site is generally poor but it is better at the eastern site. This might indicate significant sources for these components within Thailand. The samples are generally slightly acidic but pH values in the range of 4.1 - 4.4 were recorded in some cases at the western site. The acidity in these cases can be attributed to sulfuric acid. There are indications that some sulfate might be soil-derived together with many of the components traditionally considered as coming from the soil such as excess calcium. The sulfate concentration at both sites is substantially higher than predicted by global scale model calculations at both stations (five to ten times).

Compared to European conditions, the sulfate and ammonium concentrations in Thailand are equal to or lower than in the most remote areas in north-west Scandinavia while nitrate is much lower. The concentration of calcium is comparable to the concentration found in Scandinavia, is much lower than what has been obtained from other measurements in south-east Asia, and is definitely lower than a few recent measurements with the same technique in western India.

### *Iodine in Rainwater*

L. Campos, L. Spokes, T. Jickells (oral) #35

Because of the relative abundance of iodine in seawater compared to terrestrial systems, the atmospheric cycle of this element is thought to be dominated by emissions from the oceans. These emissions are in the form of seasalt-associated iodine, derived from bursting bubbles, and gaseous emissions which are probably dominated by methyl iodide. Although measurements of sea to air fluxes of methyl iodide are very limited, it seems possible that the gaseous emission flux is the larger of the two and also liable to more effective long range transport. The subsequent oxidation of the methyl iodide may play a significant role in global atmospheric chemistry via the formation of IO radicals.

We have adapted electrochemical methods to the determination of iodide and iodate (the two stable redox states under atmospheric conditions) at the low concentrations at which they are found in rainwater (about 10 nM). Using these methods we have begun perhaps the first systematic study of iodine in rainwater aimed at clarifying the geochemical cycle of this element. These results will be presented and used to address the following questions: (1) What are the atmospheric wet depositional fluxes of iodine at various locations? (2) What are the relative magnitudes of methyl iodide emissions and seasalt iodine fluxes? (3) What is the iodine redox speciation in rainwater (i.e.,  $\text{I}^-/\text{IO}_3^-$  ratio) and what does this imply about redox processes in the atmosphere?

## RICE: Rice Cultivation and Trace Gas Exchange

### *Methane Emission From Rice Fields*

H.-U. Neue, R. Sass (invited) F

Wetland rice cultivation is considered to be among the highest sources of atmospheric methane which is an important potential source of global warming. Atmospheric methane concentration is increasing at about 1% per year and it is an open question as to how much of the increase is due to increased emissions from wetland ricefields. Objectives in current research

are to reduce uncertainties of how much methane and other climatically active trace gases are annually emitted from irrigated, rainfed, and flood prone rice ecologies at present, to predict future emissions at given management scenarios, and to develop feasible rice technologies that will reduce emissions and yet will meet the required increase in rice production.

Recent global estimates of methane emission from ricefields range from 20 - 100 million t/yr corresponding to 6 - 30% of total anthropogenic methane emission. Parts of methane emitted from naturally flooded ricefields may not be considered anthropogenic. Because of the limited number and locations of comprehensive seasonal flux measurements, global extrapolations of emission rates from ricefields are still highly uncertain and tentative. They do not account for varying floodwater regimes, soil properties, organic amendments, cultural practices, and rice cultivars. Irrigated ricefields seem to be the major potential source for increased methane emission. Methane emissions are lower and highly variable in rainfed rice because of periodic droughts during the growing season. Flood prone rice may also emit less methane because of deep flooding or tidal influence. Upland rice is not a source of methane because it is grown like wheat on aerobic soils.

Flooding a ricefield cuts off the oxygen supply from the atmosphere causing an anaerobic fermentation of organic matter in the soil. Methane is a major end product of this process. Zero to over 90% of the methane produced may be oxidized in the soil depending on flood condition and time of growing season. Methane is released to the atmosphere by diffusion, ebullition, and through rice plants. A well developed vascular system, common to wetland plants, provides an effective vent to supply atmospheric oxygen to the rice roots for respiration and to release methane from the soil. Methane fluxes are influenced by temperature, water regime, low molecular carbon supply from decomposing soil organic residues and root exudates, soil physical, soil chemical and soil biological properties, plant physiology, rice cultivars, and cultural practices. Methane emission from ricefields show distinct diel and seasonal variations. Diel variation strongly correlates with soil temperature while seasonal variation seems to be more influenced by plant development.

The world's annual rice production must increase by 65% in the next 30 years. With present agronomic practices, such increased production will lead to further increases in methane emission. Promising mitigation candidates that are in accord with increased production are shortening of flooding periods through direct seeding and multiple-drainage aeration, minimizing application of easily decomposable organic matter, use of sulfate-containing fertilizer, application of chemicals that inhibit nitrification and methane formation at the same time, breeding of rice cultivars with a lower methane emission potential, and cultural practices that cause less soil disturbance.

#### *Temporal Patterns of Methane Emissions from Wetland Rice Fields Treated by Different Modes of N-Application*

R. Wassmann, H. Neue, R. Lantin, J. Aduna, M. Alberto, M. Flores, M. Tan, H. Denier van der Gon, H. Hoffmann, H. Papen, H. Rennenberg, W. Seiler (oral) #47

Methane emission rates from wetland rice fields were determined in Los Banos (Philippines) with an automatic system that allows semi-continuous measurements over extended observation periods. Methane emission was monitored in an irrigated rice field planted with rice variety IR72. The soil was classified as Andaqueptic Haplaquoll. The field design was a randomized complete block design with 19 individual plots, 4 treatments and 4 replicates. All plots received identical amounts of mineral nutrients but differed with respect to the mode of urea application: (1) broadcasting at transplanting, (2) broadcasting and incorporation at final harrowing, (3) broadcasting 10 days after transplanting, and (4) deep incorporation into the soil as super granulates. Measurements were performed in wet season 1991 (4 treatments), dry season 1992 (4 treatments), and wet season 1992 (only treatment number 2).

The emission data show pronounced temporal variations. The diel course of methane emission rates followed a persistent pattern with peak values in the early afternoon and minimum values late at night. The daily mean emission rates were lower during the wet season. In the dry season daily mean emission rates revealed a distinct seasonal pattern. Emissions increased generally over the growing season with distinct peaks early after transplanting, at panicle initiation and directly before ripening stage.

Significant amounts of methane were released when the soil was drained after harvest. Emission rates increased sharply when the drained soil started cracking. Methane emission only stopped when the soil was fully oxidized. Irrespective of the mode of N-application the total methane emitted from these wetland rice fields amounted to 10 - 20 g CH<sub>4</sub> m<sup>-2</sup> in the dry season with rice yields of 5.2 - 6.3 t ha<sup>-1</sup> and 6 - 10 g CH<sub>4</sub> m<sup>-2</sup> in the wet season with rice yields of 2.4 - 3.3 t ha<sup>-1</sup>.

#### *Recent Estimates for Methane Release from Indian Rice Paddy Fields*

D. Parashar, P. Gupta (oral) #48

Results of methane emission studies from Indian paddy fields, carried out on a national campaign basis from most of the major rice growing regions of India with different paddy water regimes in "1991 Methane Campaign" and consisting of more than 2000 observations, covering the complete 1991 kharif (wet) season are reported in this paper. These results have been used to derive the estimate of the total budget of methane from Indian paddy fields.

The methane emission rates ranged between -0.20 and 66 mg m<sup>-2</sup> hr<sup>-1</sup> in various paddy cultivation regimes. The irrigated fields had the values between -0.20 and 3.6 mg m<sup>-2</sup> hr<sup>-1</sup>, water logged fields between 0.04 to 66 mg m<sup>-2</sup> hr<sup>-1</sup>, and deep water regimes in the range between 1.10 to 23.3 mg m<sup>-2</sup> hr<sup>-1</sup>. The methane budget has been estimated by using seasonal integrated flux for the whole cropping season for each study site and extrapolating it for total paddy the cultivation area of India. The integrated flux for rainfed waterlogged areas have been found to range from 5 to 60 g m<sup>-2</sup>, for deep water areas between 14 and 24 g m<sup>-2</sup>, and for irrigated areas between 0.06 and 2.0 g m<sup>-2</sup>. The estimates of methane emission from Indian paddies has been found to have an average value of 4 t g yr<sup>-1</sup> with a minimum and maximum range between 2.4 and 6 t g yr<sup>-1</sup>. These recent Indian estimates have been discussed in relation to various factors influencing the methane emission from different rice environs.

**Seasonal Variation of Methane Flux from a Chinese Rice Paddy in a Semi-Arid Temperate Region**

Y. Heng, C. Liang (oral) #49

Methane emission from a rice field in a semi-arid, temperate region in China, viz. Beijing, has been measured, covering the whole growing period. Strong seasonal variation was observed. Two emission peaks accounting for more than 70% of the total emission occurred in early July and the middle of August. Organic fertilizer, irrigation pattern and soil temperature were found to be important factors which influence the methane emission rates. Under common management, the average flux during the entire growing season of 94 days was  $20.4 \pm 9.0 \text{ mg m}^{-2} \text{ hr}^{-1}$ . Methane emission variation from control plots with no rice or only grass has also been studied.

**Emission of Trace Gases from Agro-Ecosystem in Japan and Asia**

H. Tsuruta, K. Yagi, K. Kanda, M. Yoh, K. Minami (oral) #51

We have been studying trace gas emissions to the atmosphere from the agro-ecosystem in Japan and Asia for several years. We will report the new and interesting results of this study. (1) NO and N<sub>2</sub>O fluxes have been measured from fertilized soils and their vertical profiles in the surface soil layer. In addition to nitrification by which these emissions are caused, another mechanism is also needed to explain the NO emission. (2) Seasonal variation of biogenic sulfur gas emissions from crop fields has been measured. DMS is the predominant gas emitted from plants, but COS is absorbed by plants. (3) CH<sub>4</sub> flux has been measured from rice paddy fields in Japan, Thailand and China. The CH<sub>4</sub> flux from the central plain of Thailand is not as high as that estimated from the flux data in the mid-latitude region. Water management in irrigation systems is one of the major controlling factors of methane emission from rice paddy fields.

**Automated Monitoring of Methane Emission from a Rice Paddy Field: Effects of Temperature and Water Management**

K. Yagi, H. Tsuruta, K. Minami (poster) #46

Methane (CH<sub>4</sub>) emission from paddy fields to the atmosphere was studied in a Japanese paddy field at Ryugasaki by using an automated sampling and analyzing system during the cultivation period in 1991. This system consisted of polycarbonate chambers equipped with shutters and a GC/FID, which are both controlled by a microcomputer. By using this time-programmed system, we obtained one flux datum every 2 hours from one chamber. A test site having an area of 100 m<sup>2</sup> was divided into two plots. The paddy field was continuously flooded by irrigation from May to August at one plot (control plot), while the draining practice lasting a week was performed two times in July at the other plot (drained plot).

Methane fluxes showed pronounced diurnal and seasonal variations. Generally, the minimum flux occurred in early morning and the maximum flux occurred in the afternoon. The ranges of the diurnal fluctuation changed day by day. These variations of the flux closely correlated with variations of the temperature in the surface soil layer. From the end of July to the beginning of August, the flux at the control plot showed a rapid increase. A peak flux was observed at the beginning of August when the soil temperature was very high.

The effect of drainage was significant. Large fluxes of CH<sub>4</sub> were observed in the drained plot immediately after drainage, following rapid decrease of the fluxes. After that, the fluxes were significantly lower than those at the control plot even after re-flooding. Soil redox potential (Eh) was increased in this period at the drained plot, suggesting a decrease of CH<sub>4</sub> production rates in paddy soil. Total emission rates of CH<sub>4</sub> during the cultivation period were 14.8 and 8.6 g/m<sup>2</sup> from the control and drained plots, respectively. As well as the drained plot, the ebullition of CH<sub>4</sub> was observed at the control plot after the final drainage at the end of August, which accounts for 10% of the total emission. These results indicate that water management practices have a strong influence on CH<sub>4</sub> emission from paddy fields.

**Seasonal Variation and Transport Mechanism of Methane Emission from Rice Paddies in the Beijing Area**

Y. Heng, Z. Ya-hui, C. Zong-liang (poster) #50

Methane emissions from paddies in Beijing have been measured during the whole vegetation period in 1991. A strong seasonal variation has been observed. Two methane emission peaks accounting for more than 70% of total emission in one year occurred in early July and mid-August. We also found strong dependence of methane emission on factors like organic content, water condition, and soil temperature. Over the 150-day vegetation season the average flux was  $20.4 \text{ mg hr}^{-1} \text{ m}^2$  under normal cultivation method. Studies on the transport mechanism of methane emission from paddies to the atmosphere have been carried out over the whole vegetation period. More interestingly, similar results were also obtained in a field where there is no rice or only grass.

**PAC: Polar Atmospheric Chemistry; and PASE: Polar Air-Snow Experiment****Polar Tropospheric Chemistry and Deposition**

L. Barrie, R.J. Delmas (invited) G

In the last fifteen years, considerable progress has been made in understanding the occurrence, origin, pathways, history and relevance to global change of natural and anthropogenic substances in the polar troposphere. In addition, glacial snow and ice have provided historical records of tropospheric composition of greenhouse gases and of snow deposited in the polar regions. One of the most remarkable features of polar studies is the extreme geographical contrast between the Arctic and Antarctic. The Arctic troposphere is underlain by an active ocean surrounded by pollutant-emitting, industrialized continents while the Antarctic troposphere lies over a massive, 4 km thick, ice sheet surrounded by the pollution-free southern ocean. The Arctic troposphere is much more polluted than its southern counterpart (Arctic haze) and has different exposure to compounds of natural origin such as wind blown dust or marine gases and particles. The pollution has an impact on both

physical and chemical climate. Anthropogenic Arctic haze aerosols of black carbon and sulphate have a net warming influence in the north in contrast to elsewhere on the globe where they tend to offset the impact of anthropogenic greenhouse gases. Biogeochemical cycles of many substances including carbon, sulfur and nitrogen are perturbed. Compounds potentially toxic to polar ecosystems also accumulate.

Phenomena of interest in the polar regions include chemistry associated with Arctic haze pollution, the destruction of lower tropospheric ozone over the Arctic ocean at polar sunrise induced by marine halogens in the presence of sulfuric acid aerosols, oxidant chemistry of both polar tropospheres, chemical control of clouds and atmospheric energy budgets, and the relationship between glacial and atmospheric composition.

Historical records of atmospheric composition are available from glaciers and instrumental records of atmospheric optical properties and atmospheric composition. They indicate that the Arctic region has been polluted particularly in the winter-half of the year since at least the turn of the century.

#### ***Carboxylic Acids in High Alpine Snow***

**F. Maupetit, M. Legrand, R.J. Delmas (poster) #117**

Fresh snow was collected using a snowpit sampling technique on an event basis on the high altitude (3360 m.a.s.l) glacier de la Girose (French Alps), from the beginning of January to the end of April 1990 and 1991. Snow samples were directly obtained under ultraclean conditions from a pit wall using precleaned air-tight glass flasks, and brought back frozen to the laboratory. They were analysed for  $\text{HCOO}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  by ion chromatography. The problem of gaseous contamination by ammonia and formic and acetic acids was limited by melting these samples in their air-tight glass flasks a few minutes prior to the analysis of both cations and anions. The acidity-alkalinity of snow was measured accurately using a titration technique.

A perfect ion balance was achieved for this data set.  $\text{HCOO}^-$  and  $\text{CH}_3\text{COO}^-$  are generally present in alpine snow in very low concentrations:  $0.3 - 0.6 \mu\text{eq l}^{-1}$  in winter (January - February) and  $0.6 - 1.2 \mu\text{eq l}^{-1}$  in early spring (March - April).  $\text{HCOOH}$  and  $\text{CH}_3\text{COOH}$  contributions to the measured free acidity were estimated to be 10% and 6% to 9%, respectively. Contrary to major ions which are present in wide concentration ranges,  $\text{HCOO}^-$  and  $\text{CH}_3\text{COO}^-$  are rather stable. The only significant deviation of  $\text{HCOO}^-$  and  $\text{CH}_3\text{COO}^-$  concentrations from their mean values (up to 8.5 and  $4.5 \mu\text{eq.l}^{-1}$  respectively) was observed in the case of alkaline Saharan dust transport towards the Alps, thereby shifting the pH of precipitation from slightly acidic to alkaline conditions. These observations indicate that the incorporation of organic acids in precipitation is pH-dependent. On the other hand, our measured  $\text{HCOO}^-$  and  $\text{CH}_3\text{COO}^-$  concentrations in snow are far lower than expected from Henry's law equilibrium of measured  $\text{HCOOH}$  and  $\text{CH}_3\text{COOH}$  concentrations, suggesting that, in the absence of riming during snow crystal growth by water vapor diffusion,  $\text{HCOO}^-$  and  $\text{CH}_3\text{COO}^-$  are re-emitted from the cloudwater liquid phase to the gas phase, and therefore the incorporation of organic acids into snowflakes is rather inefficient.

### **HESS: High Latitude Ecosystems as Sources and Sinks of Trace Gases**

#### ***Terrestrial Biosphere-Atmosphere Exchange in High Latitudes***

**W. Reebergh, N. Roulet, B. Svensson (invited) H**

This paper summarizes methane flux measurements from high latitude tundra and wetland environments obtained during large field campaigns and a number of smaller projects since 1986. Areally weighted time series methane flux measurements at fixed sites in high latitude tundra and wetland environments suggest a methane source strength of about 35 TG/yr, which agrees reasonably with atmospheric model calculations. Individual flux measurements are subject to high spatial and temporal (daily to interannual) variability, and are strongly influenced by vegetation, soil temperature, thaw depth, and water table level, which influence the balance between methane production and consumption. Field studies show that these subsurface parameters and methane fluxes are poorly correlated. Laboratory studies on varying water table level in tundra soil columns have shown long lag times and hysteresis under falling and rising water table conditions. These results indicate that the soil parameters are not independent variables and that a single parameter capable of predicting methane flux is unlikely.

Boreal forest ecosystems appear to be a small net sink for methane. Microbially mediated oxidation of atmospheric methane is the dominant process; wet bogs, fens and beaver ponds are the only methane sources. Microbial methane oxidation is also an important modulator of tundra emission and has the potential to eliminate net methane emission under warmer, drier conditions.

Studies to date have emphasized methane, but future integrated studies along boreal forest and tundra transects include measurements of carbon dioxide fluxes for estimates of carbon fixation and storage. Field manipulation experiments aimed at determining the sensitivity of high latitude soils to temperature and moisture variations are also planned. High latitude biosphere-atmosphere studies to date have a strong North American bias. Collaborative studies in northern European and Siberian wetlands are essential to understanding the importance of high latitude ecosystems in trace gas budgets.

#### ***Regional Pattern of Climate Feedbacks: The Role of Northern Peatlands***

**G. Alexandrov, G. Golitsyn, I. Mokhov, V. Petukhov (oral) #55**

It is known that during the past thousand years the rate of peat formation increased. Simulation runs with a model of bog evolution and a thermodynamical model of climate show that in case of global warming this pattern of ecosystem functioning will be enhanced only in the north west of Russia. In other regions the rate of peat formation and thus sequestering

of carbon dioxide from the atmosphere will decline. Methane emission, with exception of the north east of the U.S. seems to be increased. Excluding the north west of Russia, the integrated climate feedbacks are shown to be positive, i.e., more CO<sub>2</sub> and methane stay in the atmosphere.

#### *Seasonal Trends of Isoprene, C<sub>2</sub>-C<sub>5</sub> Alkanes, and Acetylene at a Remote Site in Canada*

**B. Jobson, Z. Wu, H. Niki, L. Barrie (oral) #114**

An ongoing weekly air sampling campaign at Fraserdale, Ontario (latitude 50°N, longitude 82°W) has revealed a distinct seasonal trend in the isoprene, alkane, and acetylene concentrations over the period of April, 1990 up to the present. Concentration of the biogenic hydrocarbon isoprene peaked in July – August ( $\leq 5$  ppbV), with concentrations above 0.1 ppbV from May through September. In contrast, alkane and acetylene concentrations displayed a summer minima (July – August) and a winter maxima (February). Back trajectory data showed that prevailing air flow to Fraserdale was from the north-west sector when samples were collected, and therefore these measurements were of “background” continental air. The amplitude of the seasonal oscillation increased with hydrocarbon reaction rate. Chemical and meteorological factors were investigated in order to identify the mechanism causing the oscillation. Comparison with Toronto urban data indicates the anthropogenic origin of acetylene and C<sub>2</sub>-C<sub>5</sub> alkanes at this site during winter.

#### *Measuring Methane Emission from Northern Peatlands: Comparison of Field Observations, Laboratory Experiments, and Simulation Model Runs*

**G. Alexandrov, O. Kotsurbenko, M. Sokolov, A. Stepanov (poster) #52**

The box technique is widely used for measuring methane emission from the soil. However, installation of the box alters the soil-atmosphere temperature gradient that may lead to underestimation of methane emission rate especially in sunny days when air temperature in the box is higher than outside the box. A simple simulation model was developed to correct the results of the measurements. Coefficients of the model were identified by means of laboratory experiments. The model was then applied to the data on the methane emission measurements which were carried out monthly (March – October, 1992) at two sites (eutrophic and oligotrophic) of a mire near Moscow, and on the moving edge of mire fire (August, 1992) in order to estimate the accuracy of the box techniques.

#### *Regional Estimate of the Emission of Photochemically Active Components by Boreal and Middle-Latitude Forests*

**V. Isidorov, V. Povarov, E. Klokov (poster) #53**

Continental vegetation is one of the greatest sources of atmospheric organic carbon. The total emission of photochemically active volatile organic compounds (VOC) from this source was estimated at 1550 Tg/year (Isidorov, 1985). The more precise determination of this value requires more complete data about VOC emission rates from different plant species and production scales from individual regions.

The qualitative composition of VOC produced by 25 species of arboreous plants and some shrubs which are characteristic for boreal and middle-latitude forests has been studied. The emission rates of terpenes and isoprene from main arboreous species of coniferous and deciduous plants were determined. From the temperature and light dependence of the VOC emission rates the total emission of these compounds in the coniferous and deciduous forests of the European part of Russia and other republics of the former USSR was calculated. The total forest area, principal types of these forests, foliage biomass, and length of the vegetative period were taken into account for the calculation. Evaluation of these factors gave the estimated value of VOC emission from 5.9 to 7.4 Tg/year.

#### *CO<sub>2</sub> Uptake by Russian Forests*

**R. Karaban, A. Kokorin, I. Nazarov, A. Shvidenko (poster) #119**

Discussions about global warming tend to focus on the need to preserve tropical rainforests, yet Siberian forests have a large role to play in mitigating global warming. Russian forests contain 80 billion tons of stored carbon in above-ground living biomass, and nearly 200 billion tC in forest soils which are exposed to climate changes. This huge carbon store is comparable with tropical forests. The analysis of original data on forest carbon sinks in Russia is carried out. A calculation model is developed to assess and forecast climate change impact on carbon content dynamics in wood, green biomass, litter and soil humus of various natural zones and economic regions. The assessments obtained indicate that forest biomass increments due to warming, changing of precipitations and increased CO<sub>2</sub> concentration currently results in the uptake of 80 – 100 million tC/year. An increased CO<sub>2</sub> flux from forest soils to the atmosphere significantly reduces the effect. As a result, total CO<sub>2</sub> uptake as of 1988 and 2010 is nearly 70 and 100 million tC/year, respectively. Thus only under the effect of climatic factors Russian forests will compensate for CO<sub>2</sub> anthropogenic emission in country by 10%; by 2010 the effect may increase up to 20%. The analysis of changes in forest areas in Russia for the last 30 – 40 years shows that their increase can cause an additional uptake of 20 – 100 million tC/year. According to our assessments, a large-scale forest planting would only be effective (from the viewpoint of CO<sub>2</sub> uptake from the atmosphere) if fertilizers and high productive tree species are used.

### **TRAGEX: Trace Gas Exchange Between Mid-Latitude Terrestrial Ecosystems and Atmosphere**

#### *Exchanges of Trace Gases between the Terrestrial Biosphere and the Atmosphere in the Mid-Latitudes*

**K. Smith, P. Robertson, J. Melillo (invited) I**

Most terrestrial ecosystems of the mid-latitudes have been subjected to human influence. Large areas of forests and grasslands have been converted to agriculture; conversely, re-forestation is also extensive in many regions. These changes

in land use, the use of fertilizers on agricultural land, and high precipitation inputs of nitrogen from industrial emissions to forests and other natural ecosystems all have consequences for trace-gas exchange, and thus for the atmospheric concentrations of trace gases that contribute to climate change.

The study of these interactions, on a comprehensive world-wide basis, is the task of IGAC Activity 5.2, TRAGEX. Although TRAGEX as a coordinated program is still at the planning stage, there is a substantial current research effort in progress in North America, Western Europe and Australia that has already provided some insight into the most important processes governing trace gas exchange in the mid-latitudes. Some of the highlights of this work, and major outstanding questions, are outlined in this paper.

Soil carbon availability, temperature/moisture interactions, pH, and nutrient dynamics have been identified as key variables in methane emission from temperate wetlands, but measurement and modelling of processes of transfer to the atmosphere are in their infancy. Inputs of nitrogen and restrictions in aeration of topsoils have been shown to reduce very substantially the soil's capacity to act as a sink for  $\text{CH}_4$  by microbial oxidation to  $\text{CO}_2$ . High N inputs promote emissions of  $\text{N}_2\text{O}$ , but it has been shown that large effects on fluxes are caused by variations in soil physical conditions, the chemical form of the N, and soil pH. The very high spatial and temporal variability of  $\text{N}_2\text{O}$  and  $\text{CH}_4$  fluxes have made representative flux estimates very difficult to make, and have stimulated major research efforts in development of improved methods of analysis applicable to areas of  $10^3 - 10^4 \text{ m}^2$  and ultimately to the  $\text{km}^2$  scale. The linking of process models with GIS systems for large-scale integration is a focus of current planning activity.

Increased  $\text{CO}_2$  concentrations and N deposition, and the fact that much of the present forest area of the region is in a mid-successional stage, suggest that there may be a substantial vegetation sink for  $\text{CO}_2$  in the mid-latitudes. Changes in soil organic matter in areas of reforestation and in response to changing agricultural practices may also represent an important contemporary sink for atmospheric  $\text{CO}_2$ . Feedbacks associated with  $\text{CO}_2$  uptake by vegetation, its release during decomposition, and the nitrogen cycle processes that affect plant and microbial growth — including trace gas production — must be better understood to appreciate fully the significance of changing  $\text{CO}_2$  sink strengths.

High priority must now be given to three areas: (1) the establishment of flux measurement networks in important mid-altitude regions, especially in those such as the former Soviet Union, China, temperate South America, where comparatively little data have been obtained; (2) the development of adequate process-based models; and (3) the scaling-up of the models to predict fluxes over large regions. This should lead to a substantial improvement in the quality of the input to climate models.

#### *Surface Exchange of NO and NO<sub>2</sub> over a Wheatfield in Central Europe*

J. Ludwig, F. Meixner (oral) #58

A dynamic chamber technique was used to study the surface exchange of NO and  $\text{NO}_2$  over a wheatfield at a rural site in Lower Bavaria (south-east Germany). The measurements were performed between May and August 1990 at different development stages of the wheat plants and just after harvest. The flux measurements were accompanied by monitoring/measurement of major environmental variables (e.g., soil temperature, photosynthetic active radiation, N-content of soil) to study their role in controlling the NO and  $\text{NO}_2$  exchange. N-containing fertilizers were several times applied to the wheatfield between the measurement periods. To study the influence of fertilizer application, 3 of a total of 8 dynamic chambers were installed on plots that received only reduced fertilizer amounts.

Weather conditions during the experimental period were characterized by a considerable drought. Ambient mixing ratios at the site were generally  $< 3 \text{ ppbv}$  (NO) and  $< 10 \text{ ppbv}$  ( $\text{NO}_2$ ). Under these conditions NO was always emitted from the plant-soil system. Net emission fluxes ranged typically from  $1 - 5 \text{ ngN m}^{-2} \text{ s}^{-1}$ . Seasonal variation resulted mainly from the fertilizer application; enhanced NO emissions (up to  $30 \text{ ngN m}^{-2} \text{ s}^{-1}$ ) were observed immediately after fertilizing the harvested wheatfield. NO emission was clearly dependent on soil temperature resulting in an afternoon maximum of NO emission. The dependence was even more pronounced at high NO emission levels.

$\text{NO}_2$  fluxes were usually directed from the atmosphere to the wheatfield, they ranged between  $1 - 15 \text{ ngN m}^{-2} \text{ s}^{-1}$  and were characterized by large temporal variations. Furthermore, uptake of  $\text{NO}_2$  showed a diurnal variation, which could be related to photosynthetic active radiation. The diurnal dependence of  $\text{NO}_2$  uptake vanished as the plants got senescent. After harvest and N-fertilizer application an  $\text{NO}_2$  emission up to  $10 \text{ ngN m}^{-2} \text{ s}^{-1}$  from the (bare) soil could be observed.

During the entire vegetation period of 1991 plant covered soil cores from the same Lower Bavarian wheatfield site were routinely transferred to a plant growth chamber facility. There, in the laboratory, the samples were exposed to NO and  $\text{NO}_2$  mixing ratios varying in the same range as was observed at the field site before. Corresponding flux studies which were performed under controlled environmental conditions were used to interpret the more complex field data set. Compensation points (i.e., those mixing ratios where the observed net flux is zero) between  $5 - 80 \text{ ppbv}$  (NO) and  $0.5 - 3 \text{ ppbv}$  ( $\text{NO}_2$ ) were identified which explain the generally observed behavior of net emission of NO and net deposition of  $\text{NO}_2$  at ambient mixing ratios at the field site.

#### *On the Exchange of Carbonyl Sulfide (COS) between the Atmosphere and a Forest Ecosystem in Central Europe*

X. Xu, H. Bingemer, H. Georgii, C. Gravenhorst, H. Kreilein (oral) #66

The flux of carbonyl sulfide between the atmosphere and the underlying forest has been measured by a flux-gradient technique on the 50 m tower of the forestry faculty of the University of Goettingen in the Natural Reserve Solling in Central Germany. The site is covered by beech and spruce of 120 and 80 years of age, respectively. The canopy height is around 28 meters. Carbonyl sulfide was sampled simultaneously at 32, 38, and 50 m above the ground by cryo-trapping over 10 minute intervals. Samples were analyzed by GC/FPD. Fluxes of COS above the forest were derived from gradients and fluxes of heat



and water vapor measured simultaneously with COS. Twenty sets of profiles have been obtained during daytime under stable boundary layer conditions. Each of the individual profiles shows a decrease of COS towards the top of the canopy that exceeds the analytical uncertainty of the measurement, indicating uptake of COS by the forest canopy. Average fluxes of COS to the forest will be presented. Results for CS<sub>2</sub> will be discussed.

***Biosphere-Atmosphere Exchanges in a Forest Ecosystem in the Southwest France Landes Project***

**A. Lopez, R. Delmas, J. Fontan, Y. Brunet, L. Torres (oral) #71**

In this paper we describe the general outline of a project (the Landes Project) developed by several laboratories in connection with the Eurotrac committee and the CNRS. The overall aim of this program is to investigate modifications of atmospheric chemical composition as a result of biosphere-atmosphere exchanges in a temperate forested area. The site of this experiment is the "Landes" forest located in South Western France, along the Atlantic Ocean. This ecosystem extends over an area of 1 million hectares, with a forested component mainly constituted by resinous (maritime pines) and an agricultural component dominated by maize fields.

The vegetation in the pine-tree forest is a source of a number of hydrocarbons emitted into the atmosphere in the form of highly reactive terpenic compounds. Numerical simulation carried out in our laboratory with a Langangian photochemical model have shown that their influence on the "formation/destruction" of ozone within the atmospheric boundary layer is dependent on nitrogen oxide emissions. The reaction schemes relevant to biogenic hydrocarbon emissions do not follow linear variations laws. Depending on the intensity of NO<sub>x</sub> emissions, the introduction of a biogenic hydrocarbon source results in either an enrichment or a depletion of ozone in the air mass.

A first field experiment, carried out in June 1992 was focused on: (1) terpenic hydrocarbon emission by the vegetation (bag method); (2) nitrogen compound emissions by the soils of forested areas and of fertilized agricultural areas (static and dynamic chamber method); (3) vertical flux measurements by eddy correlation methods at the top of the canopy for ozone and aerosols, and at different levels within the vegetation for CO<sub>2</sub>.

The first results show: (1) the existence of a daily cycle for terpenic hydrocarbon emissions (diurnal maximum, nocturnal minimum). These terpenic compounds are emitted mostly as  $\alpha$  and  $\beta$  pinene (58%), with a comparable distribution; the remaining ones being myrcene, limonene and  $\Delta_3$ -carene, in homogeneous distribution. (2) A negligible emission of NO and NH<sub>3</sub>, and a significant uptake of NO<sub>2</sub> by the soils in forested areas. On the contrary the fertilization of maize fields leads to very important emissions of gaseous nitrogen compounds (NO, NH<sub>3</sub>, N<sub>2</sub>O), with variable intensities depending on the amount and composition of fertilizers and depending also on the spreading procedure used. (3) For ozone and aerosols the eddy correlation method requires a filtration of fluctuations at low frequency in order to eliminate those due to the non-homogeneity of sources. (4) The CO<sub>2</sub> fluxes measured at three different levels allows provision of a good description of the mean vertical source density profile.

Detailed results from the experiment are presented in four independent papers (posters). These results lead us to select an experimental site located in the center of the forested area. This site is presently being equipped and could constitute a site opened to the scientific community to investigate atmosphere-biosphere interactions in the case of a dual forest/agricultural ecosystem in temperate zones.

***Comparison of Methods for Measurement of Nitrous Oxide Fluxes Between Soils and the Atmosphere, Stirling, Scotland, 1992: Overview and Conclusions***

**K. Smith, H. Clayton, F. Arah, U. Skiba, S. Christensen, P. Ambus, D. Fowler, K. Hargreaves, G. Harris, F. Wienhold, L. Klemedtsson, B. Galle (oral) #109**

A comparison was made between several different methods for the determination of nitrous oxide (N<sub>2</sub>O) fluxes between the soil and the atmosphere, in an international experiment carried out in April 1992. The experiment was conceived as part of a European Community STEP programme project, involving groups from Edinburgh, Copenhagen and Mainz, and was extended to include a group from Gothenburg, Sweden.

The experiment constituted, to the best of our knowledge, the largest comparison of methods ever undertaken for the purpose of measuring a greenhouse gas flux. The site was a 10 ha field in an area of flat alluvial land in the Carse of Stirling, about 6 km west of Stirling, Central Scotland. The soil was a fluvisol (fluvaquent in USDA system) with a silty clay texture, under timothy grass. Nitrogen fertilizer (185 kg N ha<sup>-1</sup> as NH<sub>4</sub>NO<sub>3</sub>) was applied on 3 April 1992, and measurements of N<sub>2</sub>O flux were made over the period 4 - 24 April.

Three closed chamber methods (including a novel ultra-large chamber variant) and an open (flow-through) chamber method were compared against each other and against two micrometeorological methods: flux gradient and eddy correlation. Four instrumental techniques were employed: tunable diode laser absorption spectrometry (TDLAS), long-path Fourier-transform infrared spectrometry (FTIR), long-path IR spectrometry with a simple dedicated instrument, and gas chromatography. Some instrumentation was used in different modes. Details are contained in the other papers of the series.

Data from 24 40 - 70 cm closed chambers showed that N<sub>2</sub>O emissions were generally high, ranging between 100 and 300 g N<sub>2</sub>O-N ha<sup>-1</sup> d<sup>-1</sup> for most of the site, but about twice as high from the remainder, which had been grazed by cattle a few months previously. Detailed grid sampling with small (10 cm) chambers showed great heterogeneity in fluxes at the > 7 m scale, but coefficients of variation decreased as grid spacing was reduced. Generally good agreement was obtained between results from both large and small chambers and flux gradient measurements made by three different techniques: (a) automated gc analysis of bulk air samples collected over a 30 min period; (b) FTIR spectrometry; and (c) TDLAS. The FTIR system was also used inside an ultra-large chamber, and as a continuous analyzer for a small open chamber, and the TDL system was used in both flux gradient and eddy correlation modes. Comparison of results from all these approaches, and those of a direct comparison of the two IR systems inside the ultra-large chamber, showed that all the methods gave results that were

reasonably compatible with each other.

The methods employed have complementary strengths. When conditions are favorable, micrometeorological techniques offer great temporal resolution and integration of fluxes over large areas, and the more sensitive the instrument the wider the range of conditions in which it can be used. Chamber techniques, on the other hand, are extremely robust and they also provide information on spatial variability (and thus perhaps insights into processes) unavailable by other means.

#### ***Emission of Nitrogen Compounds from Fertilized Maize Fields in the Southwest of France***

**C. Jambert, R. Delmas, L. Labroue, P. Chassin, D. Plenet (poster) #59**

Since the beginning of the century, the increase of  $N_2O$  and of nitrogen oxides in broad sense in the atmosphere, is partly due to the increasing use of fertilizers in agriculture. A research program on nitrogen compounds emissions ( $NO$ ,  $NH_3$ ,  $N_2O$ ) is being developed in maize fields in the Southwest of France. Cultivated lands in the region of the Landes de Gascogne represent about  $10^5$  ha included in  $10^6$  ha of pine tree forest. The nitrogen budget of these fertilized soils shows a net imbalance of about  $100 \text{ kg(N)/ha}$  for a nitrogen input of  $300 \text{ kg(N)/ha/year}$  from fertilizers, which could be due to N losses to the atmosphere.

Emissions of  $NO$ ,  $NH_3$  and  $N_2O$  from maize fields soils were measured during preliminary experiments carried out during spring and summer of 1992. Very large fluxes were measured just after the input of fertilizers. A maximum loss of  $4.91 \text{ kg(N)/ha/day}$  was observed. The emission intensity as well as the relative proportion of the different gases emitted depend on the type of fertilization applied. The emission of ammonia is mainly due to the hydrolysis of urea at the soil surface, whereas  $NO$  production occurs in the first 10 cm of the soil and is linked to the biological activity. An intense denitrification develops in the water table (situated at less than 1 m depth) leading to high  $N_2O$  emission into the atmosphere ( $0.1 - 0.2 \text{ kg N-N}_2O/\text{ha/day}$ ). As a consequence, the increase of nitrates in the water table appears to be limited (from 8 ppm before the fertilization up to 14 ppm after).

These emissions of nitrogen oxides from fertilized maize fields associated with the emission of hydrocarbons (terpenes) from pine trees could lead to significant ozone formation. This aspect is currently being studied by modelling and regional scale experiments.

#### ***Measurement of $N_2O$ Emission from Fertilized Grassland Using Flux-Gradient Micrometeorological Techniques***

**K. Hargreaves, U. Skiba, D. Fowler, J. Arah, F. Wienhold, B. Galle (poster) #60**

Fluxes of  $N_2O$  from a recently fertilized pasture growing on a heavy clay soil were determined using flux-gradient micrometeorological techniques. Three separate techniques were employed (Gas Chromatography Fourier Transform Infra-Red Spectroscopy and Tunable Diode Laser Spectroscopy) to measure small gradients in  $N_2O$  concentration close to the surface. After application of  $185 \text{ kg NH}_4\text{NO}_3/\text{ha}$  to the site, emission fluxes in the range  $0$  to  $100 \text{ ng N}_2O\text{-N m}^{-2} \text{ s}^{-1}$  ( $0$  to  $86 \text{ g N}_2O\text{-N ha}^{-1} \text{ d}^{-1}$ ) were measured from a previously ungrazed part of the pasture. Over a grazed area of the pasture a larger emission flux of  $150 \text{ ng N}_2O\text{-N m}^{-2} \text{ s}^{-1}$  ( $130 \text{ g N}_2O\text{-N ha}^{-1} \text{ d}^{-1}$ ) was measured, due possibly to greater compaction in this part of the pasture. Agreement between the three independent techniques was good, thus establishing the suitability of micrometeorological methods for making measurements of  $N_2O$  emission at the field scale, integrating the great spatial variability in  $N_2O$  emission rates which is frequently observed using box enclosures.

#### ***Measurements of $N_2O$ Fluxes from a Fertilized Pasture Using a Fast Response Tunable Diode Laser Spectrometer***

**F. Wienhold, H. Frahm, G. Harris (poster) #61**

A fast response Tunable Diode Laser (TDL) spectrometer was used to make  $N_2O$  flux measurements by both eddy correlation and concentration gradient methods during a methods intercomparison field program in April 1992 at a site near Stirling, Scotland which is described in companion papers.

The requirements of fast time resolution and high precision imposed by the flux determination methods were met by application of the recently developed two-tone frequency modulation technique coupled with fast scanning of the laser. The use of a dedicated digital signal processor (DSP) allowed zero-overhead on-line data handling including averaging and multiple linear least squares regression at an update rate of  $10 \text{ Hz}$  such that the time response of the system was only limited by the gas exchange time in the multipass sample cell ( $200 \text{ ms}$ ). The need to introduce a correction for the water vapor flux was avoided by passing the air through an efficient Permapure Nafion dryer. The mixing ratio determinations were made at the constant temperature of the measurement cell.

The cross correlation of 30 minute segments of  $10 \text{ Hz}$   $N_2O$  mixing ratio data measured at  $2 \text{ m}$  elevation with the corresponding vertical wind velocity component resulted in a covariance signal-to-noise ratio of  $\sim 10$  for typical  $N_2O$  fluxes of  $40 \text{ ngN m}^{-2} \text{ s}^{-1}$ . Vertical concentration gradients leading to a difference of  $< 1 \text{ ppbv}$  in the  $N_2O$  mixing ratio at  $0.06$  and  $1 \text{ m}$  elevation were statistically resolved within one minute. Fluxes calculated from these concentration gradients and the vertical profile of the wind velocities agreed closely with those derived from the eddy correlation measurements. The results of this field campaign and the flexibility of the TDL instrument encourage the further application of the technique for eddy correlation flux measurements of  $N_2O$  and other trace gases.

#### ***Measurement of Nitrous Oxide Emissions from Fertilized Grassland Using Closed Chambers***

**H. Clayton, J. Arah, K. Smith (poster) #62**

Nitrous oxide emissions were measured using closed chambers at a grassland site in the Carse of Stirling, Central Scotland, in April 1992. The measurements provided a yardstick for comparison with  $N_2O$  fluxes determined simultaneously by other methods (described in other papers at this conference).

The site was a 10 ha field of timothy hay on flat alluvial land, fertilized with 185 kg N ha<sup>-1</sup> as NH<sub>4</sub>NO<sub>3</sub> on 3 April. Twenty-four closed chambers (16 of 0.126 m<sup>2</sup> and 8 of 0.49 m<sup>2</sup>) were installed at random locations across the field, 6 in a 2 – 3 ha area that had been grazed by cattle the previous summer, the remainder in the larger ungrazed area. Flux measurements were made over a 3-week period, daily for 10 days and then every 3 or 4 days. Nitrous oxide concentrations in the chambers one hour after closure were determined by taking air samples in glass syringes and analyzing them by electron-capture gas chromatography.

There was substantial spatial and temporal variability. The 360 individual measurements, made on 15 occasions, showed fluxes ranging from 6 to 1500 g N<sub>2</sub>O-N ha<sup>-1</sup> d<sup>-1</sup>, lognormally distributed. Means from all chambers in the grazed and ungrazed areas were generally 100 – 300 and 200 – 600 g N<sub>2</sub>O-N ha<sup>-1</sup> d<sup>-1</sup>, respectively, peaking 5 days after fertilization and declining to about one-sixth of the maximum by the end of 3 weeks. Spatial differences observed early on were generally maintained throughout the period.

The study showed that total emissions of N<sub>2</sub>O from this type of agricultural ecosystem are high. The loss of N as N<sub>2</sub>O was 5.8 kg ha<sup>-1</sup> and 2.5 kg ha<sup>-1</sup>, from the grazed and ungrazed areas, respectively. Measurements of soil water content, pH, nitrate, ammonium, organic matter and temperature were compared with the N<sub>2</sub>O fluxes. Preliminary analysis suggests that none of those factors alone could account for the differences between the two areas, or for the temporal variability. However, generally greater anaerobiosis in the soil of the grazed area, due to compaction, may have been an important factor; this aspect is being investigated.

#### **Field Methods for Measuring N<sub>2</sub>O Emissions from Soil: Examination of Spatial Variability**

**P. Ambus, S. Christensen (poster) #63**

N<sub>2</sub>O emission was quantified and spatial heterogeneity of the activity characterized by means of 10 cm diameter closed chambers arranged in grids with spacings of 0.11, 0.2, 1.1, and 7.1 meters (n = 35 – 64). Daily measurements on five successive dates in April 1992 gave similar N<sub>2</sub>O emission rates of 140 to 257 g N<sub>2</sub>O-N ha<sup>-1</sup> d<sup>-1</sup> independent of grid design.

Generally, the heterogeneity of N<sub>2</sub>O emission declined as grid size was diminished. The coefficient of variation (C.V.) averaged 95% at 7.1 m spacing and 50% at smaller spacings. N<sub>2</sub>O emission at 7.1 m spacing approximated a log-normal distribution whereas the distribution at smaller spacings approached normality.

The variability of N<sub>2</sub>O emission was characterized by a spatial dependence at spacings of 0.11 – 1 m and a relatively high variability at spacings < 0.11 m. Variability did not change at spacings between 1 and 5 m, but beyond 5 m there was a distinct increase in variability with increasing distance.

Within the 0.11 and 0.2 m grids glucose amendments enhanced N<sub>2</sub>O emissions 4- to 7-fold and there was a marked positive relationship between N<sub>2</sub>O and CO<sub>2</sub> fluxes after glucose addition. This suggests that N<sub>2</sub>O originated from denitrification. The N<sub>2</sub>O emission was not related to CO<sub>2</sub> production in the soil, however, suggesting that the variability at the scale below 1 m was governed by a patchy distribution of denitrifying "hot spots" having dimensions considerably smaller than 0.1 m. It is hypothesized that the variability at the larger scale was due to changes in soil aeration governed by small changes in topography across the area. This study also indicates that N<sub>2</sub>O fluxes obtained from "mega" chambers (> 10 m) should be interpreted carefully since they may not encompass the whole field variability.

#### **Soil-Atmosphere Methane Exchange by Mid-Latitude Hardwood Forest Soils and the Impact of Agricultural Practices**

**R. Burke, J. Meyer (poster) #64**

Soil-atmosphere methane exchange is presently being measured at intervals of roughly ten days at several sites within the University of Georgia (UGA) Horseshoe Bend (HSB) Agroecosystems research area in Athens. The HSB research area is located on a 100 year floodplain of the Oconee River in the southeastern U.S. piedmont physiographic region. The sites being monitored at HSB consist of five sites each from a mixed hardwood forest, a conventional till (VT) agricultural area and a no-till (NT) agricultural area. The CT and NT sites have been maintained under various crop cultural and fertilization treatments since 1978. Measurements to date indicate that the gravimetric water content of the forest soils ranges between about 5 and 20%, and the gravimetric water content of the agricultural soils ranges between about 5 and 30%. The soil-atmosphere methane exchange measurements are being performed with static, vented chambers and flame ionization gas chromatography.

Two of the HSB forest sites are about 1 meter lower in elevation and have a thinner leaf litter layer (1 to 2 cm) than the other three sites (litter layer about 3 to 5 cm thick). All five of these sites have generally been observed to be net sinks for atmospheric methane during the first six months of monitoring; the lower elevation sites are generally weaker (median values of -0.11 and 0 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>, respectively) than the more elevated sites (median values of -0.89, -1.33, and -1.54 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>, respectively with a maximum of -3.21 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>). The lower elevation sites were a weak source of methane to the atmosphere after recent heavy rains, however.

We have frequently observed erratic variations in the headspace atmosphere methane concentration with time during chamber deployments in the agricultural plots. The disturbed nature of the agricultural soils may be responsible for their variable methane exchange characteristics. To date, 47% and 49% of our deployments in the CT (n = 47) and NT (n = 47) plots, respectively have yielded linear correlations between time and methane concentration that were significant to the 80% confidence level. By comparison, 80% of the forest soil deployments (n = 68) were significant at the 90% level. Methane flux in the CT plots ranges from -0.91 to 1.03 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>, and the median flux is 0 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>. Methane flux in the NT plots ranges from -0.91 to 0.59 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> with a median flux of 0 mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>. Our data clearly indicate that the HSB soils impacted by agricultural practices have less methane sink capacity than the forest soils with the thicker litter layers. A longer time series of data will be required to determine whether or not the methane sink capacity of the agricultural soils is significantly different from that of the forest soils with less litter accumulation.

**Trace Gas Exchanges in the Temperate Region of China**

W. Su (poster) #67

The significance of Northern China in the budget of atmospheric trace gases is discussed briefly. Sites for the research work of IGAC/TRAGEX Activity and some results of preliminary measurements on  $N_2O$  flux are introduced.

Northern China near  $40^\circ N$  from  $75$  to  $135^\circ E$  includes a variety of temperate ecosystems. This region has undergone land use change for over 2000 years. However, extensive changes during the past century are evident. During the last 50 years agricultural changes related to fertilization, irrigation, and new crop varieties have contributed to marked increases in grain production. All of these play an important role in the changes of sources and sinks of  $CH_4$ ,  $N_2O$ , and  $CO_2$ .

In China, 6 sites along  $40^\circ N$  have been identified to contribute to research efforts described by the TRAGEX Activity. These sites are located in the regions of forest, grassland, agriculture, arid and semiarid, and desert.

On one of these sites, the Luancheng Comprehensive Experimental Station of Agricultural Ecology, the flux of  $N_2O$  from a typical winter wheat field has been measured. Measurements were taken during the growing season of winter wheat in fertilized and unfertilized fields. Measurements were also taken in an alfalfa field. It was shown that fertilization, irrigation and soil temperature were positively related to the emission of  $N_2O$ . Diel variability of fluxes was measured. The fluxes in different treatments varied between  $2 - 46 \mu g N m^{-2} h^{-1}$ .

**Carbon Dioxide Exchange Between a Temperate Pine Forest and the Atmosphere: Landes Project**

Y. Brunet, P. Berbigier, F. Daudet (poster) #72

An experiment devoted to carbon dioxide exchanges was conducted during summer 1992 in the pine forest of Les Landes, in South-Western France. Over a period of three months, the fluxes of momentum, sensible heat, water vapor and carbon dioxide were measured by eddy-correlation at three levels, one above the canopy, one below the crown and the other at various locations in the crown region. Simultaneously, mean profiles of wind speed, air temperature, air humidity and  $CO_2$  concentration were recorded. Assimilation and transpiration chambers were also operated in the understory. During the whole experiment, no water stress was observed. We essentially present here the results obtained on the fluxes of carbon dioxide.

The exchanges of carbon dioxide are shown to occur intermittently and to be strongly related to the instantaneous behavior of the turbulent wind field: a substantial proportion of the  $CO_2$  flux is transferred during short periods of high turbulent activity. As a consequence, counter-gradient transfer is often observed within the canopy.

For the overall experiment, a typical daily assimilation of  $15 g/m^2$  was observed; in our non-stressed conditions, the amount of carbon fixed by the trees as well as the understory is shown to depend primarily on photosynthetically active radiation and is also strongly related to the water vapor flux. These results are compared with those obtained at the same site in 1991, when the forest was suffering from severe water stress. Over the understory, a fairly good agreement was obtained between the eddy-correlation and the chamber techniques.

Finally, the flux values obtained at the three measurement levels allow provision of a good description of the mean vertical source density profile, which can be used in further modelling studies.

**Methane Consumption in Agricultural Ecosystems of the U.S. Midwest**

G. Robertson, W. Reed, S. Halstead (poster) #121

Terrestrial sources of methane responsible for a portion of its atmospheric loading are relatively poorly understood. In recent years upland soils have been identified as a potential sink for atmospheric methane due to net methane consumption by soil bacteria. Early evidence also suggests, however, that consumption in soil can be suppressed by ecosystem disturbances that affect nitrogen availability. If true, then the widespread conversion of mid-latitude forests and grasslands to fertilized cropland that no longer consumes methane may contribute to a portion of the present atmospheric methane load.

We tested this hypothesis in a series of replicated agricultural and native communities at the KBS Long-Term Ecological Research Site in southwest Michigan. We measured methane fluxes with static chambers in four separate replicates of 6 different cropping systems and 2 native successional communities. Cropping systems corresponded to conventional tillage and no-tillage high-chemical-input crops (maize-soybean-wheat rotations), and perennial crops (alfalfa and *Populus* tree plantations). Native communities corresponded to early successions (4 years since abandonment from agriculture) and mid-successional (never tilled, 30 years since forest cutting) old field communities that varied widely in chemical and biological soil properties.

Chambers were sampled 17 times over the 1992 growing season for  $CH_4$ ,  $N_2O$ , and  $CO_2$  fluxes. We found significant but highly variable  $CH_4$  uptake in all 8 of our ecosystems, including the fertilized annual crops. Methane consumption was stronger and more consistent from date to date, however, in the organic-based crops and in the old-field communities. Uptake appears to be related to a combination of soil moisture and soil organic matter status; experiments are underway to define more specifically the biotic and abiotic controls on these fluxes.

**The Influence of Nitrate on Production of Nitric Oxide and Nitrous Oxide in Agricultural Soil**

M. Maag, F. Eiland (poster) #124

Nitric oxide (NO) and nitrous oxide ( $N_2O$ ) play important roles in atmospheric chemistry. Soil acts only as a source for nitrous oxide, while soil acts both as a source and sink for nitric oxide. The uptake of NO in soil seems to be dependent upon the concentration of NO in air, and the uptake in soil is increased with increasing NO concentrations. Both gases are produced under anaerobic conditions by biological reduction of nitrate (denitrification).

The influence of the concentration of nitrate upon release and consumption of NO and  $N_2O$  formation in a sandy loam

soil was studied. The soil was incubated under anaerobic conditions using "a flow through system." Nitrogen, free of NO and N<sub>2</sub>O, was used as a flushing gas and the flow was varied between 0.6 and 1.5 l/min. The concentrations of NO and N<sub>2</sub>O at the inlet and outlet were monitored continuously using a NO<sub>x</sub> analyzer and a gas chromatograph with an electron capture detector.

Addition of nitrate (10, 20 and 50 ppm NO<sub>3</sub><sup>-</sup>-N) to the soil resulted in a lower mixing ratio of NO (<0.1 ppmv) at the outlet when compared with the mixing ratio at the outlet from unamended soil at flow rates above 1 l/min. In contrast, the mixing ratio of N<sub>2</sub>O was positively correlated with the concentration of nitrate. The mixing ratio of N<sub>2</sub>O was lower than the mixing ratio of NO regardless of the concentration of nitrate and the flow rate used.

## MILOX: Mid-Latitude Ecosystems as Sources and Sinks for Atmospheric Oxidants

### *Ozone Formation at a Rural Site in the Southeastern US*

L. Kleinman (oral) #56

Trace gas measurements pertinent to understanding the transport and photochemical formation of O<sub>3</sub> were made at a surface site in rural Georgia as part of the Southern Oxidant Study during the summer of 1991. It was found that there was a strong correlation between O<sub>3</sub> and the oxidation products of NO<sub>x</sub>: O<sub>3</sub>(ppb) = 29 + 9.9\*(NO<sub>y</sub>(ppb)-NO<sub>x</sub>(ppb)), r<sup>2</sup> = 0.74. This fit is similar to that observed at other rural sites in eastern North America and indicates a background O<sub>3</sub> level of approximately 30 ppb; values higher than 30 ppb are due to photochemical production in the recent past, which varied from near zero to 45 ppb. The origin of the O<sub>3</sub> above background was investigated by using a free radical budget equation to calculate an in situ O<sub>3</sub> production rate in terms of measured concentrations of NO and free radical precursors (O<sub>3</sub>, HCHO, and other carbonyls). A comparison of observed and predicted diurnal trends in O<sub>3</sub> indicates that in situ production accounts for approximately 1/3 to 1/2 of the morning increase in O<sub>3</sub> concentration, the remainder being due to entrainment of dirty air aloft by the growing convective boundary layer. Additional evidence for the role of vertical transport in controlling the hour to hour changes in O<sub>3</sub> is found in the diurnal cycles of SO<sub>2</sub> and HNO<sub>3</sub> which also have rapid increases in the morning. The day to day variability of O<sub>3</sub> was investigated using a back trajectory model. NO<sub>y</sub> concentration at the measurement site could be reasonably accounted for by considering NO<sub>x</sub> emission sources located within one day's transport distance. In as much as there is a strong correlation between O<sub>3</sub> and NO<sub>y</sub>, the coincidence between trajectory location and NO<sub>x</sub> emission sources appears to be an important factor influencing mid-day O<sub>3</sub> concentration. Hydrocarbon measurements are consistent with NO<sub>x</sub> being the limiting factor for formation of O<sub>3</sub>.

### *Integrated Flux Measurements in a Southern Deciduous Forest*

P. Zimmerman, A. Guenther, L. Klinger, P. Harley, D. Baldocci, H. Westberg (oral) #68

Fluxes of carbon dioxide and non-methane hydrocarbons were measured from a deciduous forest near Oak Ridge, Tennessee in July and August of 1992. Micrometeorological and ecological monitoring has occurred at the site for over a decade. Our trace gas measurements spanned several scales, and included individual leaf, branch, canopy, and landscape fluxes along with measurements of important environmental, physiological, and ecological variables. Temperature-controlled cuvettes and enclosures were used to measure leaf and branch fluxes, respectively. Canopy fluxes were measured using concentration gradients along a tower and using relaxed eddy accumulation. Landscape fluxes were calculated from a mixed-layer gradient model employing boundary layer concentration profiles obtained with a tethered-balloon.

The research program allowed for field verification of laboratory studies of temperature and light algorithms for isoprene emissions. In addition, the research allowed for the development of specific algorithms based on position of foliage within the canopy. Ecological measurements demonstrated the importance of community succession in altering isoprene emissions within the past decade, and underscored the role of ecological models in predicting future global change impacts on trace gas fluxes.

Results of the program will be presented and flux estimates using inventories of vegetation species biomass and composition will be compared to gradient fluxes, relaxed eddy accumulation fluxes, and mixed-layer gradient fluxes.

### *Isoprene Fluxes in a New England Forest*

A. Goldstein, J. Munger, B. Daube, M. Goulden, S. Wofsy (oral) #69

Isoprene (2-methyl-1, 3-butadiene, an important biogenic hydrocarbon) emissions are estimated to exceed anthropogenic hydrocarbon emissions, and to rival methane emission on a global basis. Isoprene influences the oxidation capacity of the troposphere, and can affect regional production of ozone, organic acids, and carbonyls.

The flux of isoprene was determined continuously from July 22, 1992 until October 10, 1992 in a mixed hardwood forest in central Massachusetts. Isoprene was measured using an automated GC/FID system with cryogenic preconcentration. A pair of samples was taken simultaneously from heights of 24 and 29 m, approximately 2 and 7 m respectively above the forest canopy. Every 5th sample was taken from the same level in order to determine differences between the two sample systems.

Isoprene fluxes were calculated by similarity with CO<sub>2</sub>, using the equation:

$$\Phi_{\text{iso}} = \Phi_{\text{CO}_2} (\delta[\text{isoprene}] / \delta[\text{CO}_2])$$

where  $\Phi_{\text{iso}}$  is isoprene flux,  $\Phi_{\text{CO}_2}$  is CO<sub>2</sub> flux which is measured directly by eddy correlation,  $\delta[\text{isoprene}]$  is the isoprene concentration gradient and  $\delta[\text{CO}_2]$  is the CO<sub>2</sub> concentration gradient. This approach assumes there are no sources or sinks of either CO<sub>2</sub> or isoprene between the two sample inlets.

Emission of isoprene was related to Photosynthetically Active Radiation (PAR) and temperature. Mean emissions around midday on clear days (PAR > 1000 (μE/m<sup>2</sup>/s)) were 120, 900, 1500, 2400, and 4300 (μg/m<sup>2</sup>/hr) in the respective

temperature ranges < 17, 17 - 21, 21 - 25, 25 - 29, and 29 - 33 (°C). Emissions on overcast days with low PAR were low, and emissions were zero at night. Isoprene fluxes generally peaked after solar noon, at or just before the daily temperature peak. Isoprene emissions accounted for 0.1 to 0.3% of the net CO<sub>2</sub> uptake by the forest in terms of carbon. The data support a major role for biogenic isoprene in the oxidation-reduction chemistry of the regional and global troposphere.

#### **Ecological Controls over Biogenic Non-Methane Hydrocarbon Emissions**

**M. Lerdau, R. Fall, R. Monson (oral) #65**

We examine the effects of nitrogen availability and seasonality on the concentration and emission of monoterpenes from Douglas Fir *Pseudotsuga menziesii*. We show that (1) N fertilization can change emissions by over 50% on a unit biomass basis; (2) emissions vary seasonally and the direction of these variations depends upon the N fertilization level of the plants; (3) there exists a positive correlation between the tissue concentrations of individual monoterpenes and their emission rates. We use these results in a whole forest model to calculate monoterpene emissions on a regional level. The modeling results indicate that incorporation of nutrient cycling and plant phenology into emissions algorithms helps account for variation between sites and improves our ability to predict how monoterpene emissions will change in the face of regional and global changes in atmospheric chemistry and climate.

#### **Emission of Isoprene from Deciduous Forest in North China**

**M. Hong, Z. Fuzhu (poster) #70**

Measurements of isoprene emission from deciduous forest were made in North China. According to their isoprene emission rates, ten species were classified into three groups by means of enclosure technique. The species of high emission, East-Liaoning Oak (*Q. liaotungensis*), was found to have an obvious variation from day to night. There were the maximum emission rates (1.92 µg/g hr) at 14:00 and the minimum (~0) at 2:00. Among several environmental factors, light has significant correlation ( $r = 0.86$ ) with the emission rates of East-Liaoning Oak. Factors could be ordered as follows according to the degrees of their impacts on plant emission: light > leaf temperature > ambient temperature > humidity. In deciduous forest, the concentration of isoprene varied from 13.6 ppm to 26.7 ppm with time and altitude. By the energy balance/Bowen ratio method, the flux of isoprene above the canopy was about 4800 g/m<sup>2</sup> hr in the morning.

This research used a new analysis system, a GC-PID gas phase chromatograph, by which untreated air samples can be measured directly.

#### **Measurements of Ozone and Aerosol Fluxes over a Pine Forest**

**E. Lamaud, A. Labatut, J. Fontan, A. Druilhet, F. Saïd, A. Lopez (poster) #73**

Measurements of the fluxes of ozone and aerosol particles have been made over a pine forest by the correlation method. The ozone sensor is an OSG2 ozone sonde of "Gesellschaft für angewandte systemtechnik" (Germany). The chemiluminescence reaction takes place between ozone and an organic dye, integrated in a target crossed by the air flow. The time constant is better than 0.1 second and the detection limit is less than 100 ppb. Aerosol is measured by charging the particles in a unipolar corona space charge. The air flow is about 3 m<sup>3</sup>/h, to limit the statistical fluctuations. The time constant is 0.2 s. Only the middle part of the size distribution is measured. Ozone has also been measured, at ten meters over the ground, under the canopy with a fast U.V. ozone sensor, built in the laboratory. The time constant is about 0.2 s. Flux at the two levels can be compared.

The site is sometimes polluted. For all the parameters, variances of fluctuations, energy spectra and cospectra with the vertical wind speed have been calculated. The low frequency fluctuations of concentrations mainly in the case of aerosol, due to advection from sources of pollution, has been studied and has to be eliminated by filtration during the calculation of fluxes. Diurnal variations of fluxes and dry deposition velocity has been determined and parametrized. Results are compared with those obtained over other soils and vegetation.

#### **Quantification of Terpenic Emissions: The Landes Programme**

**V. Simon, B. Clement, M. Riba, L. Torres (poster) #74**

Among emissions of vegetal origin, the emission of terpenes is likely to modify the NO<sub>2</sub>/O<sub>3</sub>/NO cycle which governs the photochemical formation and disappearance of ozone.

Indeed, terpenes can be converted into oxygenates (peroxides, aldehydes, ketones, acids) via ozonolysis or by interaction with O• and OH• radicals. They also act as precursors to nucleation germs and aerosols. The derivatives thus formed are often more aggressive toward the biosphere than the products they are derived from.

An improved knowledge of the role of terpenes in tropospheric physicochemistry requires a quantification of the corresponding emissions from various vegetal species. In this context, we have determined the emission flux of the principal monoterpenes originating from a pine forest. These experiments have been carried out in the course of a measurements campaign that took place in the Landes Forest (France) during the month of June 1992. The procedure used was the enclosure method.

Daily cycles of atmospheric concentrations in α and β-pinene, Δ<sub>3</sub>-carene and limonene have been recorded. The concentrations measured for all terpenes are seen to vary within the range of 0.2 to 3.4 ppbv, showing the minimum values at daytime and the maximum ones at night.

The daily cycles of emission rates have been also determined. In contrast to atmospheric concentrations, they exhibit maximum diurnal values and minimum nocturnal values ranging between 9 and 237 ng g<sup>-1</sup> h<sup>-1</sup>. The emission rates recorded for α and β-pinene are much higher than those corresponding to other monoterpenes. The average source emissions have been

determined from the biomass coefficient of the forest ( $0.9 \text{ kg/m}^2$ ). They are in the order of  $75 \text{ mg m}^{-2} \text{ h}^{-1}$  for  $\alpha$  and  $\beta$ -pinene or  $35 \text{ mg/m}^2 \text{ h}^{-1}$  for other monoterpenes.

The emission rates of terpenic compounds are correctly correlated with temperature, humidity and with the product of the terpene amount within the plant and the vapor pressure of the product considered. The emission rates and atmospheric concentrations of terpenes are alternatively measured with a fully automatic device designed and developed in the Laboratory (Riba et al.).

## GLOCARB: Global Tropospheric Carbon Dioxide Network

### *Sensitivity Evaluation for Oceanic Uptake of Fossil Fuel CO<sub>2</sub> Based on Global <sup>13</sup>C Distribution*

T. Peng, W. Broecker (oral) #101

Biogenic CO<sub>2</sub> (derived from fossil fuel carbon and forest-humus carbon) has a distinctive low  $\delta^{13}\text{C}$  value of about  $-27\%$ . Distribution of such  $^{13}\text{C}$  atoms in the global carbon pools should reflect the oceanic uptake of CO<sub>2</sub>. Based on measured changes in the  $\delta^{13}\text{C}$  value for atmospheric CO<sub>2</sub> and for oceanic  $\Sigma\text{CO}_2$  over a 20 year period (1970 – 1990), Quay et al. (1992) were able to estimate a sizable net uptake of fossil fuel CO<sub>2</sub> by the ocean. They concluded that the global carbon budget is balanced and hence no significant change in the inventory of carbon in the terrestrial biosphere occurred during the last 20 years. But, does the  $^{13}\text{C}$  global budget provide useful constraint on the uptake of fossil fuel CO<sub>2</sub> by the ocean? Results of our analysis of changes in the global  $^{13}\text{C}$  inventory and of model evaluations show that, while the potential is there, the data base is too inaccurate to permit a distinction to be made among the carbon budgets currently on the table (e.g., Tans et al. 1990). Box-diffusion model simulations indicate that a nearly 2.5 times change in oceanic CO<sub>2</sub> uptake corresponds to only about an 18% increase in  $\delta^{13}\text{C}$  for warm surface water  $\Sigma\text{CO}_2$ . The twenty or so percent uncertainties in the size of the effective exchange reservoir and in the magnitudes of the  $\delta^{13}\text{C}$  changes in atmospheric CO<sub>2</sub> and oceanic CO<sub>2</sub> are just too large to permit reliable estimates of CO<sub>2</sub> uptake. We conclude that uptake estimates based on ocean modeling (tracer-calibrated box models or tracer verified ocean GCMs) is a better approach.

### *ASGASEX: Air Sea Gas Exchange Experiment*

W. Oost (oral) #17

A major difficulty in the quantification of the greenhouse problem is the uncertainty in the transport of CO<sub>2</sub> and other greenhouse gases across the ocean surface. All usual measurement methods are indirect. The only absolute method to measure the transport of CO<sub>2</sub>, the eddy correlation (e.c.) method, requires high accuracy, fast responding CO<sub>2</sub> sensors. The accuracy of existing sensors is sufficient for e.c. measurements over land, but the concentration gradients over the open sea have been too small for their use so far. With the advent of new sensors this situation is changing and it appears to be possible now to make absolute CO<sub>2</sub> flux measurements at sea using the e.c. technique.

During the 1990 VIERS-1 field experiment at Meetpost Noordwijk (MPN), a research platform 5 sea miles off the Dutch coast, CO<sub>2</sub> flux measurements were made with two newly developed sensors, one from Agriculture Canada and operated by the Canadian Bedford Institute of Oceanography (BIO), the other developed (in cooperation with the National Center for Atmospheric Research, USA) at and operated by the Royal Netherlands Meteorological Institute (KNMI). Both instruments use the absorption of infrared light at 4.2  $\mu\text{m}$  to determine the CO<sub>2</sub> concentration in the air. The results of the Canadian sensor marginally exceeded the noise level. Meanwhile, the sensitivity of both sensors has been significantly improved and during a recent experiment at MPN an unequivocal fluctuating CO<sub>2</sub> signal was registered with the Dutch sensor.

A new measurement campaign, the international ASGASEX (for Air Sea GAS Exchange) experiment, will be held from September 6 until including October 1, 1993. During ASGASEX a large number of air and sea parameters and fluxes will be measured. ASGASEX will be performed at MPN and from one or more ships in its immediate neighborhood.

The aims of the experiment are: (1) to compare several techniques for the measurement of vertical gas fluxes in the atmosphere above open water, among them the eddy correlation method; (2) to test a new technique for the measurement of scalar fluxes, using heat as a tracer. This technique is intended as a stepping stone for the measurement of the CO<sub>2</sub> flux with remote sensing techniques; and (3) to find relations between the atmospheric situation (wind, stability) and the structure of the sea surface (waves, whitecaps) on one hand and gas and aerosol fluxes on the other.

### *Carbon Transfer by Chinese River Systems (CTCRS) and Its Significance to the Carbon Biogeochemical Cycle*

X. Songling (poster) #102

Characteristics of carbon concentrations of Chinese river systems. Carbon exists during CTCRS as gaseous (CO<sub>2</sub>), dissolved inorganic (CO<sub>3</sub> and HCO<sub>3</sub>), the dissolved organic (which values can be inferred BOD), and the suspended. Following are quantitative and spacial characteristics of the concentrations. Our data show that: the gaseous carbon concentration, termed GCC, is about  $1.46 \text{ mg/L}$  (a range from 0.78 to 2.77); the dissolved inorganic carbon concentration, termed DIC,  $18.71 \text{ mg/L}$  (6.93 – 39.0); the dissolved organic carbon concentration, termed DOCC,  $1.42 \text{ mg/L}$  (0 – 2.85); and the suspended carbon concentration, termed SCC,  $11.54 \text{ mg/L}$  (2.72 – 486.26). It is clear that DIC and SCC are much higher than GCC and DOCC, and therefore are two key objectives to deal with in the CTCRS study. The data show that: close interrelationships exist between GCC and DIC, and between them and degree of water mineralization. This is easy to understand on the basis of river chemistry; Referring to China's soil map, GCC and DIC spatial distribution is highly related to soil types, and GCC season variations are related to degrees of flood drowning. DIC is generally dependent on degrees of dissolvable content of humus in soil, and SCC is dependent on degree of erosion.

Formulating relations of DICC and SCC to relevant terrestrial environmental factors. DICC is related to three environmental factors. Firstly, chemical properties of earth, secondly, sediment charge of river, and thirdly, precipitation and aridity. Thus DICC can be quantitatively formulated as  $\rho_{DICC} = c(al + bS) + k$ , where  $\rho_{DICC}$  is the DICC value;  $l$ , the total exchangeable ion concentration of soil;  $S$  the sediment charge of river;  $c$ , the climatic factor (involving aridity and precipitation, and  $a$ ,  $b$  and  $k$ , constants special to particular river systems. SCC is linearly related to the sediment charge of river and the carbon content of eroded soil. The concentration can therefore be quantitatively formulated as  $\rho_{SCC} = bp_S S + k$ , where  $\rho_{SCC}$  is the SCC value;  $S$ , the sediment charge of river,  $p_S$ , the carbon content of eroded soil,  $b$  and  $k$ , constants special to particular river systems.

#### **Storage, Distribution and Transfer of the Carbon of Biotic Source in China**

**J. Fang, S. Xu, G. Liu (poster) #103**

Storage and distribution of the carbon of biotic sources was studied for terrestrial ecosystems of the entire country of China. The estimation of carbon amount was based on plant productivity data from 858 sites and data of soil organic matter from 725 soil profiles which are located all over China. Transfer of carbon to rivers and oceans from terrestrial biota was analyzed by using a river-section model and relevant hydrologic, erosive and hydro-chemical data. Main results are summarized as follows.

The total amount of carbon stored in the terrestrial vegetation of China is  $6.44 \times 10^9$  tons, which makes up 0.78–1.16% of the world's vegetation carbon pools, as estimated by Woodwell (1984). Of this amount, the carbon in forests is  $4.25 \times 10^9$  t, scrub  $0.36 \times 10^9$  t, grassland  $1.02 \times 10^9$  t, cropland  $0.80 \times 10^9$  t and desert  $0.012 \times 10^9$  t.

Carbon stored in surface soils with an average depth of 88 cm for 44 soil types is  $177.91 \times 10^9$  t, which amounts to about 28 times that in terrestrial vegetation and makes up 5.93 to 11.86% of the world's soil carbon pools. This means that China's soil is an important biotic source of carbon dioxide.

Peatland in China holds a carbon amount of  $1.10 \times 10^9$  t, about 1.7 times that stored in the terrestrial vegetation, while its area is  $4.16 \times 10^6$  ha, only about 0.43% of the whole country. Accordingly, the peatland is an important contributor to atmospheric  $CO_2$  concentration.

As an example, the transfer of carbon in the biota-river-ocean system in the Huanghe (Yellow) River Valley is studied by means of a river-section model. It is clarified that the suspended carbon and inorganic-ionic carbon are main components of the carbon transfer, comprising over 90% of a total amount of the carbon transfer. A total amount of  $3.7 \times 10^7$  Ct is transferred annually, and 66.4%, or  $2.45 \times 10^7$  Ct/yr, is carried into the Pacific Ocean. The net carbon absorption by plants is estimated at  $5.64 \times 10^7$  Ct/yr in the Valley, thus the carbon transferred to the ocean is approximately one half of the net absorption by plants.

### **GLOCHEM: Global Atmospheric Chemistry Survey**

#### **Global Measurements of Photochemically Active Compounds**

**A. Wahner, F. Rohrer, B. Ridley, E. Atlas (invited) J**

An understanding of the distribution, variation, and photochemical interactions of reactive species in the global troposphere is fundamental to questions about the budgets and trends of tropospheric ozone and other trace gases. These are among the major objectives of the IGAC/GLOCHEM Activity. Recently, several field campaigns have measured reactive trace gases and radical species in the remote troposphere to test models of transport and chemical processes. The experimental programs described here are STRATTOZ III, TROPOZ II, and MLOPEX II. Examples from each of these programs will highlight some of the results.

Global-scale distributions of trace gases were measured during June 1984 (STRATTOZ III) and January 1991 (TROPOZ II). The measurements cover latitudes from 60°N to 60°S and altitudes from 0 to 12 km. A number of different chemical species were measured during the flights, but here we focus on measurement of nitrogen oxides,  $NO_x$ , in the troposphere. The oxides of nitrogen to a large extent control hydroxyl radical concentration and ozone production in the troposphere. Thus, accurate knowledge of the global  $NO_x$  distribution is required for the understanding of tropospheric chemistry.

The northern hemispheric summertime vertical profiles are C-shaped, with high  $NO$  mixing ratios at 8–10 km altitude and a strong vertical gradient. In contrast, high concentrations were observed in the northern hemisphere during winter at all altitudes nearly without vertical gradient.

A two dimensional, zonal model with limited chemistry of  $NO$ ,  $NO_2$  and  $HNO_3$ , applied to the latitudinal band of 40–50°N, reproduces the measured vertical profiles reasonably well. Even the formation of a maximum of  $NO$  mixing ratio at 8–10 km altitude over Europe and North America during summertime can be explained by fast vertical transport of surface emitted  $NO$  and the  $NO$  emission by aircraft in the upper troposphere.

The Mauna Loa Observatory Photochemical Experiment (MLOPEX II) was conducted to measure simultaneously a large number of related chemical species to characterize the photochemical state of the remote free troposphere and to test our current understanding of photochemical interactions and processes. The measurements at this location were carried out in 1991 and 1992 during four seasonal intensive experiments, each lasting 5–6 weeks. Aircraft studies during one intensive were made to relate measurement from the ground site to trace gas concentrations on a large, regional scale. In addition to trace gas composition, radical species ( $HO_2$ ,  $RO_2$ ,  $HO$ ) and photolysis rates ( $NO_2$ ,  $O_3$ ) were measured.

Because the experiment was only recently completed, data have only begun to be integrated and analyzed. This talk will present examples of the different measurements obtained during the experiment, and we will emphasize the variations and relationships observed over diurnal, synoptic, and seasonal time scales.



**Long-Term Increase of Tropospheric Ozone****R. Bojkov (oral) #77**

Analysis of the available long-term records of surface ozone at rural stations and of ozonesonde observations confirm the continuous increase of ozone concentration, at some places by more than 1% per year, during the last 25 years. The data do not represent a global average. However, they reveal that in all major regions of the Northern Hemisphere, there is a tropospheric ozone increase. Some mountain stations, e.g., Zugspitze (3000 m) sampling free tropospheric air show increase of nearly 2% per year which is in concurrence with the nearby ozone soundings at Hohenpeissenberg. Also, the sounding stations in Canada and Japan confirm statistically significant long-term ozone increase in the entire troposphere. This is in concurrence with modelling studies highlighting the important combined effect of non-methane hydrocarbons (NMHC), as well as CO and CH<sub>4</sub>, for increasing ozone production in the troposphere.

Ozone trends in per cent per decade and their 2σ standard error at different altitudes (km) from ozone soundings at Hohenpeissenberg and Churchill show significant increase in the troposphere and decrease in the lower stratosphere.

**Large Scale Study of Ozone and Precursors (CO, CH<sub>4</sub>) in the Background Troposphere from Meridional Airborne Campaigns: TROPOZ II and STRATTOZ II****A. Marengo, P. Nedelec, H. Gouget (oral) #78**

In the course of the joint French and German program on tropospheric chemistry, two meridional airborne campaigns were conducted in opposite seasons (StratOz III, June 1984; Tropoz II, January 1991) in order to study the origins and distributions of ozone and its precursors within the troposphere. The route extended between 0 and 12 km altitude and from 70°N to 60°S latitude, along the American, African and European continents. The vertical and meridional distributions of O<sub>3</sub>, CO and CH<sub>4</sub>, obtained during the last Tropoz II mission, are presented here. The results confirm the predominance of the northern hemisphere over the southern one, as a consequence of the distributions of their sources. The ozone distribution reflects the influences of photochemistry, stratospheric air intrusions and biomass burning. An important layer, containing high concentrations of CO and CH<sub>4</sub>, is found above 7 km altitude over the major part of South America, in contrast with the low mixing ratios measured in the mid- and lower troposphere. The results confirm the importance of the CH<sub>4</sub> sources at the high latitudes of the northern hemisphere and in the northern part of South America (Amazonia). The comparison of data obtained during the two campaigns allows study of the seasonal variations.

**An Investigation of the Atmospheric Sources and Sinks of Methyl Bromide****M. Kanakidou, H. Singh (oral) #81**

Methyl Bromide (CH<sub>3</sub>Br) has been implicated as an important player in the depletion of stratospheric ozone. Atmospheric measurements of CH<sub>3</sub>Br, interhemispheric gradients, oceanic concentrations, man-made emissions, and removal processes have been analyzed and interpreted with the help of a 2-D global photochemical model (Kanakidou et al., 1992). The atmospheric lifetime of CH<sub>3</sub>Br is calculated to be about 1.9 years based on reaction with OH radicals. Consequences of a much shorter lifetime of 1.2 years, due to possible deposition losses, are also considered. A global source of about 100 Gg (10<sup>9</sup>g)/year best fits the observational data. The partitioning of this global source into natural and man-made sources is discussed. A global trend of about 0.1–0.2 pptv/year, from man-made sources of CH<sub>3</sub>Br is predicted. Model results show significant vertical and seasonal variations in the atmospheric abundances and interhemispheric gradients of CH<sub>3</sub>Br.

**Atmospheric Composition and Radiative Forcing Response to Greenhouse Gas Perturbations****C. Granier, D. Gauglustaine, G. Brasseur (oral) #86**

Both tropospheric and stratospheric ozone play a significant role in the radiative forcing of the atmosphere. The ozone concentration is controlled in the troposphere by the distributions of CH<sub>4</sub>, CO, NO<sub>x</sub>, and NMHCs, and by chlorine and bromine compounds in the stratosphere. OH is also a key compound as it governs the loss of a large number of greenhouse gases. Results of a two-dimensional model of the lower atmosphere, which treats interactively chemical, radiative and dynamical processes will be presented. Because of many feedback mechanisms included in its formulation, this model is particularly adapted to simulate the atmospheric response to human or natural perturbations. Simulations of the evolution of the atmospheric composition and of the radiative forcing of the atmosphere to increasing emissions of carbon dioxide, nitrous oxide, methane, CFCs and HCFCs will be discussed. Satellite measurements have shown a global decrease of the stratospheric ozone over the last decade, which should induce changes in tropospheric photodissociation rates. The impact of such changes on tropospheric species and on their trends will be discussed.

**Seasonal Measurements of Non-Methane Hydrocarbons and Carbon Monoxide at the Mauna Loa Observatory During MLOPEXII****J. Greenberg, D. Helmig, P. Zimmerman (oral) #83**

Atmospheric non-methane hydrocarbons (NMHCs) and carbon monoxide (CO) were measured at the Mauna Loa Observatory, Hawaii during four 5-week periods in each season, from September 1991 through August 1992, as part of the Mauna Loa Photochemical Experiment (MLOPEXII). NMHCs were measured 12 times daily and CO was measured 48 times daily by fully automated gas chromatographs with flame ionization and reduction gas detectors, respectively. These measurements describe background mixing ratios of these gases which should be typical for wide regions of the Pacific marine mid-troposphere. Mixing ratios of most trace gases measured showed marked seasonal differences; passage of synoptic systems was also seen to affect mixing ratios dramatically. Several gases with relatively short atmospheric lifetimes were typically found in free tropospheric air samples: ethylene and propylene, probably from marine sources, were always

detected; isoprene, an emission from island vegetation, was frequently measured in the downslope, free tropospheric sampling periods. The spring sampling period was supplemented by aircraft measurements from the boundary layer up to 11 kilometers. In addition, canister samples were taken daily and shipped to our Boulder laboratory for analysis.

The variability of these measurements with respect to season, meteorological conditions, and island influences will be discussed. Analytical details concerning calibrations, instrument automation, and sampling techniques will be described briefly.

***Twenty Years of Balloonborne Tropospheric Aerosol Measurements at Laramie, Wyoming***

**D. Hofmann (oral) #85**

Over the period 1971 to 1990, 265 high altitude balloons with optical particle counters were launched at Laramie, Wyoming in a long term study of the stratospheric sulfate aerosol layer. The tropospheric aerosol record obtained at this background continental site is examined here. All aerosol particle size ranges display pronounced seasonal variations, with the condensation nuclei concentration and the optically active ( $r \geq 0.15 \mu\text{m}$ ) component showing a summer maximum throughout the troposphere. The dominant source of these particles is believed to be photochemically-driven gas to particle conversion. Larger particles ( $r \geq 1 \mu\text{m}$ ) peak in spring and are probably the result of long range transport of Asian desert dust, although there is evidence that sulfate aerosol is also present in these air masses. Mass estimates, assuming spherical sulfate particles, indicate an average column mass between altitudes of 2.5 km and 10 km of about 4 and 17  $\text{mg m}^{-2}$  in winter and summer, respectively. The annual average of about 10  $\text{mg m}^{-2}$  is somewhat larger than recent model calculations for sulfate aerosol but within the uncertainties of model and measurements. Calculated optical depths are in reasonable agreement with measurements made at Boulder, Colorado. The estimated mass scattering cross section is near 5  $\text{mg}^2 \text{g}^{-1}$  throughout the troposphere. A distinct anti-correlation exists between the optically active and the condensation nuclei components, resulting in a maximum in the mixing ratio of the latter just below the tropopause where the larger particles generally show a minimum. This relation is due to coagulation of the small, newly nucleated particles with the existing larger particles and to the competition for available condensable vapors presented by the larger particles, resulting in the most effective new particle source region occurring in the upper troposphere. There is no evidence for a long-term variation in the optically active aerosol component anywhere in the troposphere; however, normally minimal winter levels of newly nucleated aerosol particles in the upper troposphere have increased since about 1986. The contribution of sulfur from jet aircraft effluent in this region is investigated and it is shown that this source is capable of providing about  $1/2$  the mass required to sustain the upper tropospheric aerosol in winter.

***Evidence of Long-Term Evolution of Ozone at Mid-Latitudes of the Northern Hemisphere from the Series of Pic Du Midi Observatory: Consequences for Radiative Forcing***

**A. Marengo, P. Dedelec, H. Gouget, J. Pages (poster) #76**

The rate of ozone increase in the troposphere is debated and there is a lack of long-term accurate measurements in representative areas. The scope of old data series performed at the end of the 19th century is relatively limited by the strong interferences induced by the location of the stations in the boundary layer (vertical exchanges) and on the border of important towns (pollution). The Pic du Midi Observatory (3000 m altitude in SW France) is representative of the free troposphere in clean conditions and is very convenient for tracing the ozone evolution at the mid northern latitudes. Here are presented four sets of data available at this station: (1) 1874 - 1881 and (2) 1881 - 1909 by the Schoenbein method, (3) 1981 - 1984 and (4) 1990 - 1992 by UV absorption analyzers.

The results show an ozone increase by a factor of 5 since the beginning of the century, corresponding to a mean rate of 1.6% per year, the tendency being higher (2.4% per year) in the last decades. A stable 10 ppb ozone mixing ratio is observed for the pre-industrial era, and the increase started around 1890. Other data obtained in other European altitude stations between 1920 and 1980, are in excellent agreement with the Pic du Midi evolution. A comparison with other representative data around the world shows that ozone is actually the second most significant greenhouse gas in the northern hemisphere (25% in radiative forcing) and will have in the future a disymmetrical evolution in the two hemispheres, which is not taken into account in radiative models. If such rates would maintain over the next century, the concentrations of ozone in the northern free troposphere will exceed the 100 ppb in the 40 years to come, and ozone could become as important as carbon dioxide in the radiative forcing of the northern atmosphere.

***Large Scale Meridional and Vertical Distribution of Carbon Monoxide Measured in January 1991***

**G. Harris, J. Roths (poster) #79**

As part of the TROPOZ II large scale measurement campaign we deployed our Four Laser Airborne Infra Red (FLAIR) tunable diode laser spectrometer on board the Caravelle 116 aircraft operated by the French Centre d'Essais en Vol. In situ measurements of CO, NO<sub>2</sub>, HCHO and H<sub>2</sub>O<sub>2</sub> were made using the spectrometer between 68°N (Greenland) and 53°S (Tierra del Fuego) at altitudes from near the surface to 11 km. The flight route followed the Atlantic coast of North America, the Pacific and Atlantic coasts of South America and the Atlantic coasts of West Africa and Europe.

We report here our CO measurements which were obtained with either one or two minute time resolution and use the data set to construct a representation of the 2D meridional and vertical distribution of this trace species during southern hemispheric summer.

Polewards of 30°S the CO distribution was very homogeneous with a mean mixing ratio of 54 ppbv. Between 20°S and 30°S a sharp north south gradient was observed at all altitudes between the surface and the tropopause. Throughout the region from 20°S to the equator we obtained anomalous vertical profiles of CO with mixing ratios 10-30 ppbv higher above

7 km than in the mid free troposphere. Three day back trajectories for these CO rich airmasses originated over Amazonia and supporting measurements suggested that the airmasses were of northern hemispheric origin and had been rapidly convected to the upper troposphere over that region. The influence of biomass burning in West Africa on the regional scale distribution of CO is clearly apparent from the measurements, with CO mixing ratios at 10°N on the African side of the Atlantic being 50 - 100% higher than on the Central American side. CO mixing ratios farther north ranged from 80 - 150 ppbv and showed distributions reasonably similar to those predicted for January by the Mainz MOGUNTIA 3D model (P. Zimmerman, private communication).

#### **Variability of the Baring Head <sup>14</sup>CO Record**

**C. Brenninkmeijer, K. Lassey, A. Gomez (poster) #80**

Like methylchloroform, <sup>14</sup>CO can be used to verify OH radical distribution and its seasonality. While both tracers have this dominant OH sink in common, their source characteristics are different in the extreme. Given that the major source, i.e. cosmogenic <sup>14</sup>C production leading to mainly <sup>14</sup>CO, is concentrated in the upper atmosphere and at high latitudes, and that CO lifetime is relatively short, a challenging picture emerges. Indeed model calculations using OH distribution have only been partially successful in explaining <sup>14</sup>CO measurement results.

In this work we analyze the 3 1/2 year long <sup>14</sup>CO record from Baring Head, 41°S, for its variability. The precision of a <sup>14</sup>CO determination is about 2%, which provides a very favorable signal to noise ratio. However, short term variability as we have observed is well in excess of this, occasionally amounting to 10% in a matter of days. Using meteorological data, it can be shown that in most instances this scatter is caused by sampling air transported from different latitudes, with southern air masses having a higher <sup>14</sup>CO content. The seasonal variation of <sup>14</sup>CO reflects OH seasonality which causes most of the 30% modulation around the average value of 9 <sup>14</sup>CO molecules per cm<sup>3</sup>. By using the concurrent CO concentration record an estimate is made of the <sup>14</sup>CO contribution derived from biogenic sources (recycled <sup>14</sup>CO). This contribution to <sup>14</sup>CO is small. Further analysis of the data shows the existence of year to year differences of up to 15%. The various causes of these are discussed including changes in mixing, solar activity and OH abundance. It is not likely that the observed changes are due to a bias in meteorological conditions during the days selected for sampling. Finally, the longer term variation in the record is considered. In particular the decreasing solar activity, now that we are leaving solar cycle 22 behind, should lead to increased <sup>14</sup>CO values, and an estimate of the change in this very important component of the <sup>14</sup>CO source is necessary. So far the data show a rather large response of the <sup>14</sup>CO inventory to the waning of solar activity.

Although CO itself is not used to constrain OH, mainly due to uncertainties about its sources, a comparison between CO and <sup>14</sup>CO proves to be useful as several aspects of these two records appear to be correlated and the reasons for this are explored.

#### **Organic Trace Gases in the Atmosphere at Maunaloa Observatory**

**D. Helmig, W. Pollock, J. Greenberg, P. Zimmerman (poster) #84**

Gas-phase organic chemicals at tropospheric background levels in the northern hemisphere were measured during four 5-week periods from September 1991 to August 1992 as part of the Mauna Loa Observatory Photochemical Experiment (MLOPEX-II). In addition to two gas chromatography/flame ionization detection (GC/FID) systems for quantification of light hydrocarbons in the C<sub>2</sub> to C<sub>7</sub> range, a fully automated gas chromatography/mass spectrometry (GC/MS) system was employed for in situ measurements during the fourth field experiment. Sample volumes on the order of up to 50 - 80 liters were collected by using a variety of different concentration and separation techniques. Compound identifications of non- and semi-polar atmospheric organic trace chemicals down to the lower ppt level were achieved.

The analytical system employed will be described briefly and the identification of individual compounds will be presented. The occurrence of certain compound classes under different meteorological and environmental conditions will be discussed and a comparison of the obtained results with the GC/FID measurements and with available analytical data from other background sampling sites will be given.

### **GEIA: Global Emissions Inventory Activity**

#### **Global Emissions and Models of Photochemically Active Compounds**

**J. Penner, C. Atherton, T. Graedel (invited) K**

Anthropogenic emissions from industrial activity, fossil fuel combustion, and biomass burning are now known to be large enough (relative to natural sources) to perturb the chemistry of vast regions of the troposphere. A goal of the IGAC Global Emissions Inventory Activity (GEIA) is to provide authoritative and reliable emissions inventories on a 1° x 1° grid. We can then combine high quality emissions inventories with atmospheric photochemical models and compare the model results with measurements of pertinent species to understand whether there are major shortcomings in our understanding of tropospheric photochemistry, the budgets of trace species, and their effects in the atmosphere. Through this activity, we are building towards the capability of predicting the future consequences of anthropogenic emissions. This paper presents results from the 3-D LLNL atmospheric chemistry model using the newly completed IGAC recommended emissions inventories for reactive nitrogen and sulfur dioxide.

#### **Fire, Biogenic Soil Emissions and the IGAC Global Emissions Inventory of Biomass Burning**

**J. Levine, W. Cofer, D. Cahoon, B. Stocks, E. Winstead, D. Sebacher (oral) #41**

Recent measurements indicate significantly enhanced biogenic fluxes of nitric oxide (NO) and, in some ecosystems, of NO and nitrous oxide (N<sub>2</sub>O), following burning. These measurements were obtained before and after burning at chaparral and temperate sites in the United States and in tropical savanna grasslands in Kruger National Park, South Africa. Artificial wetting of the burned and unburned (control) sites to simulate natural rainfall resulted in elevated fluxes of NO and, in some ecosystems, of NO and N<sub>2</sub>O. Post-fire enhanced nitrogen fluxes may be related to elevated concentrations of soil ammonium produced during the fire. The enhanced post-burn production of NO + N<sub>2</sub>O vs. NO in a particular ecosystem may be related to the microbial community of the system, i.e., certain microbial species may produce NO at the expense of N<sub>2</sub>O production. This point will be discussed in detail.

As part of the IGAC Global Emissions Inventory Activity (GEIA) on Biomass Burning, we have assessed the regional and global impact of burning on the biogenic fluxes of nitrogen oxides from Africa. The objective of GEIA on Biomass Burning is to develop the global inventory of biomass burning for a base year, chosen to be 1987. This database is being developed by acquiring various satellite and groundbased observations of biomass burning. Satellite measurements include those obtained by the NOAA AVHRR, LANDSAT and DMSF. We will discuss the status and progress of this activity and give an example of its use. Nighttime low-light images acquired by the Defense Meteorological Satellite Program (DMSP) Block 5 satellites were used to determine the monthly distribution of burning over Africa for 1986 and 1987. The geographical distribution of burning over Africa shows variability from month-to-month, but is strikingly similar for the same month separated by a year. This important and unique satellite data base will be described. These measurements, coupled with meteorological data on rainfall over Africa, provide information on the importance of post-burn biogenic emissions of nitrogen oxides on the African regional and global budgets of these environmentally important gases and the value of the IGAC / GEIA on Biomass Burning.

#### *Emissions from the Combustion of Biomass on a Global Scale: Progress in Temporal and Spatial Modeling*

D. Ward, W. Hao, M. Liu, C. Justice (oral) #45

Improvements in the assessment of emissions from global burning of biomass suggest that  $\approx 6000$  Tg are consumed annually. Combustion efficiency, or the ratio of actual CO<sub>2</sub> released to that from complete combustion, was used to estimate the distribution of carbon-containing compounds and particulate matter based on ecological types and fire conditions. Data from our field research in Brazil, South Africa, Zambia, USA, and Canada are used for the analysis. Results provide estimates of the total emissions of 10500, 360, 28, 21 and 50 Tg per year of CO<sub>2</sub>, CO, CH<sub>4</sub>, nonmethane hydrocarbons, and fine particles, respectively. The same technique has been used to estimate on a global scale the release of several air toxics including formaldehyde, benzene, and benzof[a]pyrene of 2.8, 2.1, and  $1 \times 10^{-3}$  Tg/y, respectively. We are now developing methods for improving estimates of the temporal and spatial release of trace gases, air toxics, and particles. The temporal release has been based on the occurrence and length of the dry season by geographic locations. Spatial distributions have resulted from deducing burning frequency and burned area from land-use maps, population census information and satellite imagery. More specific information is being developed to estimate emissions of trace gases and particulate matter based on broad characteristics of vegetation that respond to weather in producing predictable fire behavior. These models are being tempered with information of land-use, weather, and fire frequency derived from satellites and other sources.

#### *Global Natural VOC Emissions: An GEIA Inventory and Assessment of Uncertainties*

A. Guenther, C. Hewitt, G. Allwine, J. Berdowski, G. Dollard, J. Duyzer, C. Ennis, D. Erickson, R. Fall, C. Geron, T. Gould, T. Graedel, P. Harley, E. Holland, R. Janson, L. Klínger, B. Lamb, M. Lerda, B. McKay, P. Middleton, R. Monson, T. Pierce, B. Reed, R. Scholes, D. Simpson, G. Seuert, R. Steinbrecher, R. Tallamraju, L. Tarrason, J. Taylor, M. Trainer, C. Veldt, Y. Yokouchi, H. Westberg, P. Zimmerman (oral) #88

The IGAC Global Emissions Inventory Activity (GEIA) has established international working groups to develop and evaluate global inventories of trace gas emissions for the international community. The natural volatile organic compound (VOC) working group has completed an initial gridded, monthly inventory of emission rates for terrestrial and marine surfaces. Individual estimates are given for three classes of compounds: isoprene, monoterpenes, and other VOC. The inventory estimates are based on emission factors representative of individual surface types, light and temperature dependent emission algorithms, and seasonal biomass adjustments. Monthly temperatures and surface types are based on existing  $1^\circ \times 1^\circ$  global gridded inventories. Light intensity is estimated with a model that accounts for hourly and monthly variations due to changes in cloudiness, and light extinction within a plant canopy.

Uncertainties exist in two major areas: assignment of emission factors to individual surface types and modeling the processes that control variations in emissions from a given surface type. VOC emission rates vary greatly among different plant species. This results in large uncertainties associated with the emission factors assigned to landscapes where emission rates of the dominant plant species are unknown. Temperature, light intensity, stresses (e.g. drought, injury), phenology and other factors play a role in regulating the emission of some, but not all, natural VOC compounds. Many of these relationships are not well understood and numerical algorithms exist for only a few processes (e.g. temperature and light dependence). The results of the initial inventory suggest that a majority of global natural VOC emissions are from regions, e.g. tropical forest, with the highest uncertainties. Recommendations for future mechanistic studies and field measurement programs are given, with emphasis on research that will reduce the major uncertainties in the global VOC emission inventory.

#### *Uncertainties in the Calculation of Atmospheric Releases of Chlorofluorocarbons*

D. Fisher, P. Midgley (oral) #91

For many years, the chemical industry has voluntarily reported the annual production and sales of chlorofluorocarbons (CFCs) through a survey conducted by an independent auditor. Data are available through 1991 for CFCs 11, 12, 113,

114 and 115, as well as for HCFC 22 and methyl chloroform. The purpose of the survey is to provide the scientific community with data on the atmospheric release of these compounds. This requires an analysis of the use profile for each compound as well as the pattern and timescale of release from the various uses. In the absence of firm information for countries not involved in the industry surveys, assumptions have been made about the amount of production and type of use. These assumptions can significantly impact the world estimates for emissions.

The uncertainties involved in deriving atmospheric releases, and ultimately lifetimes, will be discussed. For instance, it is estimated that the most recent data now represent only 70% of the worldwide production for CFCs 11 and 12. Hence, production reported through the industry survey covers a decreasing fraction of world production. A sensitivity analysis has been carried out to estimate the impact of this and other uncertainties on calculated emissions. Uncertainties of greatest significance are thus identified and programs to resolve these are outlined.

#### **Changes in Tropospheric Photochemistry Owing to Stratospheric Ozone Depletion Between 1980 and 1990**

**J. Lelieveld, P. Crutzen (oral) #99**

Observed total column ozone changes obtained with the satellite-borne TOMS instrument between 1980 and 1990 have been used to estimate with a radiative transfer model changes in tropospheric ozone photolysis frequencies. We have implemented the latter in a 3-D global transport/chemistry model of the troposphere to calculate  $O(^1D)$  and subsequent OH radical concentrations. Hence, we have simulated chemical  $CH_4$  removal from the troposphere due to reaction with OH using measured  $CH_4$  concentrations and trends. The latter indicate that the atmospheric  $CH_4$  increase ascribed to anthropogenic emissions has decreased from about 1% per year during the 1970s and early 1980s to about 0.6% per year by the end of the 1980s. Our calculations suggest that stratospheric ozone depletion caused by photochemical breakdown of chlorofluorocarbons may significantly affect tropospheric photochemistry by allowing more photochemically active shortwave radiation to penetrate the troposphere. Thus, enhanced OH formation may slow down the growth of  $CH_4$ . Moreover, our calculations suggest that the influence of increasing emissions of trace gases such as  $CH_4$ , CO and  $NO_x$  also play a large role in anthropogenic changes in the chemistry of the troposphere.

#### **A Comparison of Atmospheric $^{14}CO$ Results from the Northern Hemisphere and Implications to Tropospheric OH**

**J. Mak, C. Brenninkmeijer (oral) #95**

The determination and subsequent analysis of  $^{14}CO$  in atmospheric carbon monoxide has led to an hypothesis that there may exist a relatively large interhemispheric asymmetry in the OH abundance. This was based on a comparison of the established temporal record at Baring Head, New Zealand and Scott Base, Antarctica, with multiple samples from two separate sites in Germany. To further confirm or deny the data set from Germany as being representative of the Northern Hemisphere troposphere, we have carried out two sampling campaigns from clean air sites along the American northwest coastline, ranging from 33°N (Scripps Pier, La Jolla) to 56°N (Telegraphy Creek, British Columbia), and were arranged to coincide with the observed seasonal maximum and minimum  $^{14}CO$  values in Germany, which are 6 months out of phase with the Southern Hemisphere temporal records. Samples were collected and processed using a previously established protocol, and along with  $^{14}CO$ , CO concentration,  $\delta^{13}C$  and  $\delta^{18}O$  were also determined.

These new Pacific northwest data reveal lower  $^{14}CO$  values than the German values, however they are still appreciably larger than the corresponding data from the southern hemisphere. We present the new data along with 2-D model simulations using a revised version of the Plumb and Mahlman model and the LLNL radiative chemical transport model. We also discuss possible explanations to the observed range in NH data.

#### **Geological Sources of Organic Atmospheric Compounds**

**V. Isidorov, V. Povarov, E. Prilepskii (oral) #100**

The problem of prognosticating unpremeditated changes of radiation regime and oxidative potential of the atmosphere requires taking careful account of various sources of optically and photochemically active volatile organic components (VOC). Apart from anthropogenic and biological sources of VOC, there exist geological sources investigated to much lesser degree, which are connected with natural processes of degassing of the Earth crust and upper mantle, as well as with extraction and processing of minerals. In this connection problems of genesis, composition, and emission magnitude of geogenic VOC arouse intense interest.

In the present communication results of GC and GC-MS investigation of gases emitted by volcanoes of Kurile-Kamochatka insular arch and Central America as well as spontaneous gases of hydrothermal sources connected with deep fractures of the Earth crust in seismically active regions are reported. In their composition more than 100  $C_1-C_{10}$  VOC have been identified, the principal one invariably being methane. Of great interest is the presence of halogenated hydrocarbons among which chloromethanes  $CH_3Cl-CCl_4$  predominate (10 - 1500 ppbv). Similarity in VOC composition of volcanic gases and hydrothermal gases from seismically active regions suggests uniform mechanism of their formation.

Thermodynamical calculations of depth gases taking account of their impoverishment in water vapor caused by the dissolution of the latter in magma have shown that gas phase is enriched with non-polar and weakly polar components (CO,  $CH_4$ ,  $CH_3Cl$ , etc.). This allows one to explain the presence of organic compounds in depth gases without resorting to other hypotheses (e.g. on VOC emission resulting from pyrolysis of sedimentary  $C_{org}$ ).

Rocks of the Earth crust, as well as various minerals, contain VOC in the form of gas inclusions and/or in adsorbed form. Analysis of gases contained in some widely used minerals (sylvinites, halites, carnallites, and apatite) showed presence of dozens of  $C_1-C_9$  VOC, including a series of halogenated methanes. Contents of  $CHCl_3$  and  $CCl_4$  in sylvinites from various deposits of Russia, Byelorussia, and Turkmenistan are reported. Preliminary estimates of  $CCl_4$  emission based on the

magnitude of world sylvinitic extraction amounts to 20 – 50 kt/year. Possible mechanisms of formation of halogenated methanes present in some minerals and rocks are discussed.

Available experimental and theoretical material indicates an important role of geological sources in the formation of a global background of some photochemically active atmospheric VOC.

#### ***World Inventory of Soil Emission Potentials: Development of a Global Soil Database***

**N. Batjes, E. Bridges (poster) #90**

The role of soil in controlling production and fluxes of biotic greenhouse gases is the focus of work in progress at the International Soil Reference and Information Centre (ISRIC) at Wageningen. This 3-year project, with the acronym WISE, is a part of a wider research activity funded by the Netherlands National Research Programme on Global Air Pollution and Climate Change (NOP).

During the first phase of the project (September 1991 – September 1992), literature on the soil conditions and biological, chemical and physical processes that regulate the fluxes of heat, moisture and carbon dioxide, methane and nitrous oxide between the soil and the atmosphere has been compiled into a background booklet. These initial studies served to organize an international workshop (Wageningen, August 1992) to refine the broad lines of the project outlined in the research proposal.

The second phase of WISE (October 1992 – September 1994) includes two main objectives. The first one will be to assemble a global soil data base in association with the Land and Water Division of the Food and Agricultural Organization (FAO). A cleaned, vector-version of the 1:5 million scale FAO-Unesco Soil Map of the World will be used to create a 30 by 30 minute grid of geographic soil data. The "area" data on the distribution of the FAO soil units of the respective grids will be linked to a data base of soil profile "attribute" data using a Geographical Information System. It has been proposed that management of the soil data base will be through the use of SOTER, the World Soils and Terrain Digital Data Base, a data handling system developed at ISRIC on behalf of the International Society of Soil Science (ISSS). The foundations for this work have now been put in place and providing the soil data collection programme proceeds satisfactorily, it is anticipated that a preliminary data base should begin to emerge by the end of 1993.

Once a prototype for the WISE data base is in place, the second main objective will be to develop and test a procedure for handling soil data to refine estimates of methane production potentials from hydromorphic soils. A model of potential methane production in wetland rice soils, which still requires further elaboration and testing before it can be used, was proposed during the WISE workshop. Work related to model development will take place in close cooperation with specialist research institutes such as the International Rice Research Institute (IRRI) in the Philippines, Nagoya University in Japan, and the Fraunhofer Institute, Germany. The need for further interaction and cooperation with other specialist groups of e.g. the International Geosphere-Biosphere Project (IGBP) was emphasized by the WISE workshop.

An important spin-off from the development of a global soil data base is that many requests are being received for soil information relevant for studies of "global change". At present much of this information does not exist in an adequate format, so ISRIC is proceeding as rapidly as possible to implement the WISE digital data base in a format which is compatible and user-friendly.

#### ***Future Emissions of N<sub>2</sub>O from Fertilized Soils***

**C. Anastasi, D. Bird, V. Simpson (poster) #97**

The emission of N<sub>2</sub>O from soils treated with nitrogenous fertilizers have been estimated to the year 2025. The estimates are based on a model which combines current understanding of fertilizer use per capita, conversion factors associated with N<sub>2</sub>O production, and United Nations population predictions up to 2025, an average annual increase of 1.3%. A detailed variational analysis is presented which assesses the robustness of the model. The future contribution of N<sub>2</sub>O to the greenhouse effect will also be presented.

#### ***Estimation of Emissions of Greenhouse Gases and their Increases in China, 1950 to 1990***

**B. Naibin (poster) #98**

Emissions of greenhouse gases, such as CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O and others, and their increases in China from 1950 – 1990, were estimated in this paper. Most of the data used were collected from statistical yearbooks of China, and relevant parameters came from several references. The results show that in China the present emissions of greenhouse gases are 995.18 Tg C/yr for carbon dioxide, 52.19 Tg CH<sub>4</sub>/yr for methane and 0.882 Tg N/yr for nitrous oxide. The contribution of greenhouse gases emitted in China to emissions in the world is obvious: the ratio of China/world is about 11 – 13% at the end of the 1980s. In a period of 40 years, as industrialization is advancing, the emissions of greenhouse gases from China have increased; the emissions at present are about 4 – 8 times the emissions in 1950. Lastly, the ration of natural sources/anthropogenic sources for emissions of greenhouse gases from China is also discussed.

### **GIM: Global Integration and Modeling**

#### ***The Global Sulfur Cycle in the Atmosphere: A 3-Dimensional Model Study***

**M. Pham, G. Megie, G. Brasseur, C. Granier, J. Müller (oral) #93**

Sulfur compounds play a major role in the atmosphere. Besides their direct impact on the environment, they influence the budget of both tropospheric and stratospheric ozone and have an impact on the climate through the formation

of aerosols and the backscattering of solar radiation. The global cycle of eight sulfur compounds (DMS, SO<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>, COS, DMSO, MSA, H<sub>2</sub>S and CS<sub>2</sub>) has been implemented in the 3D tropospheric chemistry-transport model IMAGES. The emission and deposition at the surface and the 3D distributions of these compounds will be presented and compared with measurements and other model results. The different production terms in the sulfate budget have been estimated to show the contribution of the different compounds and the role of heterogeneous chemistry in the conversion of reduced sulfur compounds to sulfates. In order to assess the relative importance of man-made and natural sources, simulations have been made for pre-industrial and industrial cases and will be discussed in terms of sulfur deposition, global sulfate aerosol distribution, and climate forcing.

***The Global Atmospheric Sulfur Cycle: An Evaluation of Model Predictions and Observations***

J. Langner, T. Bates, R. Charlson, A. Clarke, P. Durkee, J. Gras, J. Heintzenberg, B. Huebert, J. Lelieveld, J. Ogren, J. Prospero, P. Quinn, A. Ryaboshapko, H. Rodhe, C. Leck (oral) #96

In June 1991 a workshop was held in Stockholm, Sweden, involving scientists active in the IGAC activity MAC and from the atmospheric chemistry group at Stockholm University. The principal goal of the workshop was to compare existing observations of DMS, SO<sub>2</sub> and sulfate aerosol with the predictions of the global tropospheric sulfur model available in Stockholm. The exercise had two primary aims: validating the model and evaluating the usefulness of experiments for refining this and other models. From the standpoint of the modelers it is essential to determine whether or not the model makes sense relative to observations, and to identify ways in which it needs to be improved. Experimentalists need to know what forms of data they should collect to best stress models and parameterizations, since models are the means by which observations are extrapolated to other times and places. In this paper we present the results from comparisons of model calculations with a wide range of observational data. Recommendations for future model development and measurement strategies are given.

***Ocean-Atmosphere Trace Gas Biogeochemistry and Climate Related Global Atmospheric Effects***

D. Erickson (oral) #105

The ocean has long been recognized as an important contributor to the global surface source/sink patterns for trace species that interact with atmospheric chemistry cycles. An approach whereby satellite data is merged with 3-D general circulation model (GCM) fields has been developed to estimate the oceanic exchange of trace gases with the atmosphere. These global surface flux terms are amenable for inclusion in 3-D tracer transport models of atmospheric chemistry and climate. The Coastal Zone Color Scanner (CZCS) monthly mean data on chlorophyll content of surface ocean waters are used to estimate the "photochemical lability" of dissolved organic matter. Surface radiation, wind, sea surface temperature and atmospheric boundary layer temperature information from a GCM are coupled with the CZCS data to estimate the ocean to atmosphere flux of biogeochemically important gases. To examine the sensitivity of atmospheric chemistry to the oceanic fluxes, the semi-Lagrangian transport scheme in the NCAR CCM2 is used to simulate the atmospheric cycles of several trace species that exchange with the ocean.

A variety of feedbacks exist between the air-sea exchange of trace gases and possible alterations of climatically active trace gases concentrations that influence the dynamical and radiative balances operative in the atmosphere. CO, OCS, CO<sub>2</sub>, DMS, N<sub>2</sub>O, non-methane hydrocarbons and Cl and Br containing organic compounds are some of the species whose oceanic fluxes may influence atmospheric concentrations. Photochemical process in surface ocean waters containing varying amounts and proportions of dissolved and particulate organic matter may be related to the magnitude and direction of the air-sea flux of these trace gases. These trace gases may participate in determining the oxidative capacity and radiative state of the atmosphere. Changes in photochemical forcings in the surface ocean, due to ozone depletion, "self-shading" aerosols, changes in cloud distributions and properties or surface ocean organic chemical makeup would feedback onto the climate system via air-sea gas exchange. Conceptual and numerical modeling studies designed to address these possible feedbacks will be discussed.

***Impact on the Global Troposphere of Biomass Burning and Anthropogenic Emissions***

J.F. Müller, G. Brasseur (oral) #118

The IMAGES 3-D chemical-transport model is used to quantify the respective influence of biomass burning and anthropogenic emissions on the chemical composition of the global troposphere. The model includes approximately 50 chemical species (O<sub>3</sub>, NO<sub>x</sub>, PAN, HNO<sub>3</sub>, CO, CH<sub>4</sub>, several hydrocarbons and their oxidation products, OH, HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, etc.). The advective transport is treated by a semi-Lagrangian method and is driven by monthly mean winds, which are taken from the ECMWF climatology. The effect of wind variability is accounted for by an eddy diffusion formulation. Convection in clouds is parameterized. A detailed emission inventory is used to specify lower boundary conditions. Dry and wet deposition are taken into account.

Model simulations performed with IMAGES for different conditions will be presented, with emphasis on the contributions of different biogenic and anthropogenic surface emissions. The impact of these sources on the global budget of chemical constituents will be discussed.

***Atmospheric Concentrations of DMS and its Oxidation Products Estimated in a Global 3-Dimensional Model***

J. Langner, H. Rodhe (poster) #92

A global 3-D transport model (MOGUNITA), originally developed at Max-Planck-Institute for Chemistry in Mainz, has been used to simulate the atmospheric distribution of sulfur species (DMS, SO<sub>2</sub> and aerosol sulfate) from natural and anthropogenic sources (Langner and Rodhe, 1991). The model treats emission, transport, chemistry and removal processes

with a grid resolution of  $10^\circ$  longitude by  $10^\circ$  latitude and with ten layers in the vertical between the surface and 100 hPa. Advection takes place by climatological monthly mean winds. Transport processes occurring on smaller space and time scales are parameterized as eddy diffusion, except for transport in deep convective clouds which is treated separately. The simulations are broadly consistent with observations of sulfur concentrations in air and precipitation in and around polluted regions in Europe and North America.

In this paper we focus on the contribution to the atmospheric sulfur burden of DMS emissions from the oceans. The total oceanic emission of DMS was assumed to be  $16 \text{ Tg S a}^{-1}$  with geographical and seasonal distribution estimated based on the work of Bates et al. (1987), and Leck and Rodhe (1991).

Such emissions are shown to be reasonably consistent with observed concentrations of DMS,  $\text{SO}_2$  and excess aerosol sulfate at remote marine locations. We present maps of estimated concentrations in surface air of DMS,  $\text{SO}_2$  and aerosol sulfate originating from the oxidation of DMS. We also show comparisons of calculated and measured concentrations of DMS and  $\text{SO}_2$  at a few remote sites. Finally, we discuss the potential effect on radiation fluxes and climate of aerosol sulfate derived from oxidation of DMS.

***On the Validation of the Fast Photo-Chemistry of the Troposphere: Comparison of Field Data for OH with Model Calculations***  
**D. Poppe, M. Wallasch, J. Zimmermann, T. Brauers, H-P. Dorn, D.H. Ehhalt, A. Hofzumahaus, R. Koppmann, F. Rohrer, J. Rudolph (poster) #94**

A very important step in the validation of a chemical reaction scheme for the gas phase chemistry of the troposphere is given by a comparison of measured and calculated OH concentrations. The hydroxyl radical is one of the key species of atmospheric chemistry. The influence of the ambient OH concentration on the degradation of oxidizable compounds and also on the chemical formation of ozone can hardly be overestimated. The OH-measurements were obtained at different sites in Germany utilizing a long-path-absorption technique. The precursors of OH ( $\text{O}_3$ ,  $\text{H}_2\text{O}$ , CO,  $\text{NO}_x$ , NMHC,  $\text{SO}_2$  and HCHO) and the photolysis rates of  $\text{O}_3$  and  $\text{NO}_2$  were also measured, so that the air mass containing OH is chemically well characterized. The comparison using the chemical scheme of the Regional Acid Deposition Model (RADM2) shows rather good agreement between OH field data and calculated OH for campaigns in Deuselbach and Schauinsland, remote areas with low burdens of hydrocarbons and nitrogen oxides. The correlation ( $r = 0.73$ ) between measured and calculated OH can be explained by the experimental uncertainty of the measurements. The model overpredicts the hydroxyl concentration on the average by 20%. For the measurements in Jülich one finds a slightly larger overprediction of 24% with a significantly lower correlation ( $r = 0.62$ ). Both effects most likely are caused by the higher hydrocarbon level. The accuracy of the comparison is limited by the uncertainty of the chemical rate constants.

***Sensitivity Studies Using a Photochemical Trajectory Model***  
**J. Wild, S. Bekki (poster) #122**

A photochemical box model has been developed for use in modelling the chemistry of the troposphere on a diurnal timescale. It has been designed with the capability of moving along prescribed trajectories, provided by meteorological services or obtained from the UGAMP (U.K. Universities Global Atmospheric Modelling Project) 3-D Model. Sensitivity studies are performed with this trajectory model. These studies include determining the effect on the chemistry of using different trajectories, different conditions of cloud cover, variations in the emission and deposition rates, and the diurnal variation of the mixing height of the boundary layer. The effect of rapid variations in temperature on sulphate aerosol and subsequent heterogeneous chemistry is also investigated.

***The UGAMP Global 3-Dimensional Tropospheric Chemistry Model***  
**P. Brown, K. Law, G. Carver (poster) #123**

A tropospheric chemistry model is being incorporated into the U.K. Universities Global Atmospheric Modelling Programme's (UGAMP) GCM. This is a spectral model developed from the ECMWF forecast model. Reaction with the hydroxyl radical is the dominant destruction mechanism for many atmospheric pollutants. However, to calculate the concentration of OH explicitly in a full GCM is very expensive computationally, both in terms of CPU time and data storage. Therefore, in our early experiments we have used specified fields for the concentrations of OH,  $\text{O}(^1\text{D})$  and Cl, and for photolysis rates. The 24 hour average fields are taken from the UGAMP 2-D model.

We describe the results from a 10 year simulation of CFC-11,  $\text{CH}_3\text{CCl}_3$  and HCFC-123, and from an investigation into different possible budget scenarios for  $\text{CH}_4$ . We discuss the role of transport in determining the seasonal cycles of these gases, the interhemispheric exchange rate, and compare our calculated abundances with those measured at the ALE/GAGE and NOAA/CMDL sites. The tracer transport is also compared with that found in the UGAMP 2-D model.

Finally, we have included a parameterisation for the deep convective transport of tracers. We describe how this affects the transport of inert tracers, and discuss the implications for tropospheric chemistry.

## **Fundamental Focus: Intercomparisons, and Techniques**

***The International Non-Methane Hydrocarbon Intercomparison Experiment***  
**E. Apel, J. Calvert (oral) #106**

The non-methane hydrocarbons (terpenes, isoprene, alkanes, alkynes, and aromatics) play several crucial roles in atmospheric chemistry: they are involved in ozone formation; they form the carriers of active nitrogen compounds, they are tracers of atmospheric motions; they are sources of carbon monoxide and of reactive hydrogen species. Thus, information on



their global distributions is needed currently in atmospheric chemistry. To form a global picture of these abundances, there is a need to know whether there are any systematic differences between the methods used by various investigators. In recognition of the great difficulties involved in ambient hydrocarbon measurements and the unevaluated reliability of the results of the analysis techniques currently employed, IGAC approved this international intercomparison program as Task 2 (Non-Methane Hydrocarbon Intercomparison Experiment (NOMHICE)). The main objective of this study is to assess how accurately the non-methane hydrocarbons can be measured and to compare the techniques employed by the various laboratories. The intercomparison has been designed to answer several important questions related to current state-of-the-art analyses of hydrocarbons in air: (1) Can individual scientists and laboratories measure hydrocarbon concentrations accurately for a large range of compounds from  $C_2$  to  $C_{10}$ ? (2) Does the sampling method give a true picture of the atmospheric composition? (3) Does the analytical method employed give rise to artifacts or lose individual hydrocarbons? (4) How reliable are the standards used by individual laboratories? (5) Are the storage techniques employed adequate? (6) Is the error introduced from the overlap of chromatographic peaks, and the oxidation products of the hydrocarbons from air, a serious problem?

This study is designed to answer these questions through a series of planned experiments in which the challenge to participants, in terms of complexity of required analysis, is increased with time. We now have 35 active participants in the program from all over the globe. We will report on the results of the first two tasks of a 5-task program. The first task required the individual laboratories to analyze a simple mixture of n-butane and benzene (known compounds). The second task required participants to analyze an unknown compound containing 16 different compounds.

***Application of an FTIR System for Measurements of Nitrous Oxide Fluxes Using Micrometeorological Methods, an Ultra-Large Chamber System and Conventional Field Chambers***

**B. Galle, L. Klemedtsson (poster) #107**

A medium resolution ( $1\text{ cm}^{-1}$ ) FTIR spectrometer is applied in various configurations for measurement of fluxes of  $N_2O$  from a fertilized ryegrass field. In the various configurations the instrument's potential for doing area integrated measurements, simultaneous multicomponent measurements and continuous real-time measurements was tested.

In FTIR (Fourier Transform Infra Red) spectroscopy infrared light is transmitted over an optical path and the absorption spectra of the air mass along the path is recorded with an FTIR spectrometer. A wide band spectrum is simultaneously recorded making possible simultaneous measurements of various compounds, e.g.  $N_2O$ ,  $CH_4$ ,  $CO$ ,  $CO_2$ , and  $H_2O$ . The simultaneous wide band recording also strongly suppresses the influence of intensity fluctuations due to atmospheric turbulence when doing open long path measurements. By fitting the measured spectra with reference spectra of the studied compounds, mean concentrations along the optical paths are derived. The sensitivity of the method is dependent on the optical pathlength and may be highly improved by multipath (White cell) techniques. The inherent line integration of the technique can be exploited to find novel area integrating methods.

Three applications of measurements of  $N_2O$  fluxes with FTIR are demonstrated and discussed: (1) Real time measurements in a conventional field chamber. In this application a closed (25 liter) White cell giving 139 m optical path is connected to a conventional field chamber and the build up of various gases in the chamber is monitored. (2) Area integration using an ultra-large chamber system. The FTIR is coupled to a unique open White cell with base 25 m giving an optical path length of 1 km. The system is covered with a large gas-tight tent, covering  $64\text{ m}^2$ , that can be easily opened and closed. With this system area-integrated flux measurements of various gases can be made with high sensitivity and time resolution. (3) Area integration using gradient techniques. By using the above mentioned closed White cell arrangement, and pumping air from different heights into the instrument vertical concentration gradients can be measured and, via support from micrometeorological measurements, converted to fluxes. Various techniques to take advantage of the unique possibilities to measure small gradients with FTIR are discussed.

***Development of an Automated Gas Chromatographic Analysis System for Flux Gradient Micrometeorological Measurements of Greenhouse Gases***

**J. Arah, I. Crichton, K. Smith, H. Clayton, U. Skiba (poster) #108**

Micrometeorological methods measure fluxes of trace gases over relatively large areas ( $> 1\text{ ha}$ ). Where fluxes exhibit great spatial variability, these methods offer a considerable advantage over chamber methods.

The flux gradient method requires measurements of wind speed and direction, relative humidity and temperature, and the concentration of the trace gas of interest, at different heights above the soil surface. A system has been developed to apply gas chromatographic analysis to the method for measurement of  $N_2O$  emissions from fertilized agricultural soils. By adding a programmable automatic sample injector to a gas chromatograph fitted with an electron capture detector, we were able to measure  $N_2O$  concentration gradients in free air, with a resolution of about 1 ppbv, against an atmospheric background of 310 ppbv. This degree of resolution is required even for relatively high fluxes.

In the field, 25 liter airtight gas bags were filled over a period of 30 minutes by pumps sampling the atmosphere at usually five different heights, logarithmically spaced between 10 cm and 2 m. The bags were returned to the laboratory for analysis overnight. The necessary analytical precision was achieved by taking the mean of 15 - 20 replicate analyses of each bulk sample and of standards of known concentration difference. Samples were introduced into the gas chromatograph via an auto-injector, consisting of a PC-controlled rotary switching valve, which connects each bag in turn to an evacuated sampling loop. Gas flows from the bag into the loop, and the contents of the loop are then injected into the chromatograph. At the end of the series of 5 bags, the procedure is repeated for the preset number of cycles.

Flux gradient measurements using this system, reported in another presentation at this conference, indicate that

results obtained in this way were of the same order as those obtained using chambers. The gc-based method offers a relatively low-cost alternative to more expensive analysis systems usually used for micrometeorological flux measurements, provided the fluxes are sufficiently high and/or the wind speed is sufficiently low, to give concentration differences of 1 ppb or more.

**Use of Long-Path Infra-Red Gas Monitor for Measurement of Nitrous Oxide Flux from Soil**

K. Smith, A. Scott, B. Galle, L. Klemetsson (poster) #111

The Siemens-Plessey "Hawk" Long-Path Gas Monitor is a dedicated infra-red absorption instrument for measuring trace gases in the atmosphere. It contains a filter allowing transmission of radiation in one narrow region of the IR spectrum, to allow the dedicated measurement of one particular gas. Suitably fitted versions can be used to measure small changes in the concentration of a greenhouse gas such as  $N_2O$  or  $CH_4$ .

A Hawk system was used to measure fluxes of  $N_2O$  from grassland near Stirling, Central Scotland, in April 1992, as part of an international comparison of methods for measuring  $N_2O$  fluxes from fertilized agricultural soils. Calibration studies showed that the Hawk was capable of detecting an  $N_2O$  concentration change of ca. 10 ppb, i.e. 3% of ambient concentration – significantly better than the manufacturer's specification.

Flux measurements were made simultaneously with the Hawk and with an FTIR long-path spectrometer system, described in another paper presented at this conference. The two systems were mounted side by side in a large purpose-made tent, 25 m long and 64 m<sup>2</sup> in area. The instruments were located at one end and the reflectors at the other, giving an absorption path for the Hawk of 50 m. Concentration measurements made with the two systems, during periods of canopy enclosure of up to 1 hour, correlated very well.

Measurements with conventional (0.126 m<sup>2</sup>) closed chambers placed within the tent indicated that the emissions varied about 4-fold along the area enclosed. The mean agreed reasonably well with the flux determined from the Hawk and FTIR data.

The use of a long-path instrument in a tent, or some other suitable canopy, has one particular potential advantage compared with open-air micrometeorological methods for flux measurements, which deserves to be exploited; it should allow the comparison of emissions from plots receiving different treatments in multiple-plot field experiments where emissions from adjacent plots would otherwise interfere. It is intended to apply the Hawk in this way.

**Pulse Radiolysis Study of  $CH_3SCH_3$  and  $CH_3SCH_2O_2$  Radicals in the Gas Phase at 298K**

O. Nielsen, T. Ellermann, T. Wallington (poster) #110

Dimethyl sulfide (DMS) is a reduced sulfur compound involved in the feedback mechanisms in the earth's ecosystem and climate. In the atmosphere DMS is oxidized to  $CH_3SCH_2$  and, hence,  $CH_3SCH_2O_2$  radicals. Using the technique of pulse radiolysis combined with kinetic UV spectroscopy the ultraviolet spectra of  $CH_3SCH_2$  and  $CH_3SCH_2O_2$  radicals have been obtained over the wavelength range 220 – 300 nm. Also, the kinetics of the self-reactions were investigated. Furthermore, the rate constant for the reaction of  $CH_3SCH_2O_2$  with NO was determined.

**Recent Developments in the Isotopic Analysis of Trace Gases at Ambient Levels**

G. Atkins, S. Prosser, A. Barrie, S. Debney (poster) #115

The analytical performance of the Roboprep-TG (Europa Scientific Ltd, Crewe, UK) thermal desorption interface for isotopic analysis of  $^{15}N$  as  $N_2$  and  $N_2O$ , and  $^{13}C$  as  $CO_2$  and  $CH_4$  is reported. When coupled with Photoacoustic Spectrometry (PAS), the analytical system also provides a powerful tool for the simultaneous quantification of a number of radiatively active trace gases. A discussion of the applications of this instrumentation is presented, together with data obtained from a series of soil cover experiments. Analysis of trace gases at atmospheric levels allows sensitive *in vivo* measurement of denitrification and other processes, providing a convenient diagnostic tool in determining sources and sinks of these gases. In conjunction with  $^{13}CH_4$ ,  $^{13}CO_2$  measurements identify the sources of land-fill gas reservoirs.

**Effect of Simulated Acid Rain on *Triticum Aestivum***

N. Zibbu, T. Khan (poster) #116

This paper describes the results of a laboratory experiment to observe the effects of simulated acid rain on two varieties of wheat, i.e. *Triticum aestivum* variation *Raj. 1452* and variation *Raj. 1972*. For the study of the effect of acid rain on *Raj. 1452*, ten pH levels (from pH 5.0 to 0.5) were prepared, while eight pH levels (same range) were prepared for *Raj. 1972*. The effect was observed on different growth parameters, viz. root length, shoot length, root and shoot dry weight, and chlorophyll contents. Three replicates were maintained for each level. A uniform population of five seedlings was maintained in each petriplate. The results revealed that the seedlings of *Raj. 1452* tolerated simulated acid rain exposure down to pH 2.5. Below pH 2.5, the growth of the seedlings were adversely affected. The seeds faced mortality at pH level 0.5. The chlorophyll content was not affected even down to pH level 1.0. The seedlings of the *Raj. 1972* could grow well down to pH level 2.0. The adverse effects on the growth parameters started from pH level below 2.0. Seeds faced mortality at pH 0.5, and the chlorophyll contents remained unaffected down to pH level 1.0.