IGACtivities Newsletter

INTERNATIONAL GLOBAL ATMOSPHERIC CHEMISTRY

of the International Global Atmospheric Chemistry Project

Issue No. 28
May 2003

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A Note from the IGAC Co-Chairs:

Tim Bates, Sandro Fuzzi, and Shaw Liu

The new IGAC Science Plan and Implementation Strategy, available on the IGAC web page (www.igac.noaa.gov), has been approved by our parent organizations, IGBP and CACGP. We would again like to thank all those who have commented so positively and provided written material and graphics. The new IGAC Scientific Steering Committee (SSC) has also been approved by IGBP. Tim Bates (USA), Sandro Fuzzi (ITA), and Shaw Liu (CHN-Taipei) will be sharing the duties of co-chairs of the SSC. We would like to welcome the other members of the SSC: John Burrows (DEU), Laura Gallardo (CHL), Ilia Illyin (RUS), Achuthan Jayaraman (IND), Makoto Koike (JPN), Kathy Law (FRA), Ulrike Lohmann (CAN), Dave Lowe (NZL), Martin Manning (USA), David Parrish (USA), Phil Rasch (USA), Mary Scholes (ZAF), Eric Wolff (UK), and Yongfu Xu (CHN-Beijing). We look forward to working with them as we begin the second phase of IGAC.

The International Project Office (IPO) responsibilities for the new IGAC will be split between three offices: a North American IPO in Seattle USA, an Asian IPO in China – Taipei, and a European IPO in Italy. The North American IPO will be the main point of contact for IGAC for the next two years while the Asian and European IPOs are coming on line. With the move of the North American IPO from New Hampshire to Seattle we would like to welcome the new North American IGAC Executive Officer, Dr. Sarah Masonis. Sarah will be working for IGAC half time and continuing her research on optical properties of atmospheric aerosol particles at the University of Washington half time. Sarah can be contacted at igac@noaa.gov; www.igac.noaa.gov. We would like to thank our outgoing Executive Officer, Peter Czepiel, for his many contributions to IGAC over the past year and a half. Peter will be returning to a research position at the University of New Hampshire.

Certainly a highlight of IGAC is the biannual international science symposium. Our last symposium, held jointly with the CACGP in September 2002 in Crete, Greece was a tremendous success with over 550 participants. We would like to again extend our sincere appreciation to Maria Kanakidou, the local organizing committee, the international scientific steering committee, and our many sponsors for this outstanding event. The science articles in this issue of IGACtivities highlight some of the invited presentations and scientific discussions We envision that many of these topics (e.g., the oxidizing capacity of the atmosphere; intercontinental transport and chemical transformation; developing the potential of satellite remote sensing through the integration of in-situ measurements, models and satellite observations; processes controlling tropospheric ozone concentrations) will become the first “Tasks” of the new IGAC. A guide to submitting proposals for IGAC Tasks can be found on the IGAC website at http://www.igac.noaa.gov/proposals.php.

GLOBAL IGBP CHANGE

CACGP

SCIENCE FEATURES

Investigation of the Global Atmospheric Oxidation Efficiency and Its Trends: A Proposal to Initiate IGAC-GHOST (Global HO Systematic Tests)

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Introduction

The main chemical characteristic of the earth's atmosphere is its self cleansing efficiency, which for instance limits the average lifetime of methane molecules to less than 10 years. By and large, the input of reduced gases into the atmosphere and their rate of removal are in dynamical balance.

The main tropospheric cleansing agent, the "detergent of the atmosphere", is the OH radical (hydroxyl, sometimes designated HO). Its presence is due to the photolysis of ozone by which excited oxygen atoms are formed. When these react with water molecules before becoming quenched through collision with other air molecules leading to the re-formation of ozone, two OH radicals are formed. Other primary sources of OH may also exist and can be important, such as for instance organic molecules like acetone in the upper troposphere.

Tropospheric ozone, the presence of which is of fundamental importance, has 2 source categories. One is its import from the stratosphere, the other is in situ photochemical formation within the troposphere. The only significant chemical source of tropospheric ozone is the photolysis of NO_2, followed by direct $O + O_2 \rightarrow O_3$. A lot of O_3 net production takes place in the upper troposphere.

In the background troposphere, hydroxyl radicals react mainly with methane (CH_4) and carbon monoxide (CO), providing the main removal process of these gases from the atmosphere. The reactions, however, constitute not necessarily a sink for OH. In the presence of NO, hydroxyl radicals can be recycled, for instance via the reaction sequences

$$OH + CO(+O_2) \rightarrow CO_2 + HO_2 \quad (1)$$
$$HO_2 + NO \rightarrow OH + NO_2 \quad (2)$$
$$NO_2 + h\nu\ (+O_2) \rightarrow NO + O_3 \quad (3)$$
$$\text{net: } CO + 2O_2 \rightarrow CO_2 + O_3 \quad (4)$$

or via

$$OH + CH_4(+O_2) \rightarrow CH_3O_2 + H_2O \quad (5)$$
$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \quad (6)$$
$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \quad (7)$$
$$HO_2 + NO \rightarrow OH + NO_2 \quad (8)$$
$$2\times\ \ NO_2 + h\nu + O_2 \rightarrow NO + O_3 \quad (9)$$
$$\text{net: } CH_4 + 4O_2 \rightarrow CH_2O + H_2O + 2O_3, \quad (10)$$

providing sources for tropospheric ozone. Photolysis of CH_2O can next lead to the production of HO_2 radicals, which are converted into OH radicals by reaction with NO. The importance of OH for the chemistry of the troposphere is undisputed. Yet, although our knowledge has increased considerably since OH was recognized for its importance (Levy, 1971), it has remained a rather elusive species. Its very high reactivity towards many trace gases makes it responsible for ridding the atmosphere of a host of reduced gases, but at the same time this extreme reactivity reduces its lifetime to less than a second. This leads to a low abundance and to extreme spatial and temporal variability. But also the sources of OH are highly variable. Its primary production depends on UV radiation, that is diurnally variable, and particularly the amount of water vapor is very variable. All in all we are dealing with a highly variable trace species at a concentration of only about 1 million per cm^3, corresponding to about 3 OH radicals per 10^{14} air molecules. As a result, we cannot reconstruct the ever changing global tropospheric distribution of OH from direct measurements of OH. Also important is the question, how stable the global OH abundance is on the time scale of decades (Crutzen and Zimmermann, 1991; Prinn et al., 2001; Lelieveld et al., 2002).

Enormous progress has been made in the detection of OH. Several groups worldwide master the techniques for reliably detecting OH, even from aircraft (Crosley, 1995; Hausmann et al., 1997; Hofzumahaus et al., 1998; Hard et al., 1995; Wennberg et al., 1998; Tan et al., 2001; Tanner et al., 1997; Crosley, 1997; Brune et al., 1999). This all has contributed enormously to our improved understanding of the basic chemistry of the atmosphere.

Since one cannot reconstruct the global distribution of OH, and therefore, the atmosphere's oxidation efficiency from in situ measurements, much of what is known about the distribution of OH is derived from modeling (e.g. Spivakovsky et al., 2000). However, it is largely unknown how closely the global tropospheric OH distributions as derived from 3D chemistry-transport models reflect reality. There are quite different global OH distributions "in use", all of them showing the characteristic maximum in the tropics, but showing differences between the hemispheres for instance (e.g, Lawrence et al., 2001, and references therein).

Because direct measurements only offer limited help, indirect methods are being used. The basic idea is to measure the concentration and change in time of a trace gas that is predominantly removed from the troposphere through reaction by OH, and whose source strength is known (Singh, 1977a). In this way the 'global average' OH abundance, and its changes can be derived (Lovelock, 1977; Singh, 1977a,b). In the simplest case a box model is used, but 2D and 3D models have become more common. At the outset, and parts of the following discussion will touch upon this, it is clear that this indirect estimation of OH is biased by the choice of model, and of the trace gas that is scavenged by OH.

One could propose to use methane as a tracer for OH, yet, the sources of methane are far from being accurately defined. In fact, there are basically 2 serious options for assessing OH. One is based on industrial tracers, the other uses a cosmogenic tracer.

For over 20 years the increase and subsequent decline of the tropospheric abundance of the industrial tracer methylchloroform (MCF) (phased out under the Montreal Protocol) has been followed with increasingly more refined methods from several measurement sites with the important goal to obtain a measure of the total amount of OH, and to obtain information about possible trends. The measurement of MCF by several researchers forms by far the main basis for the independent experimental verification of model derived distributions of OH (Spivakovsky et al., 1990; Prinn et al., 1995; Krol et al., 1998; Montzka et al., 2000; Prinn et al., 2001; Krol et al., 2003). Other studies focused on the use of HCFCs (Prather and Spivakovsky, 1990; Kanakidou et al., 1995; Ehhalt et al., 1998; Miller et al., 1998).

Besides the use of MCF, some groups have measured the abundance of ^{14}CO, the concentration of which is mainly determined by its production from cosmogenically generated ^{14}C, by the degree of importation from the stratosphere where about 50% is formed, and by its reaction with OH. Because ^{14}CO measurements (abundance a mere 5 to 25 molecules per cm^3 STP) are elaborate and expensive, the ^{14}CO method has been applied on a small scale only (Volz et al., 1981; Brenninkmeijer et al., 1992; Mak and Southon, 1998; Tyler et al., 1999; Quay et al., 2000; Jöckel and Brenninkmeijer, 2002; Jöckel et al., 2002b).

Basically what is done in using the indirect methods (MCF, or occasionally ^{14}CO, and in the future other industrial or perhaps 'dedicated' tracers), is to verify to what degree a given model, and its corresponding OH distribution correctly simulates the behavior of a tracer. If this simulation is excellent, we have successfully tested very important aspects of the model, and it is probable that the model will do a reasonable job concerning the removal of other trace gases, e.g. methane or carbon monoxide. We could then also predict future changes of OH by knowing the future changes in the input parameters of the model.

However, thus far there seems to be considerable uncertainties about what MCF tells us, as is witnessed by the vivid debates in the literature (Butler et al., 1991; Hartley and Prinn, 1991; Spivakovsky et al., 1991; Cunnold and Prinn, 1991; Spivakovsky, 1991; Prinn and Huang, 2001; Krol et al., 2001).

The idea to assess the local OH concentration by injecting dedicated OH tracers at least on short time scales (< 1 day) has been discussed earlier (Davenport and Singh, 1987 and references therein), but has never been successfully implemented.

In a recent paper some issues related to the determination of "global average OH" have been explored (Jöckel et al., 2002a), and briefly the following issues were raised:

1. the use of a dedicated tracer on the global scale, so that the quantitative input of tracer is undisputed
2. the use of 2 tracers of different lifetimes to partially separate the effects of transport from those of chemistry
3. the optimization of such a tracer (reaction rate constant, temperature dependence)
4. the optimization of the observation sites for following the decay of the tracer
5. the possibility of deriving "global average OH", independent of a chemistry-transport model

At the IGAC/CACGP meeting in Crete, September 2002, preliminary discussions were held concerning steps to increase our knowledge to derive the global average oxidation efficiency ("global average OH") and its potential trend. As a result of these discussions it was proposed to develop an IGAC activity 'IGAC-GHOST' to optimize progress. IGAC-GHOST is an integrated initiative that is global in scope and cuts across many disciplines such as modeling, ultra-sensitive analytical methods, synthesis of idealized chemicals, and the necessary kinetic and physical property determinations including toxity.

Proposed Tasks

The following questions should be addressed:

- Which properties of the global OH abundance/distribution have to be known and for what reason? (spatio-temporal distribution, total abundance, trends, variability, time scale)
- How variable is the global OH distribution?
- How and to what degree do natural processes (e.g. El Niño) and man made disturbances perturb the global OH distribution? Can these perturbations be observed?
- What are the benefits and limitations of tracer methods?
    - What can tracer methods actually tell us about the OH distribution?
    - What is the relationship between the effective tracer lifetime and global OH distribution?
    - How sensitive are tracer methods to the boundary conditions?
    - Which information is needed for scaling tracer lifetimes of different tracers?

- Which spatio-temporal averaging of the OH distribution is implied in tracer methods?
- Which additional information can be gained by using multiple tracers?
- How well can dynamical and chemical effects be distinguished from observations of tracer abundances?
- What are the fundamental limitations resulting from the lack of information? (How) can the spatio-temporal OH distribution be re-constructed from a limited number of observations?

- What are the benefits and limitations of in-situ methods; how can in-situ measurements be used to complement the global tracer methods?
- Can a "global atmospheric oxidation efficiency" be defined unambiguously as an intrinsic property of the atmosphere, and what is its relation to the OH distribution?

In using tracers, two approaches can be distinguished:

1. existing natural and industrial tracers (i.e.,"tracers of opportunity")
    - What are the largest uncertainties which limit the quantification of the global OH abundance?
    - With what accuracy can emission estimates be established?
    - Which tracers can be used for probing which property of the global OH abundance?
    - What is the optimal sampling strategy to gain maximum information?

    (Note: Much of this is already ongoing!)

2. dedicated tracers (tailor-made)
    - What property of the OH abundance/distribution can be addressed by the use of dedicated tracers (time scale, spatial scale)
    - Which are the properties of the 'ideal' tracer(s) (pressure-, temperature- dependence of the reaction coefficient, additional sinks (ocean, photolysis, soil, chemistry, ...))? Which of these properties can be designed as 'real' tracers?
    - What is the optimal sampling strategy to gain maximum information?

We suggest the following questions to be considered:

1. Theoretical investigations, e.g., Computer Aided Gedanken Experiments (CAGEs) of dedicated tracers to answer the following questions:
    - Are tracer method 1 (tracers of opportunity) and/or 2 (dedicated tracers) feasible to measure the required properties of the global OH distribution.
    - Which tracers are best suited?
    - What can be gained by using multiple tracers of different lifetimes / properties?
    - What is the optimal release strategy to gain maximum information?
    - What is the optimal sampling strategy to gain maximum information?
    - How can the spatio-temporal OH abundance/ distribution be reconstructed from tracer observations?
    - What can we learn from applying statistical methods (e.g. lifetime versus variability)?
    - Advanced inversion techniques: What are the limitations?
    - 3D global atmospheric models: What are the largest uncertainties?
    - The issue of lacking information: How robust are the results of the 'reconstruction methods'? Which additional information can profitably be added? How sensitive are the results to uncertainties of this additional information?
    - Is it possible to trace accurately the uncertainties of the various methods?
    - Can systematic errors be investigated?

2. If the outcome of 1. is favorable to perform a real, dedicated tracer experiment:
    - Which tracer compounds can be used?
    - What are the necessary detection limits for reasonable tracer release rates?
    - Which measurement techniques are available?
    - Which observational accuracy/precision is needed?
    - Cost calculations
    - Where and how to release the tracers?
    - Where and how to monitor the tracer decay?
    - Execution of dedicated tracer experiments

We further suggest an approach starting from an 'ideal' world, i.e., addressing the fundamental issues (e.g. lack of information, sampling strategy, etc.), passing successively over to more and more 'realistic' conditions, i.e., addressing at the end also the practical issues (e.g. tracer mass, cost, measurement technique, etc.). This allows a complete trace of uncertainties and limitations of the method:

1. Feasibility of the tracer method: General considerations and limitations
2. Additional information: How robust are model / inversion results; what are the limitations
3. Design of an 'optimal experiment' in an 'ideal world'
4. Transition from the 'ideal world' to the 'real world'

For a start, we suggest the following Computer Aided Gedanken Experiment (CAGE):

1. A 3D atmospheric model is used to generate 'pseudo-tracer observations' at a number of sites with
   perfectly known rate coefficient of OH with the tracer
   complete knowledge of emitted tracer mass
   OH as the only sink of the tracer

2. Reconstruction methods' are applied to the 'pseudo-observations' in order to retrieve global average information about the original 3D OH distribution.

3. Comparison of the results (retrieved information) with the original 3D OH distribution: Differences between original and reconstructed OH are due to the lack of information from a limited number of sites and uncertainties of the additional information used for the various reconstruction methods.

4. Model inter-comparison: Repetition of 3., using different chemistry-transport models (CTMs) and general circulation models (GCMs) using the same 3D OH distribution.

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Tropical Tropospheric Ozone: A Perspective on Photochemical and Dynamical Interactions from Observations in the Past Five Years

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Background: Chemistry and Dynamics in Tropical Tropospheric Ozone

For many years ozone was regarded as a passive tracer in the troposphere, in balance between a stratospheric source and destruction at the surface. With the realization that free-radical chemical reactions among trace gases emitted through human activities ("ozone precursors," NO, CO, hydrocarbons) can lead to ozone formation, attention was directed at photochemical sources of ozone. To complicate matters, note that various natural processes also produce ozone precursors, e.g. vegetation releases fast-reacting hydrocarbons; soils and lightning release nitric oxide.

In the tropics, field experiments and satellite data of the 1980's [Fishman et al., 1986] emphasized pollution sources of ozone. Causes of pollution include urban activities in developing countries and biomass fires. The latter are natural or related to agriculture, domestic cooking and heating, or to deforestation. Lightning production of NO is also thought to be a significant ozone source because the tropics is the region of most concentrated lightning on earth. A series of field campaigns in the 1990's (some under the auspices of IGAC BIBEX), confirmed the importance of biomass burning sources, lightning and the ubiquity of ozone pollution throughout the tropics.

In 1984 and again a decade later, global plumes of carbon monoxide were measured from space on the Shuttle MAPS instrument (Reichle et al., 1990; Pougatchev et al., 1999). The lifetime of each pollutant is sufficiently long (3-6 weeks for free tropospheric ozone, several months for CO) that long-range transport (thousands of km) can occur (Chatfield et al., 1998). The ubiquity of ozone pollution layers as surveyed by aircraft over the remote Pacific was pointed out by Newell et al. (1999) In general, the thin layers of elevated ozone alternated with cleaner background amounts of ozone (5-20 ppbv), occasionally < 5 ppbv as was discovered in the late 1970's (Routhier et al., 1980).

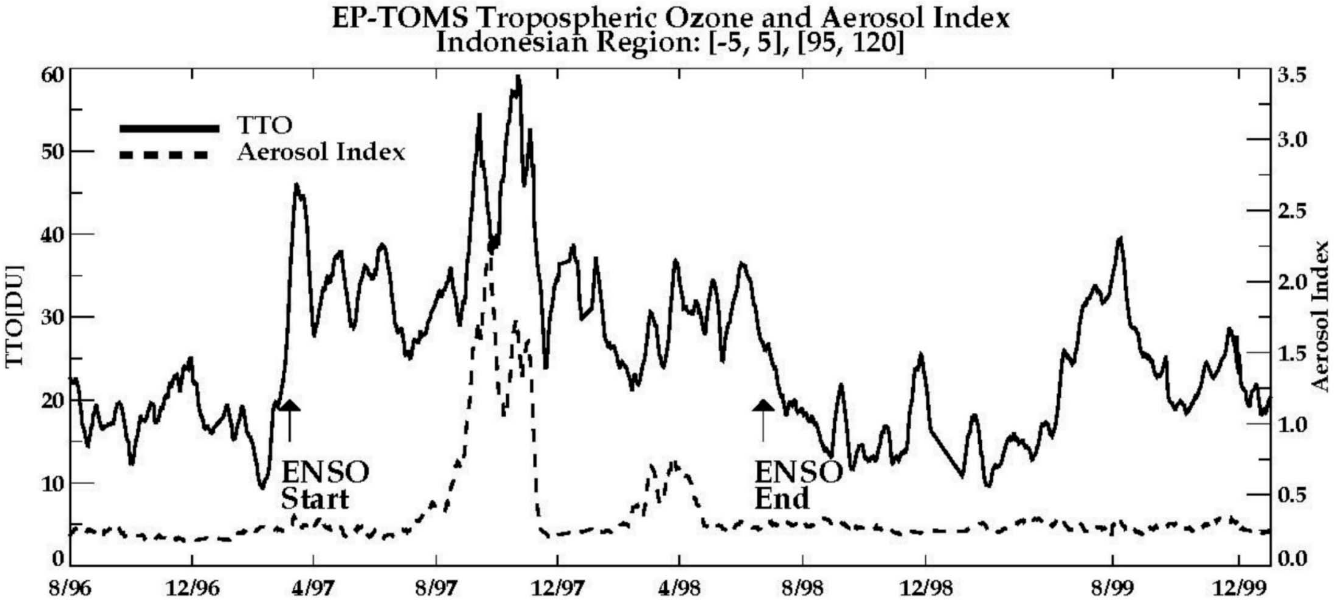

Figure 1 - Time-series of tropospheric ozone column (solid) and absorbing aerosols (dashed, for smoke from biomass fires) as measured from Earth-Probe/TOMS over the Indonesian region [Thompson et al., 2001].

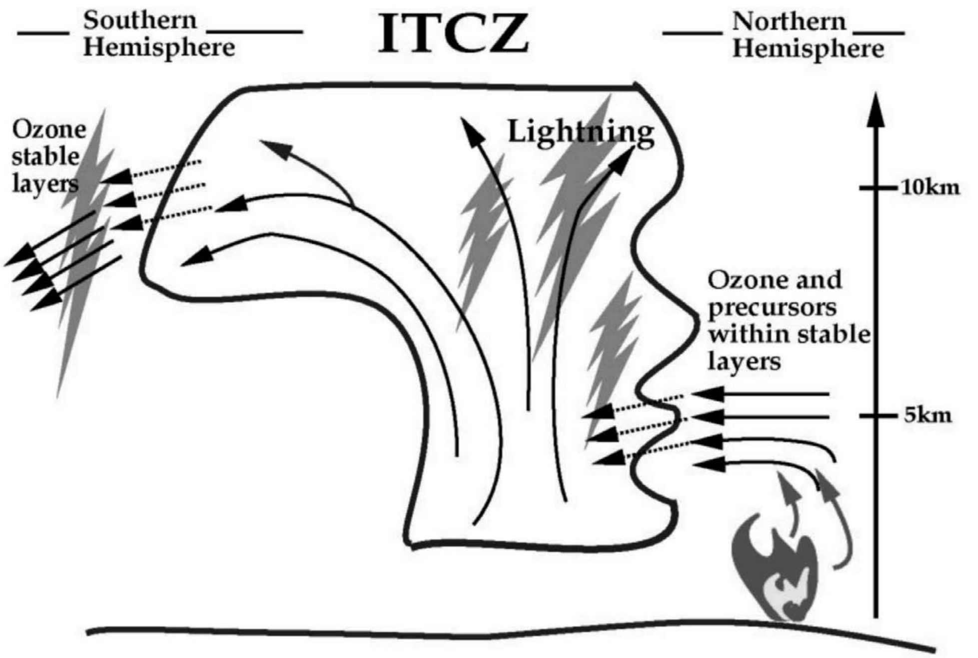

Figure 2 - Mechanisms interacting to produce the tropical Atlantic ozone paradox (Thompson et al., 2000). Pollution ozone and ozone precursors from north of the ITCZ are entrained into convection at low levels, transported upward and redistributed on either side of the ITCZ. See also Edwards et al. (2003) and Jenkins et al. (2003).

Shipboard studies of ozone and ozone precursors in the tropical Pacific (Thompson et al., 1993) demonstrated net photochemical loss of surface ozone. In convectively active regions, low ozone at the surface is transported rapidly upward, leading to low column ozone amounts and the pockets of low ozone observed from aircraft and sondes (Kley et al., 1996).

Even as evidence for photochemical control of ozone was accumulating in regions affected by human activity, closer examination of the data pointed to dynamical impacts. For example, in southern Africa, where biomass burning is a major contributor to ozone formation, recirculation of extremely stable layers (Cosijn and Tyson, 1996) is a decisive factor in the accumulation of ozone over that continent and the adjacent oceans (Thompson et al., 1996). Analysis of the satellite tropospheric ozone record since 1980 (Thompson and Hudson, 1999) shows photochemically-induced variations as biomass burning patterns are modified by drought associated with El-Niño-Southern Oscillation (ENSO) events. El-Niño episodes also alter patterns of convection, leading to perturbed tropospheric ozone in non-burning regions. The TROPOZ aircraft sampling in 1991 detected ozone and other trace gases from biomass fires crossing the ITCZ (Intertropical Convergence Zone; Jonquières and Marenco, 1998).

Recent Examples of Chemical-Dynamical Interactions Affecting Ozone

Satellite View of El-Niño-Southern Oscillation Interactions. In Figure 1 a time history of tropospheric column ozone, from the Earth-Probe TOMS instrument sampling over the Indonesian maritime continent, reveals the highest ozone resulting from fires that erupted in the wake of the 1997 ENSO (Thompson et al., 2001). The TOMS absorbing aerosol time-series (a proxy for smoke from biomass fires) is also illustrated. The ozone evolution reveals two sharp increases and only the second one is due to the fires (increased smoke between August and November 1997). The first increase occurred in March 1997 at the onset of the El Niño when a shift in Indian and Pacific Ocean temperature gradients led to intense subsidence and an increased ozone column. Thus, the earlier response to the ENSO was associated with perturbed regional dynamics.

Evidence from Ozone Soundings. The location of the enhanced ozone (above 8 km prior to the burning, 3-5 km ozone maxima in early September 1997) over Indonesia during the ENSO period was detected in sondes launched at Java (Fujiwara et al., 1999). Complexity in chemical and dynamical interactions in tropical ozone has been identified in other sets of ozone soundings. A phenomenon characterized as the “tropical Atlantic ozone paradox” (Thompson et al., 2000) was discovered during an oceano-

Figure 3 - Location of ozone sounding stations in the SHADOZ network (Thompson et al., 2003a,b)

graphic cruise in early 1999. The paradox refers to the persistent appearance of more tropospheric ozone south of the ITCZ during the time of year (December-January-February) when the greatest amount of biomass burning is north of the ITCZ. The causes include north-to-south inter-hemispheric transport of pollution through interaction with convection, subsidence and lightning in the southern hemisphere, as illustrated in Figure 2. The mechanisms are explored in greater detail using satellite data and meteorological analyses (Edwards et al., 2003; Jenkins et al., 2003).

Insights into Tropical Ozone from SHADOZ Soundings. The above examples show the way in which multiple chemical and dynamical factors affect tropical tropospheric ozone. Further insights are gained by examining profiles from a tropical ozone sounding network, the SHADOZ (Southern Hemisphere Additional Ozonesondes) project (Thompson et al., 2003a). Through comprehensive longitudinal coverage (as shown in Figure 3) and frequent launches, it is possible to examine seasonality, week-to-week variability and differences in ozone from station-to-station. Presently nearly 2000 ozone, temperature and relative humidity profiles from SHADOZ are available to the community at < Most of the profiles include the stratospheric maximum (~25 km) because the balloon-borne sondes normally reach 7 hPa pressure (Thompson et al., 2003b)

1. Zonal Wave-One in Tropospheric Ozone

A feature that can be studied with SHADOZ data is the zonal distribution of ozone. As noted by Shiotani (1992), a greater thickness of ozone over the Atlantic relative to the Pacific leads to a roughly wave-one pattern in the column amount of total ozone. This discovery, which was made with TOMS satellite data, led to debate over whether the "excess" ozone over the Atlantic is concentrated in the stratosphere, the troposphere, or both. Satellite data are not sufficiently precise to determine whether or not the wave-one is the lower stratosphere. SHADOZ sonde data show an absence of a wave pattern in that region. However, when the ozone profiles are viewed zonally, a statistically significant wave-one is observed in total and troposphere ozone [Thompson et al., 2003a]. The ozone cross-section (Figure 4) shows the vertical and longitudinal structure of the tropospheric wave. A broader and lower tropopause layer (the so-called "tropical tropopause layer" or TTL) is one contributor to the greater concentration of ozone over the Atlantic. Although the thickness and location of the TTL varies over the course of a year, the general appearance of the ozone zonal structure is always similar to the March-April-May view (Figure 4). The wave-one feature may explain the northern hemisphere-southern hemisphere gradient in tropospheric ozone that gives rise to the "paradox" feature. Satellite observations (Thompson and Hudson, 1999) suggest that at all times of year southern tropical Atlantic tropospheric ozone is greater than over the northern tropical Atlantic.

A second contribution to the wave-one ozone is subsidence over the Atlantic, that causes the ozone column to be denser than over the Pacific, where convection leads to a thinner ozone column amount. This contrast reflects the atmospheric general circulation. Photochemical contributions to the wave feature include lightning, biomass burning, both of which are more concentrated over South America, Africa and the south Atlantic between than they are over the Pacific.

The sole northern tropical station in the SHADOZ network is in Surinam (Figure 3). Peters et al. (2003) show that ozone seasonality at that location is distinct from the closest southern hemisphere stations because transport patterns and the location of the ITCZ subject Surinam to different influences.

2. Variability - Week-to-week, Seasonal, Interannual

The wave-one phenomenon illustrates the large scale dynamical impact on tropospheric ozone distributions in the southern tropics. When ozone data are examined at individual stations, meteorologically related short-term variability is the dominant feature. The SHADOZ stations are remote from strong sources, so the highest ozone concentrations due to pollution usually occur in the free troposphere. Convection tends to bring clean surface air into the middle troposphere. In all cases, pollution episodes alternate with nearly pristine conditions, often on a week-to-week basis (Thompson et al, 2003a).

A seasonality in tropospheric ozone is normally defined

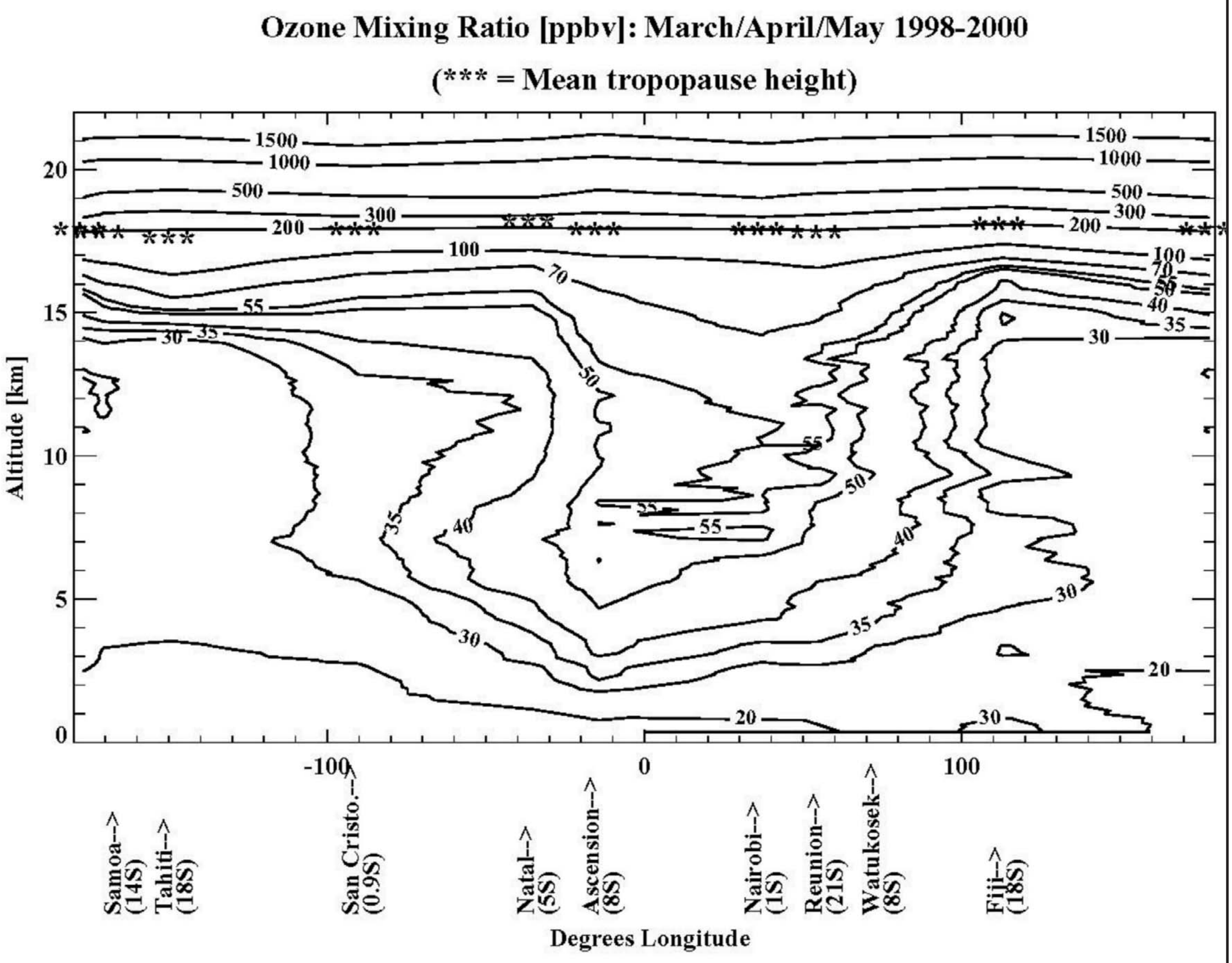

Figure 4 - Cross-sectional view of mean ozone mixing ratio in March-April-May taken from sondes at the stations indicated along the abscissa. Tropopause denoted by stars. The greater concentration of ozone over the Atlantic relative to the Pacific is responsible for the wave-one pattern first detected from satellite.

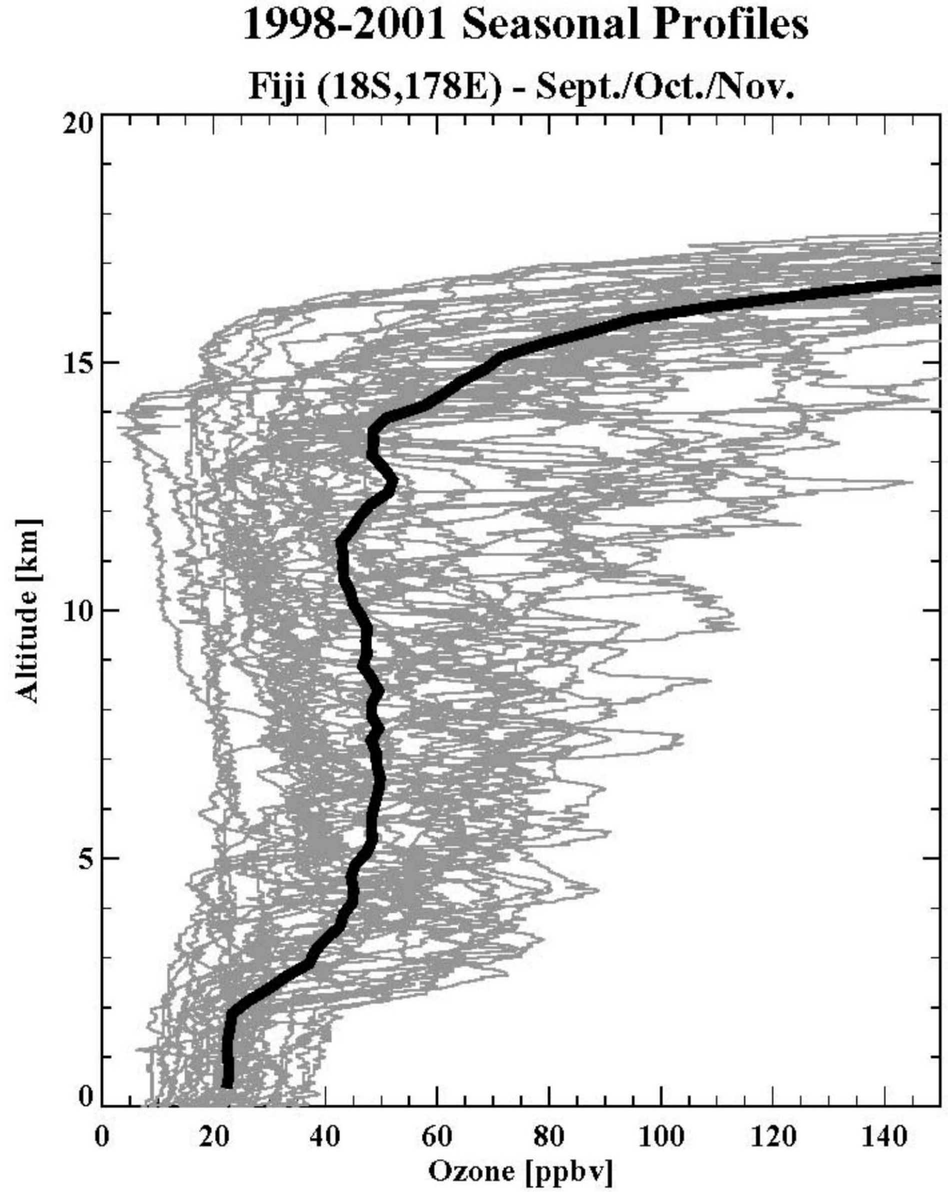

Figure 5 - Seasonal mean ozone profile below 20 km with all individual soundings taken in September-October-November (1998-2001) at Fiji. Note the large variability in the soundings.

in terms of a mean. Tropospheric ozone is a maximum in September-October-November (Figure 5) and a minimum in March-April-May. However, when the individual profiles are compared to the seasonal average, the variability is so extreme that the mean has little statistical significance. A cluster method of classifying tropical tropospheric ozone has shown that distinct distributions of profiles are associated with different synoptic conditions (Diab et al., 2003). Classification may be a better way of developing tropospheric ozone climatologies for remote sensing applications and determination of tropospheric ozone trends. A satellite retrieval of ozone in the lower troposphere may be compromised by the discrepancy between the SHADOZ observations and the simple climatological profile employed in a typical algorithm.

Summary

Observations of tropospheric ozone in the tropics in the past five years have been greatly enhanced by satellite measurements, aircraft and ground measurements and by more than 1600 ozone profiles from the SHADOZ network. We have gained insights into the complexity of dynamical and photochemical influences through a view from space, from detailed soundings, and from ancillary data that give information about mechanisms. The variability of tropospheric ozone at remote stations is surprisingly high, reflecting localized short-term meteorological shifts within a generally stable environment. The structure of the zonal wave-one, the tropical Atlantic ozone “paradox,” and El-Niño influences on ozone variability are examples of the decisive role meteorological influences play in tropical tropospheric ozone.

Further progress in evaluating processes affecting ozone and budgets of this and related trace gases will require models of various scales. Although the data caution against oversimplified approaches to ozone climatologies, today's models are challenged to simulate the variability captured by recent tropical observations.

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Composition of Asian Deposition (CAD): A Task Within the IGAC DEBITS Activity

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One of the original tasks of IGAC (Galbally, 1989) was entitled "Composition and Acidity of Asian Precipitation" (CAAP), with the objectives:

1) to quantify the wet deposition of S, N, C, P and sea-salt species, and
2) to assess the state of rainwater acidity in south and south-east Asia.

The prime motivation was a concern that rapidly increasing emissions of S and N compounds in south and south-east Asian countries could create acid deposition and other regional pollution problems (Rodhe and Herrera, 1988). At that time the number of regionally representative observations of the chemical composition of precipitation was very limited (to a large degree this is still true).

Until 2000 the task was coordinated by Greg Ayers and Henning Rodhe. At this time the focus was shifted by de-emphasizing the rainwater acidity issue and by expanding the goal to include dry deposition. As a consequence the task was given its new name, CAD, (composition of Asian Deposition) and the leadership was taken up by Leong Chow Peng from Malaysia and Rajasekhar Bala from Singapore.

CAAP/CAD has operated as a rather loosely coordinated network, primarily of observational activities, but supplemented more recently by modeling studies. In parallel with well-focused national and bi-national measurement programs, mainly in India, Thailand, Malaysia, Singapore and Indonesia, a most important component of CAAP/CAD has been the convening of workshops, the last one held in Kuala Lumpur in November 2002. At these workshops the results of the various measurement programs have been presented and issues of common concern discussed. Great efforts have been made to assure the quality of the data and their representativeness for regions rather than just for urban situations. An important component of technology transfer/capacity building has also prevailed throughout the lifetime of the task.

The backbone of CAAP/CAD has been, and still is, precipitation chemistry measurements. In recent years several of the observational stations have included measurement of the gases SO_2, NO_2 and NH_3, (using passive samplers, c.f. separate article by Ferm and Carmichael) to enable dry deposition of these gases to be estimated. At a few sites measurements are also made of aerosol particles, separated into sub-micrometer and super-micrometer sizes.

A strong commitment to publication has seen most results of the CAAP/CAD studies reported in the open literature; a selection of these papers is given below. Some of the highlights are summarized here.

- A significant number of papers documenting the state of the regional environment in terms of chemical gradients of acidity and acidic substances.
- Identification of areas of very high acidic deposition (in Malaysia and in Indonesia) (Ayers et al., 2002; Gillett et al., 2000).
- Assessment of the impact of Indonesian smoke haze episodes on regional air quality (Balasubramanian et al., 1999).
- Identification of areas where calcium carbonate and ammonia were important sources of alkalinity in rainwater (e.g. India: Pillai et al., 2001 and in Thailand: Granat et al., 1996).
- To the extent that ecosytems are nitrogen saturated, soils in regions with high ammonia deposition (e.g. northern India) may be receiving a substantial input of acidity even though the pH of rainwater exceeds 5.0 most of the time (Granat et al., 2001).
- Identification of high levels of organic acidity in rainfall throughout tropical regions, and the role played by these acids in changing apparent rainfall composition after collection (Zhung and Balasubramanian, 2001)).
- Characterisation of the relative roles of S and N in various regions, related to regional source balance.

In addition, CAAP/CAD has provided a legacy that includes a modest network of people within S and SE Asia who are now knowledgeable about reactive atmospheric chemistry and modern measurement techniques as it relates to sources and sinks of anthropogenic S and N emissions. Several of these people are now providing advice to governments on these matters, and are also now included in international networks such that they have access to the latest scientific knowledge and are more and more being included in regional, international collaborative experiments and environmental assessments.

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SCIAMACHY on ENVISAT: Some Highlights from the First Year in Orbit

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Introduction

SCIAMACHY is a Greek word, which means chasing or hunting shadows, in the sense of doing an impossible task. In spite of this and in addition, SCIAMACHY (SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY) is also an innovative and novel Earth observation experiment successfully making measurements from the European environmental research satellite ENVISAT operated by ESA. SCIAMACHY is a national contribution to ENVISAT, being funded by the space agencies of Germany, The Netherlands and Belgium. The main objective of ENVISAT is the investigation and monitoring of the Earth's environment from the surface to the mesosphere. Using a variety of instruments, it will determine the state and provide a health check of the Earth-Atmosphere System. ENVISAT was launched successfully by ESA in March 2002, comprises ESA and European experiments and has an intended minimum operational lifetime of five years. It has ten instruments on board, which make a variety of different observations of our environment. ENVISAT flies in a sun synchronous polar orbit in 800 km height, having an equator crossing time of 10.00 am and an equivalent ground speed of ~7 km^{-1}. Within the ENVISAT atmospheric chemistry mission (SCIAMACHY, GOMOS, MIPAS), SCIAMACHY aims to deliver important and relevant data about the changing composition of the atmosphere from the troposphere up to the mesosphere from the local to the global scale. Its unique role aboard ENVISAT is to provide measurements, which yield unambiguously the composition of trace constituents within the troposphere down to the boundary layer under cloud free conditions. In addition, the combination of SCIAMACHY observations with those of MERIS, AATSR and MIPAS provides some unique synergistic scientific opportunities for earth observation.

SCIAMACHY's Mission

SCIAMACHY was conceived end of the 1980's to improve our knowledge and understanding of a variety of issues of importance for the chemistry and physics of the Earth's atmosphere (troposphere, stratosphere and mesosphere) and potential changes resulting from either increasing anthropogenic activity or the variability of natural phenomena (Burrows et al., 1988). Topics of relevance for SCIAMACHY are:

- tropospheric pollution arising from industrial activity and biomass burning
- troposphere - stratosphere exchange processes
- stratospheric ozone chemistry focusing on the development of the global ozone layer
- mesospheric chemistry and dynamics
- solar variability and special events such as volcanic eruptions, and related regional and globa phenomena.

The SCIAMACHY instrument is a spectrometer designed to measure sunlight transmitted, reflected and scattered by the Earth's atmosphere or surface in the ultraviolet, visible and near infrared wavelength region (214 nm - 2380 nm) at a moderate, channel dependent, spectral resolution (0.2 nm - 1.5 nm) (Bovensmann et al., 1999). For the majority of an orbit, SCIAMACHY measures alternately the Earthshine radiance in limb or nadir viewing geometry. Close to the terminator in the northern and southern hemispheres, the solar or lunar light transmitted through the atmosphere are observed in occultation. In addition to a complete calibration procedure, the extra-terrestrial solar irradiance and lunar radiance are determined from observations of the sun and the moon above the atmosphere. The absorption, reflection and scattering behaviour of the atmosphere and the Earth's surface is inferred from a comparison of Earthshine radiance and solar irradiance. Appropriate mathematical inversion of the ratio of Earthshine radiance and solar irradiance yields information about the amounts and distribution of important atmospheric constituents (see Figure 1) and the spectral reflectance (or albedo) of the Earth's surface. GOME, a small scale version of SCIAMACHY flying on ERS-2 since 1995, also observes back scattered solar radiation but only in nadir mode and restricted to the wavelength range of 240 nm to 790 nm (Burrows et al., 1999). GOME has made 7 years of successful measurements and has been a proof of concept mission for SCIAMACHY. The extended spectral range of SCIAMACHY enables many more constituents to be measured than with GOME.

A special feature of SCIAMACHY is its ability to combine near simultaneous limb and nadir measurements. The inversion of this combination of limb and nadir measurements yields the tropospheric column amounts of the gases O_3, CO, SO_2, NO_2, BrO, CH_4, H_2O, N_2O, H_2CO and aerosol parameters.

SCIAMACHY was constructed, tested and delivered to ESA in the period from 1994 to 2000. In May of 2001 ENVISAT was successfully transported to Kourou and launched into a polar sun-synchronous orbit in March

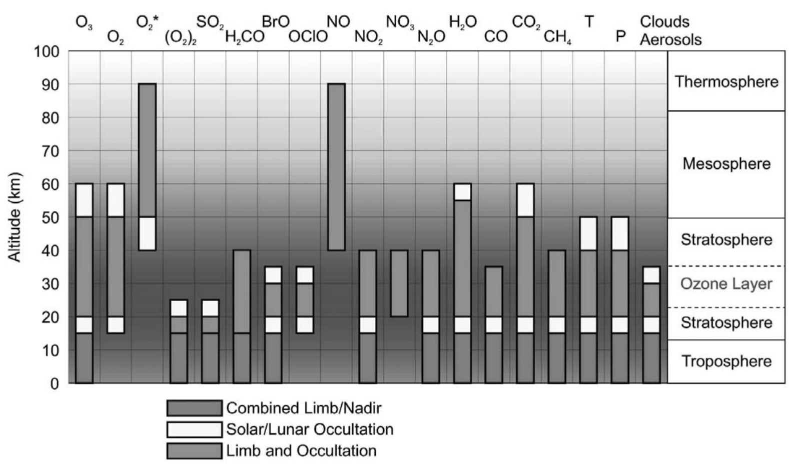

Figure 1 - Altitude ranges of atmospheric constituents targeted by SCIAMACHY. Retrieval from the occultation measurements yield information over a wider altitude range than the limb measurements, due to its higher S/N.

2002. After a few weeks of out-gassing in-orbit, SCIAMACHY was switched on successfully. A complex procedure to open the different covers protecting the light path, to check out the instrument in orbit and to tune it to the optimum in-flight performance was initiated. Solar and atmospheric spectra were already taken from the beginning of April 2002. During this so-called commissioning phase the instruments functional and optical performance was verified and instrument calibration activities were started, with the result that since end of July 2002 SCIAMACHY is fully functional. It achieves the performance expected from on-ground tests with only one exception, which results from ice formation on two of the SWIR detectors. This issue required some changes in operational planning to minimise its impact. SCIAMACHY has been performing its regular measurement program since the beginning of August 2002 just in time to be ready for validation. Two intensive validation campaigns organised by ESA and DLR were executed in late summer/autumn 2002 and winter/spring 2003. Since August 2002 the instrument is continuously and successfully performing its nominal measurement programme (limb, nadir, occultation, calibration) and over 99.5 % of all scientific measurements are working as expected.

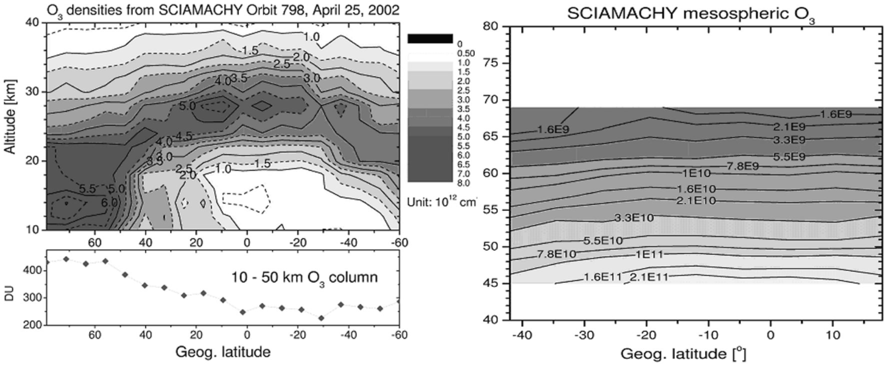

Figure 2 - Left: Preliminary upper tropospheric and stratospheric Ozone vertical profile (top) distribution and stratospheric column amount (bottom) derived from limb backscatter measurements in the spectral range of the Chappuis band of ozone and integrated column amount on April 25, 20032. Right: Preliminary upper stratospheric and mesospheric Ozone distribution, on July 3, 2002 (Orbit 1779), derived from limb backscatter measurements in the spectral range of the Hartley band of ozone..

SCIAMACHY Instrument and Observation Modes

The SCIAMACHY instrument is a passive remote sensing moderate resolution imaging spectrometer. It comprises a mirror system, a telescope, a spectrometer, and thermal and electronic sub systems. With exception of the scan mirrors and slit mechanism, all spectrometer parts within SCIAMACHY are fixed. As a result of the instrument design, spectra are recorded simultaneously from 214 nm to 1750 nm, and in two smaller windows, 1940 nm - 2040 nm and 2265 nm – 2380 nm, in the short wave infrared. The spectral and radiometric performance of the SCIAMACHY spectrometer as well as more details about the instrument are described elsewhere (Bovensmann et al., 1999). The incoming radiation enters the instrument via one of three entrances:

(i) the nadir port, which directs the radiation from the Earth's scene by the elevation mirror into a telescope (off axis parabolic mirror) and thereby focuses the beam onto the entrance slit of the spectrometer;

(ii) the limb port which is used for both atmospheric limb and solar/lunar occultation measurements. In this case the radiation is reflected by the azimuth mirror to the elevation mirror and then into the telescope,

(iii) the sub solar port, which directs solar radiation via the elevation mirror into the telescope.

In addition the instrument has on board spectral line and broad band light sources for in flight calibration, which are observed via the elevation mirror. Two diffuser plates are mounted on the back side of the elevation and azimuth mirrors to facilitate the solar observations.

Measurements of SCIAMACHY are performed in the three different viewing geometries: nadir, limb, and solar/lunar occultation. A typical orbit starts with a limb measurement of the twilit atmosphere, followed by the solar occultation measurement during sunrise over the north pole and an optimised limb-nadir sequence: lunar occultations being made where possible. All these different

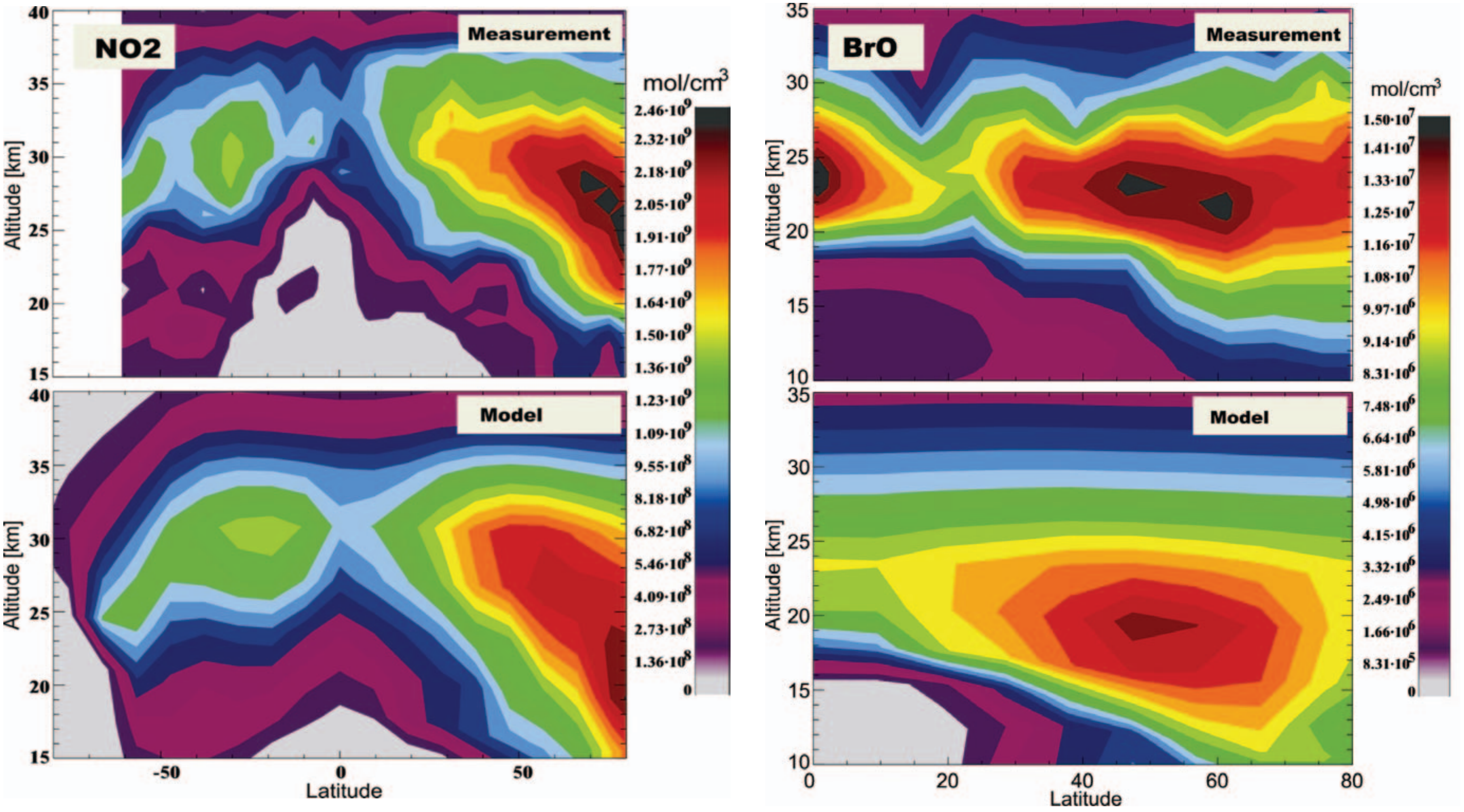

Figure 3 - Left: Preliminary global stratospheric NO_2 distribution from limb backscatter measurements (top) on August 8, 2002 (orbit 2302) compared to noontime values of a 2D climatological-photochemical model (bottom). Right: Preliminary global stratospheric BrO distribution from limb backscatter measurements (top) on August 8, 2002 (orbit 2302) compared to 2D climatological model (bottom).

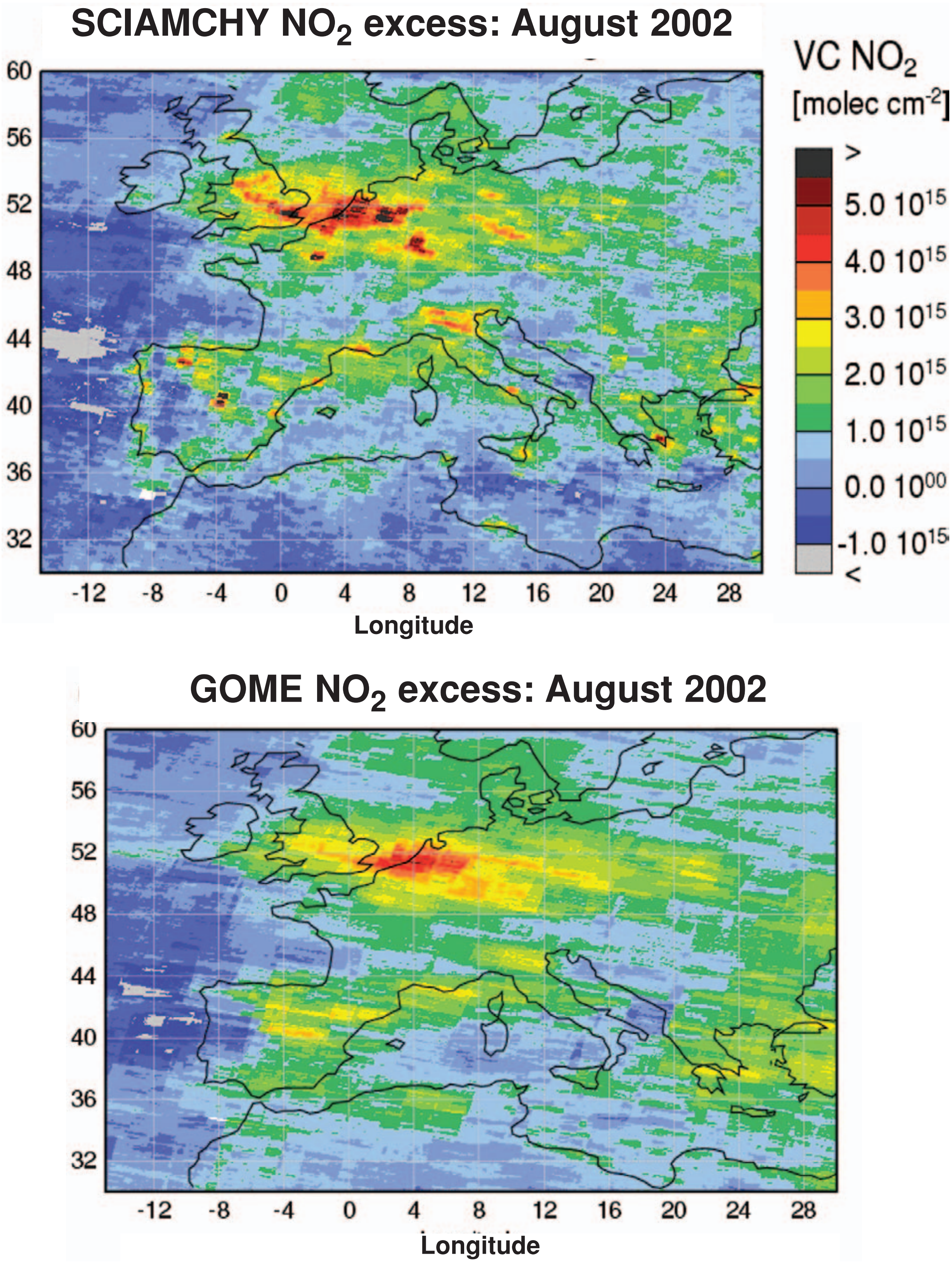

Figure 4 - Comparison of tropospheric excess column NO_2 as seen by GOME-1 on ERS-2 (spatial resolution 40 x 320 km^2) and SCIAMACHY on ENVISAT (30 x 60 km^2).

measurements, with the exception of lunar occultation, are made every orbit, i.e. 14 orbits per day.

To calibrate the Earthshine spectra, to guarantee the optical performance and to detect long term changes in the instrument throughput arising from degradation, calibration measurements are regularly performed. These include solar irradiance measurements, spectral calibration, relative radiometric calibration, and dark current measurements. The degradation of the limb and nadir mirrors is monitored by using the on board lamps, the lunar and solar observations via the mirrors and the diffuser plates. This enables the throughput of the spectrometer optics to be monitored throughout the mission lifetime. The data processing is designed to incorporate these calibration measurements and provide a dynamic update of the spectral and radiometric calibration.

First Results from Limb Measurements

In April 2002 the limb light path was opened by removing the relevant cover and first solar and limb spectra were recorded. In limb mode the spectrometer slit is projected parallel to the horizon in-flight direction tangentially to the Earth's atmosphere. In this measurement mode the limb mirror scans the atmosphere in horizontal (azimuth) direction whereas a step scan of the nadir mirror results in the vertical (elevation) scan direction from the ground to approx. 150 km. Each horizontal scan of the atmosphere in limb covers 960 km in the horizontal (across track direction). The vertical resolution is approximately 3 km. The ability of the SCIAMACHY instrument to observe the same atmospheric volume first in limb and thereafter in nadir viewing geometries within about 7 min is one of the novel features. For the dedicated limb-nadir scanning strategy and a total swath width of 960 km global coverage is achieved after 6 days at the equator. Figure 2 (left) shows an example of one of the first analysis of global upper tropospheric and stratospheric Ozone retrieved from the spectral signature of O_3 in the Chappius band around 600 nm [4]. Clearly visible is the tropopause and its typical behaviour as function of latitude.

The SCIAMACHY limb measurements also enable mesospheric ozone to be determined directly. Figure 2 shows a preliminary analysis of global upper stratospheric to mesospheric O_3 derived from the UV absorption of O_3 in the Hartley bands using wavelengths between 240 and 300 nm. A first comparison with the Canadian Middle Atmosphere Model (CMAM) data corresponding to an August mean reveals that the overall structure is well represented. Further work is required to validate the measurements.

In addition to O_3, SCIAMACHY measurements yield profiles of other important trace gases in the upper troposphere and stratosphere such as NO_2 (Eichmann et al., 2002) and BrO (see Figure 3). Especially the latter will allow now a more detailed characterisation of the global stratospheric Bromine budget.

As expected, the stratospheric profile of OClO has observed during periods of chlorine activation in the polar vortex in late winter and spring. The presence of both noctilucent clouds in the mesosphere (Von Savigny et al., 2002) and Polar Stratospheric Clouds are readily observed to be detectable by SCIAMACHY. Additional stratospheric profiles of O_3 and NO_2 were also derived from the occultation measurements.

First Results from Nadir Measurements

In June 2002 the nadir cover was opened as part of the last phase of switch on activity. In nadir mode up welling radiation from the atmospheric volume beneath the spacecraft is observed. The nadir mirror scans across the satellite track. Each full scan covers an area on ground of approximately 30 km along track by 960 km across track. By reading the data out at an appropriate rate a typical spatial resolution of 30 km by 60 km for the spectral data is achieved.

Figure 4 shows the tropospheric NO_2 amounts, derived from GOME and SCIAMACHY using the tropospheric excess or residual method averaged for August, 2002. (Richter and Burrows, 2002) The improvement of the horizontal resolution from 40 km x 320 km (GOME) to 30 km x 60 km (SCIAMACHY) is obvious. This enables unambiguously the accurate detection of the enhanced NO_2 values originating from industrialised areas (Birmingham, Manchester, Po valley etc.) and large cities (Vienna, Roma etc.) which are in comparison smoothed out or smeared over the larger ground scene in the GOME observations. It should also noted that the maximum column amounts in the SCIAMACHY measurements are roughly a factor of two higher than in the GOME data, which demonstrates the large and expected inhomogeneity of the NO_2 plumes. The good spatial resolution and the high data quality of tropospheric NO_2 measurements will yield a much improved quantification of global emissions of NO_2.

In addition to the first results on NO_2, it has already been demonstrated that the column amounts of O_3, SO_2, BrO, OClO, CH_4, CO_2 and CO (see Buchwitz et al., 2002; Brastedt et al., 2002) can be retrieved. The retrieval of the other trace gases is progressing. Furthermore, first attempts to derive cloud information (cloud top height, cloud optical thickness, effective droplet radius etc.) and aerosol parameters from nadir backscatter measurements are showing promising results

Data Products

Operational data products are defined for SCIAMACHY and ENVISAT purposes as being a regularly generated, quality controlled and archived data products. For SCIAMACHY it is planned that limb and nadir measurements will be processed operationally within the ENVISAT ground segment. SCIAMACHY operational data products are divided into two categories: the fast delivery (FD) products and the off-line (OL) products. FD products are to be generated directly after downlink at the ESA ground stations in near-real time, a few hours after the spectrum is acquired. OL products comprise a set of consolidated and fully calibrated products. The latter are to be processed off-line at the German Processing and Archiving Center (D-PAC) as part of the ENVISAT ground segment. Scientific products for process studies from lunar and solar occultation measurements as well as special scientific products from limb and nadir measurements are also planned to be generated for the atmospheric research and related communities by specific scientific groups. Currently calibration and algorithm improvements coupled with validation and an iterative systematic data analysis is in progress. Finally, to ensure a high data quality over the mission lifetime instrument performance is monitored continuously and an intensive validation campaign and activity are currently on-going.

Summary and Outlook

It has shown in the first year that global data sets of profiles and/or total column measurements of O_3, NO_2, BrO, OClO, SO_2, CO, CO_2 and CH_4 can be derived from SCIAMACHY solar backscatter measurements. On the remaining gases, aerosol and cloud parameters first progress is made. Currently algorithm improvements, validation and an iterative systematic data analysis is ongoing. SCIAMACHY has now the potential to be a unique milestone for research into the Earth-Atmosphere system. It provides a wealth of information both in its own right and in combination with the synergistic measurements from other instruments aboard ENVISAT about atmospheric composition of relevance and significance for many of the IGAC research objectives. It is intended to measure for at least five years but the mission will hopefully continue its measurements for a significantly longer period. The fact that there is already a 9 month overlap with GOME-1 data provides the opportunity to generate a consistent set of data products from GOME and SCIAMACHY nadir measurements having the potential to be extended over more than a decade. Provided SCIAMACHY is successful in meeting its objectives there is little doubt that the continuity of these measurements, incorporating technical improvements and developments, are needed. This could be made within the follow on to the ESA and EUMETSAT Metop series of platforms in the 2015.

It is also now well accepted that measurements of tropospheric constituents with higher spatial and temporal resolution are and will be needed for atmospheric and climate research as well as for operational meteorological applications in both traditional and new (e.g. numerical environmental prediction) areas (Lelieveld, 2003). A unique opportunity to achieve this are synoptic measurements from geostationary orbit (Lelieveld, 2003; Bovensmann et al., 2002). The Geostationary SCanning Imaging Absorption spectrometer (GeoSCIA) (Bovensmann et al, 2002), an evolutionary version of SCIAMACHY, proposed to ESA as a demonstration mission for post-MSG atmospheric instrumentation, aims to meet the above objective.

Acknowledgements

There are too many scientists and engineers, who have contributed to the success of SCIAMACHY, thus far to name individually. The industrial development of SCIAMACHY was managed by a joint agency team formed between the German Space Agency DLR (then DARA) and the Dutch space agency NIVR. The University of Bremen team has performed the role of Principal Investigator Institution for SCIAMACHY. The mission has been scientifically supported by scientists from BIRA-IASB, DLR, KNMI, Max Planck Institute for Chemistry Mainz, NASA, RAL, SAO, SRON, University of Heidelberg, and University of Bremen. The work at the University of Bremen was partly funded by the BMBF (FKZ 07 UFE 12/8), DLR (FKZ 50 EE 0027) and the Land Bremen.

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Links:

ENVISAT and operational data products: **http://envisat.esa.int**
SCIAMACHY "Link Center": **http://www.sciamachy.de**

The Regional Integrated Project Mediterranean

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Introduction

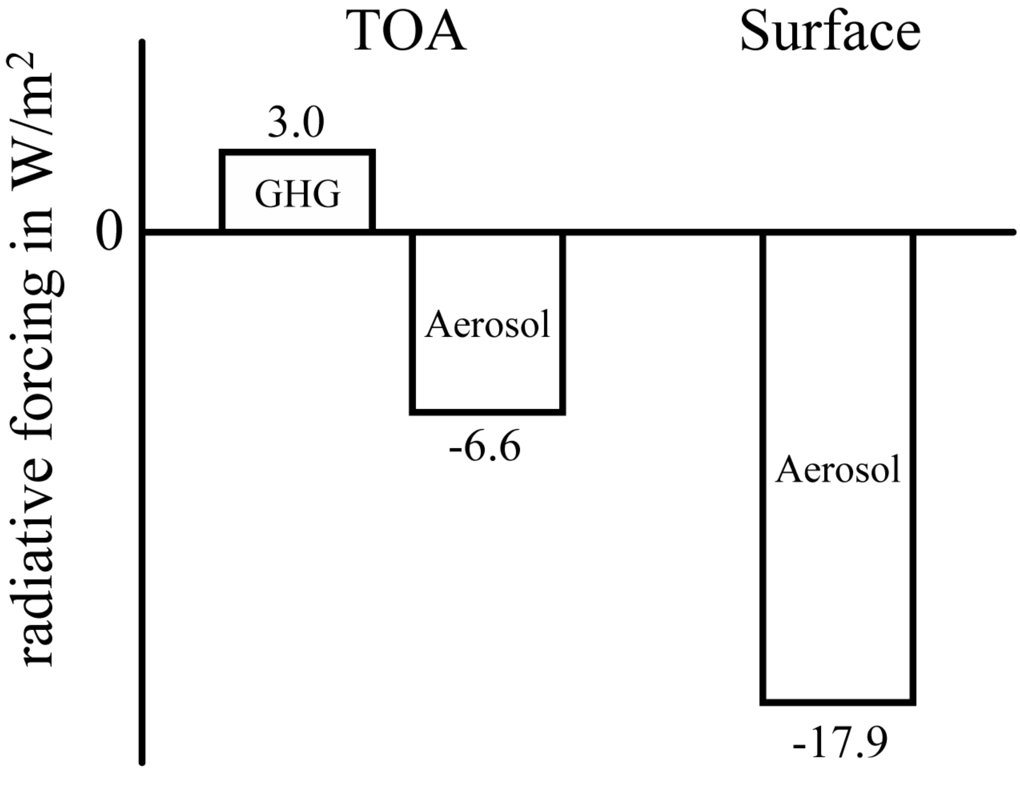
In the Mediterranean Intensive Oxidant Study (MINOS) an international team of scientists from eight countries has investigated the Mediterranean atmosphere during six weeks in July-August 2001. Measurements of the chemical composition and the radiation budget of the Mediterranean troposphere were performed both from a ground-station and with the use of aircraft. The objective was to study long-distance transport of natural and anthropogenic trace gases and aerosols and their effects on air quality and climate. The results indicate that anthropogenic emissions cause a large-scale air quality decrease and may contribute to a reduction of precipitation.

The operational base of MINOS was Crete, where a monitoring station was equipped to measure a large number of gaseous and particulate air constituents as well as solar radiation scattering and absorption. Measurement details are provided through the following website, which includes a link to the MINOS special issue of the online journal *Atmospheric Chemistry and Physics*: http://www.mpch-mainz.mpg.de/~reus/minos/. The measurement campaign was hosted by the University of Crete in Heraklion. Two aircraft, a twinjet Falcon and a King Air, performed more than 20 research flights to sample the air over the Mediterranean Sea.

Air pollution "crossroads"

The measurements give evidence of a remarkably high level of air pollution from the surface to the top of the troposphere up to15 km altitude. The strongest anthropogenic influence was observed in the lower 4 km, originating from both West and East Europe transported by the northerly flow (Lelieveld *et al*., 2002; Traub *et al*., 2003). The sources are industrial activity, traffic, forest fires, agricultural and domestic burning (Gros *et al.,* 2003; Salisbury *et al*., 2003; Xu *et al*., 2003). Especially over the eastern Mediterranean Sea biomass burning effluents from the region north of the Black Sea were abundant during the campaign (Holzinger *et al*., 2003). Since the Mediterranean region has only few clouds in summer, the solar radiation levels are high so that noxious reaction

Figure 1- Direct radiative forcing by greenhouse gases (GHG) and aerosols over the summertime Mediterranean Sea, both for the top of the atmosphere (TOA) and at the surface. The GHG effects are based on model results, that of the aerosols on measurements during MINOS.



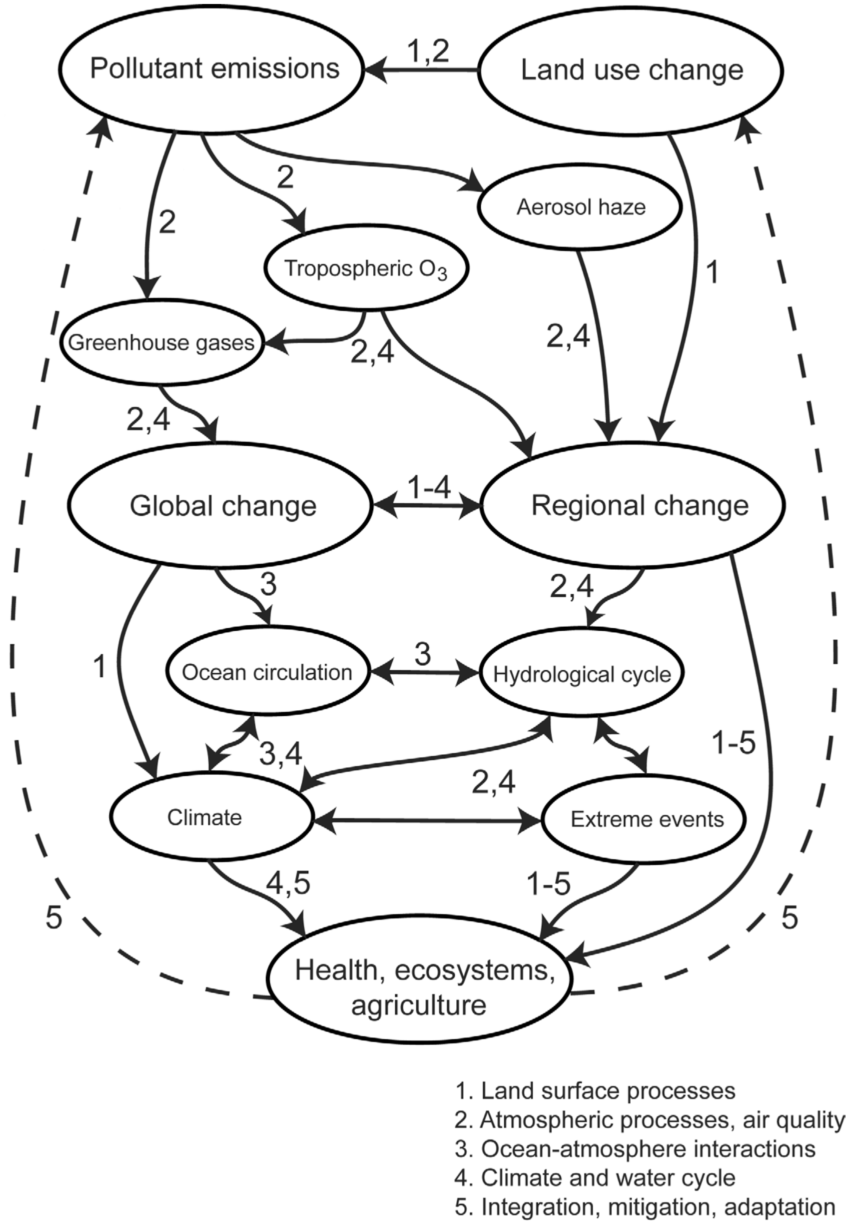


Figure 2- Schematic representation of the system forcings and responses, and how they are investigated in the 5 thematic components of ProMed. The dashed lines imply mitigation-adaptation responses by society.

products such as ozone and peroxyacetyl nitrate (PAN) are formed in photochemical smog. The oxidation efficiency of these air masses is high, with diurnal average hydroxyl concentrations of about $4.5x10^6$ radicals/cm^3 and daytime maximum levels of about $1.5\text{-}2x10^7$ radicals/cm^3 (Berresheim *et al*., 2003).

At higher altitudes, above 4 km, strong contributions from long-distance pollution transport from North America and Asia were found, for example, for carbon monoxide (CO) (Lawrence *et al.,* 2002). It is quite remarkable that about half of the mid-tropospheric CO over the Mediterranean originates from Asia and 25-30% from North America. These transports follow the prevailing westerly winds that are typical for the extra-tropics. These layers are moreover substantially affected by ozone that is mixed down from the stratosphere (Roelofs *et al.,* 2003). It appears that especially the middle troposphere in summer is influenced by stratosphere-troposphere exchange, leading to a stratospheric contribution to column O_3 in the troposphere up to 25-30%. In addition, transport of anthropogenic O_3 and its precursor gases from the USA exerts a significant influence in the free troposphere (Heland *et al.,* 2003).

In the upper troposphere, above 8 km altitude, another distinct layer can be distinguished, especially over the eastern Mediterranean, associated with high levels of reactive species such as formaldehyde (Kormann *et al.,* 2003). This is caused by anthropogenic emissions transported from South Asia, following convective lifting into the upper troposphere by thunderstorms in the Indian monsoon (Traub *et al.*, 2003). Subsequently these air parcels follow the easterly tropical jet and turn north over the eastern Mediterranean in a large upper level anticyclone. The chemical "fingerprint" of biomass burning (e.g. enhanced CH_3CN, CH_3Cl, C_2H_2), in particular by biofuel use in India as also observed during the Indian Ocean Experiment, is evident (Scheeren *et al*., 2003). From the upper troposphere over the eastern Mediterranean these species can even penetrate the lowermost stratosphere. It appears that the Mediterranean region is a preferred location for cross-tropopause exchanges, partly related to direct convective penetration of the lower stratosphere over southern Europe (Fischer *et al*., 2002; Traub *et al*., 2003).

Air quality and climate

Near the surface the air pollution has several undesirable consequences. First, the European Union eight-hourly air quality standard for ozone (53 nmol/mol) is exceeded throughout the summer in the entire Mediterranean region. High ozone concentrations are harmful for human health and ecosystems, and they also cause agricultural crop loss. Typical ozone mixing ratios in summer are 55-70 nmol/mol, and the diurnal variability is small (~10%)

(Kouvarakis *et al*., 2002; Nolle *et al*., 2002). Because the Mediterranean background O_3 levels are so high, it is difficult to control ozone in urban and industrial areas. Second, the concentrations of aerosols are high as well, affecting human health. The fine aerosol fraction (<1µm) is mainly composed of sulfate (35-40%), organics (30-35%), ammonium (10-15%) and black carbon (5-10%), mostly from fossil fuel and biomass combustion (Lelieveld *et al*., 2002; Sciare *et al*., 2003). The persistent northerly winds in summer carry large pollution loads from Europe that can deposit onto the Mediterranean Sea, which affects the water quality and contributes to eutrophication (Kouvarakis *et al*., 2001).The aerosols furthermore influence the Mediterranean atmospheric energy budget by scattering and absorbing solar radiation (Figure 1). They reduce solar radiation absorption by the sea by about 10% and they alter the heating profile of the lower troposphere (Markowicz *et al*., 2002). As a consequence, evaporation and moisture transport, in particular to North Africa and the Middle East, are suppressed. Furthermore, Rosenfeld (2000; and by personal communication) studied satellite observations, indicating important perturbations of the cloud microstructure and convection by aerosols, probably decreasing precipitation. These effects by aerosols are substantial today, even though sulfate from Europe has actually decreased in the past two decades through the abatement of acidification. Therefore, it is likely that the climate effects of the aerosols have been much larger in the past.

The radiative forcing by aerosols also influences the energy budget of the Mediterranean Sea, of which the consequences are yet poorly understood. The Mediterranean Sea is a small-scale ocean, which has the same phenomenology of large oceans, including a thermohaline circulation, showing signs of large perturbations in the 1990s (Lascaratos *et al*., 1999). It is quite conceivable that the changing energy budget and anomalous winds have influenced the ocean circulation (Tragou and Lascaratos, 2003). It is conceivable that changes in evaporation, for example, owing to changes in surface heating resulting from aerosol radiative forcing, substantially influence the Mediterranean overturning (Myers and Haines, 2002). The aerosols may thus affect several components of the regional atmosphere-ocean system and the water cycle.

Project Mediterranean: ProMed

The atmospheric forcings to the ocean, climate and water cycle do not act in isolation. Firstly, the regional effects are linked to large-scale phenomena through teleconnections, for example, with the Indian monsoon and the North Atlantic Oscillation. It is not known, however, how these system components are linked and interact under global change. Climate change scenarios nevertheless consistently predict drying of the Mediterranean region, already being under water stress. Secondly, water availability is also determined by many other factors, in particular agriculture. Even if the total amount of precipitation would remain constant, soil crust formation in dry years and heavy short-duration rainfall in other years can have dramatic effects, as indicated by anomalous weather events in the past decade (Bolle, 2003).

Thus a wide range of environmental processes and societal conditions are in many ways linked. The goal of ProMed is to obtain a better understanding of these linkages, and to improve the skill to predict how the system may be affected under climate change and human activities. The project builds upon previous projects that have focused on system components. ProMed must bring together the necessary information to help mitigate problems, or to adapt to them. Already today several Mediterranean countries need to make difficult choices how to use the limited water resources. Others have problems with the compliance to air pollution and climate change policies, which sometimes include conflicting directives.

Table 1 summarizes several of the main arguments why an *integrated project* is needed with a focus on the Mediterranean region. The project, which is presently being established, has four thematic components that primarily address biogeophysical and -chemical processes and feedback mechanisms:

1. Land surface processes;
2. Atmospheric processes and air quality;
3. Ocean-atmosphere interactions;
4. Climate and water cycle;

An additional component aims at:

5. Integration, mitigation and adaptation.

- Small-scale coupled ocean-atmosphere system
- Water resources are vulnerable and under stress
- Climate change scenarios indicate further drying
- Strong influences by long-range air pollution transport
- Large perturbations of the atmospheric energy budget
- Recent changes in weather and ocean circulation
- Environmental changes have large-scale effects
- Collaborations with North-Africa and Middle-East needed

Table 1 - Why an *integrated project* for the Mediterranean region?

The latter must support the development of societal strategies and policies. Figure 2 indicates how these five thematic components are linked to investigate the relationships between human activities, system forcings and responses. The project furthermore includes "integrating" experiments to bring together data from anchor stations, satellites, field measurement campaigns and modeling.

In addition to the environmental and societal arguments, an important scientific merit of ProMed is that the Mediterranean Basin is an excellent "natural laboratory" to investigate feedback mechanisms between the atmosphere and ocean that control the hydrological cycle and climate, in particular because the Mediterranean Sea is an "integrator" of natural and anthropogenic changes over long time periods. The Mediterranean coupled ocean-atmosphere system moreover responds relatively rapidly to atmospheric forcings, so that research in this area provides clues on how the global climate system may respond to a changing environment.

Considering the different levels of knowledge and skills in the region, capacity building will be prerequisite, to train young scientists, develop a quality assurance and control program associated with the regional network of anchor stations, and to help answer questions of decision makers and stakeholders. The project must moreover organize networks that further the communication between the disciplines and activities, and provide links with (inter)national meteorological and hydrological services and international programs. Although it is a major challenge to establish integrated projects such as ProMed, it is an inevitable next step in environmental science to expand multi-disciplinary collaborations, and bring the results of atmospheric and climate change research to the *regional* level at which the questions are asked by science and society.

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Comparison of Regional Aerosol Chemical and Optical Properties from the European, Asian, and North American Plumes

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Introduction

Global distributions of aerosol optical depth (AOD) derived from satellite observations of backscattered radiation indicate persistent seasonal aerosol plumes downwind of many continental regions (Husar et al., 1997). In March through May a plume extends from Asia eastward across the North Pacific Ocean. During the winter monsoon period (December through April), a plume is located off the southwest coast of India over the Indian Ocean. In the summer months of June through August an aerosol plume originates from the mid-Atlantic states of the United States and extends across the North Atlantic Ocean. Likewise, in the spring and summer months a plume is transported from Europe to the North Atlantic Ocean. Satellite observations reveal the seasonal regularity and relative magnitude of regional plumes in terms of backscattered radiation but are not able to provide information about aerosol chemical composition, size distributions, optical properties, or mass loading in the boundary layer. Such information can be obtained from *in situ* measurements and is required to fully understand the regional climate and health effects of the haze. Recent field campaigns have characterized aerosol properties in these plumes to better understand their impacts on regional atmospheric chemistry and climate. The first Aerosol Characterization Experiment (ACE 1) purposefully steered clear of any continental plumes in order to characterize the "background" aerosol upon which anthropogenic perturbations could be imposed. Following ACE 1, ACE 2 focused on the European plume, INDOEX (Indian Ocean Experiment) on the plume emanating from the Indian subcontinent, ACE Asia on the Asian plume, and TARFOX (Tropospheric Aerosol Radiative Forcing Observational Experiment) and NEAQS (New England Air Quality Study) on the eastern U.S. plume. Table 1 lists the details of these experiments.

Results from these experiments have been reported or soon will be reported in a variety of peer-reviewed journals. We will not summarize already-reported results here but rather will use (almost exclusively) the data set collected by NOAA PMEL to compare regional aerosol chemical and optical properties. Our approach in these experiments has been twofold. First, sampling has been done with standardized protocols so that sampling biases are minimized and data from the different regions are directly comparable. Second, we have collected over-determined data sets so that a measured property such as aerosol mass or light extinction can be compared to mass or extinction calculated from an independent set of measurements. Hence, we can test for internal consistency in our data sets, determine and quantify sources of uncertainty in the measurement and model methods, and objectively assess how well we understand the regional aerosol. Our goal in this short article is to point out a few of the intriguing findings from these regional experiments; and, based on closure studies using the over-determined data sets, some of the successes and some of the areas where improvements are needed in measurement and modeling capabilities.

Methodology

The regional comparisons shown in Figures 1 and 2 and discussed throughout the text are based on data collected during ACE 1, ACE 2, INDOEX, ACE Asia, and NEAQS onboard a variety of ships using identical inlets, sampling humidities, aerosol samplers, and analysis methods (Quinn et al., 2002; Quinn and Bates, 2003). Even though different sampling protocols were used in TARFOX (Hegg et al., 1997; Novakov et al., 1997), we include it in these comparisons since it took place in the vicinity of NEAQS and contributes to the eastern U.S. plume data set. Since TARFOX was an aircraft study we include only data collected at altitudes less than or equal to 300 m.

The samples collected during each of these experiments were categorized according to air mass back trajectories (Draxler, 1992). "Marine" refers to sampled air masses that had not been in contact with land for 5 or more days prior to reaching the ship. "Continental", "Polluted", and "Polluted with Dust" refer to sampled air masses that had recent (< 3 days) contact with continental regions with known sources of pollution and/or dust aerosol.

The degree of variability presented here reflects only that which was measured during these short-lived campaigns. However, results from the 1999 INDOEX field campaign are expected to be representative of other years based on satellite data for 1996 to 2000 (Ramanathan et al., 2001a). Seasonally (January to March) and spatially (0∞ to 30∞N) averaged AOD for these 5 years varied by less than 10% of the 1999 values. Similarly, the summer mean values of AOD measured at Greenbelt, MD varied by less than 15% between 1993 and 1996 indicating that the 1996 TARFOX values were representative of other years (Remer et al., 1999). In addition, the regional mean AOD measured during NEAQS was within 18% of regional mean summer values derived from 5 Aeronet sites along the mid-Atlantic coast in 1993 and 1996 (Remer et al., 1999). Dust storms from northern China and Mongolia have increased notice-

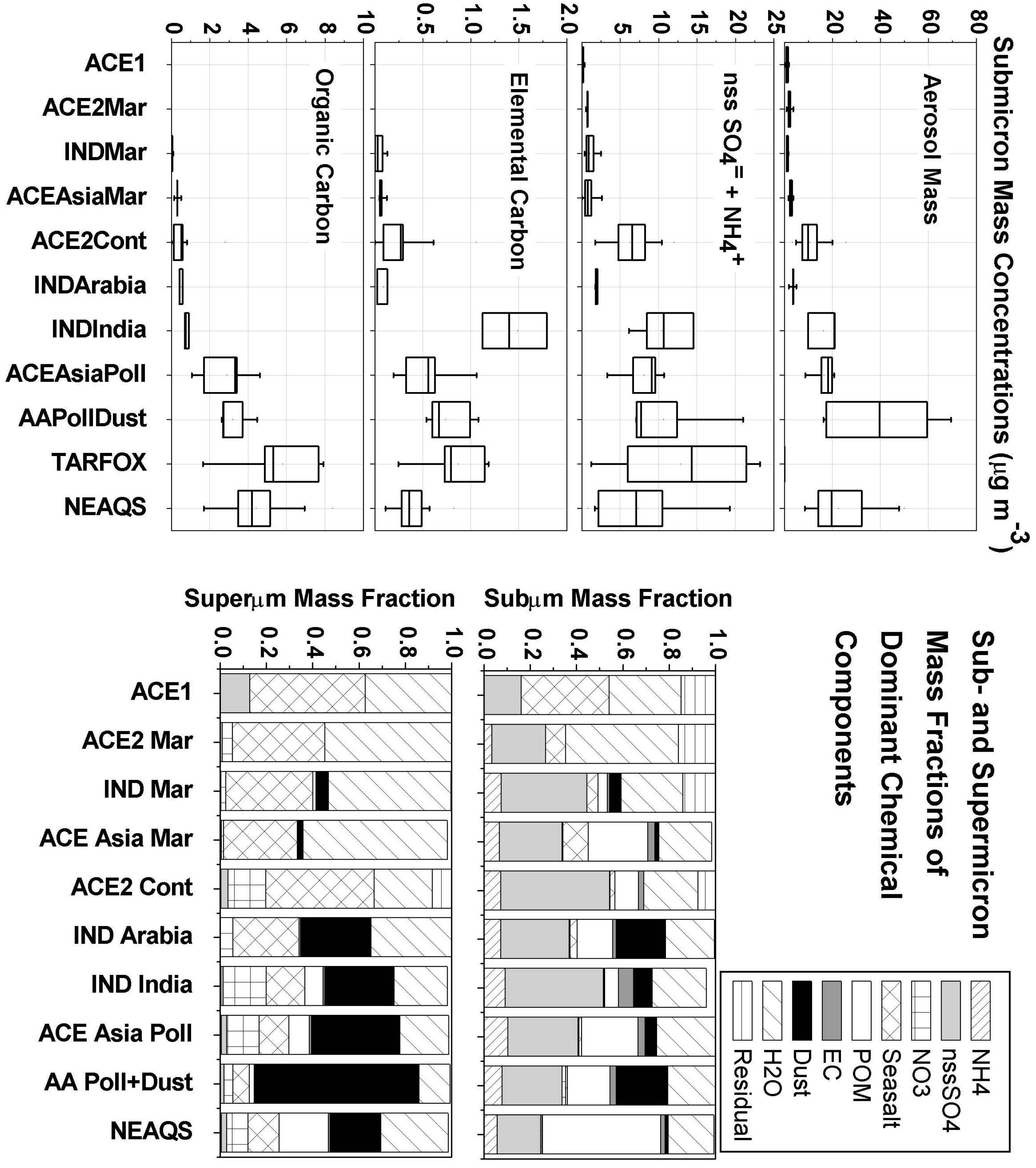

Figure 1 - Left panel: Absolute submicron concentrations of aerosol mass, non-sea salt (nss) $SO_4^=$ + NH_4^+, elemental carbon (EC), and organic carbon (OC) for the different regions. All are in mg m^{-3} except OC which is mg C m^{-3}. Horizontal lines denote the 25th, 50th, and 75th percentiles. The solid square in the box denotes the mean. Right panel: Average mass fractions of sub- and supermicron dominant chemical components for the different regions. Mass fractions are based on the gravimetrically-determined aerosol mass and concentrations of the chemical species. The mass fraction of H_2O is that calculated to be associated with the ionic chemical species at 55% RH. POM is estimated by multiplying the measured concentration of OC by a factor of 1.6 to 2.1 to account for associated H and O [*Turpin and Lim,* 2001].

ably in frequency and intensity during the past three years. The dust storm sampled during ACE Asia was a major event that extended across the Pacific, North America, and the Atlantic (Huebert et al., 2003). Hence, the ACE Asia time period may represent an upper bound in dust emissions.

The distance of the measurements from the haze source may also lead to variability in the compared data sets. During NEAQS, measurements were made 20 to 100 km downwind of the eastern shore of the U.S. During ACE Asia measurements were made 100 to 400 km from the upwind shore, during INDOEX 900 to 1400 km, and during ACE 2 20 to 900 km. During NEAQS, ACE Asia, and INDOEX, back trajectories indicated that the travel time from the upwind shore to the measurement platform was less than 2 days. During ACE 2 the travel time was less than 3 days. The global estimate of the average lifetime of sulfate aerosol is about 5 days (Langer and Rodhe, 1991). During INDOEX, the aerosol lifetime was estimated to be 7 to 8 days due to a lack of wet deposition (Rasch et al., 2001). Similarly dry conditions during NEAQS and ACE Asia are expected to have led to equivalent lifetimes. Given short transport times relative to the aerosol lifetime and assuming minimal dilution of the air from mixing across the marine boundary layer inversion, the concentration of particulates in the plume should remain fairly constant 100 to 1400 km from shore. The uniformity of the aerosol concentration downwind of India is confirmed by satellite-derived average AOD for a two week period during INDOEX (Collins et al., 2001). Values ranged from 0.35 to 0.4 for the region extending westward from the coast of India to 68°E longitude. This region encompassed the area of the ship measurements.

The height of the marine boundary layer was highly variable within and between regions ranging from 0.25 to 3.5 km. Elevated particulate concentrations occurred irrespective of boundary layer height.

Intriguing Results

1. Sea salt dominates sub- and supermicron aerosol mass and light extinction in the remote marine atmosphere. Prior to a series of Pacific and Southern Ocean cruises, including ACE 1, it was commonly believed that sea salt was a supermicron or coarse mode aerosol chemical component. As a coarse mode component, it was thought to persist in a particle size range that is not very efficient in terms of light scattering and to have a relatively short atmospheric lifetime. Shipboard measurements during ACE 1 revealed that ~ 70% and 100% of the sub- and supermicron aerosol mass, respectively, was sea salt with associated water at 55% RH (Figure 1) (Murphy et al., 1998; Quinn et al., 1998). As a result, sea salt controlled aerosol extinction in the ACE Asia region. This Southern Ocean result corroborated earlier findings for a wide latitude range of the Pacific Ocean where sea salt was found to dominate aerosol mass and light extinction in the sub- and supermicron size ranges (Quinn and Coffman, 1999). In addition, in all marine air masses shown in Figure 1, sea salt makes a significant contribution to the submicron aerosol mass and dominates the supermicron mass. These results showed the necessity of including submicron sea salt in coupled chemical transport/radiative transfer models to provide an accurate estimate of the radiative properties of the background marine aerosol.

An extension of the sea salt finding from ACE 1 was that non-sea salt (nss) $SO_4^{=}$ derived from oceanic dimethylsulfide (DMS) did not make a significant contribution to aerosol mass or light extinction nor did it play a role in new particle production in the marine boundary layer. DMS-derived sulfur did, however, appear to contribute to the growth of existing particles in the marine boundary layer (Bates et al., 1998) and the nucleation of new particles in the free troposphere in the outflow regions of clouds (Clarke et al., 1998).

2. A large fraction of submicron aerosol mass is not sulfate. Until the late 1990s, most model estimates as well as the 1996 IPCC summary of direct aerosol radiative forcing focused on a highly simplified sulfate-only aerosol. A major advance derived from the aerosol experiments discussed here, was the identification and quantification of the chemical components and their relative importance in the different study regions. Figure 1 shows a regional comparison of the absolute submicron concentrations of a few of the chemical components and the sub- and supermicron mass fractions of all dominant chemical components. At the sampling RH of 55 ± 5%, average submicron mass fractions of nss SO_4^{+} plus associated NH_4^{+} ranged from 16 to 54% over all study regions. Hence, a large and variable fraction of the submicron aerosol was not sulfate. This same result has been reported for the Pacific Ocean and aerosol monitoring stations located across North America (Quinn et al., 2000). Since aerosol optical and cloud-nucleating properties are composition dependent, a complete chemical characterization of aerosol mass is required for estimating aerosol direct and indirect radiative effects.

3. Absorbing aerosols have a complex impact on radiative forcing at the surface. The largest submicron concentrations and mass fractions of EC were observed in air masses from the Indian subcontinent (Figure 1) (Ramanathan et al., 2001a and b; Quinn et al., 2002). As a result, the lowest SSA were observed in these same air masses. Solar radiation flux measurements from space and the surface during INDOEX revealed that the haze-induced reduction in surface solar radiation was three times larger than the reflected solar radiation at the top of the atmosphere for clear skies (Satheesh and Ramanathan, 2000). The large negative surface forcing resulted from the absorption by EC in the Indian haze. The hydrological

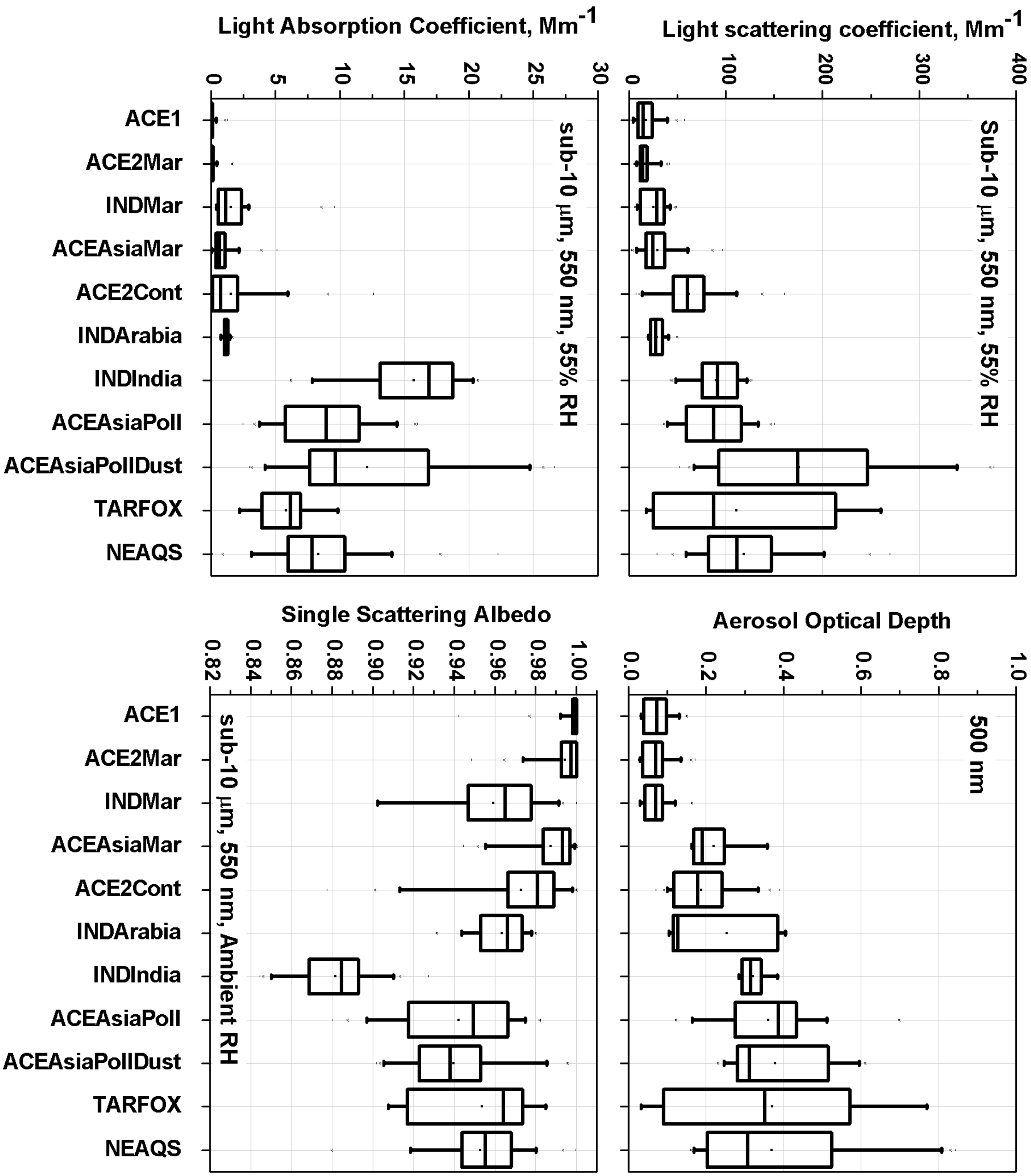

Figure 2 - Aerosol optical properties including light scattering coefficient, light absorption coefficient, aerosol optical depth, and single scattering albedo for the different regions. Percentile information is the same as in Figure 1.

impacts of this reduction in solar radiation to the surface may be significant but currently are not well understood. Conversely, solar heating of the boundary layer by EC can lead to the evaporation of some clouds which may result in more solar radiation reaching the surface and a subsequent warming of the surface (Ackerman et al., 2000). All aspects of EC in the atmosphere including (but not limited to) emission rate, size distribution, mixing state, cloud processing, radiative effects, lifetime, and deposition rate need more study to understand its complex impact on climate.

4. The NE U.S. plume is comparable to the Indian and Asian plumes in terms of aerosol mass, surface extinction, and aerosol optical depth. The Indian and Asian plumes have been well documented by field campaigns and satellite observations and the environmental implications of the "Asian Brown Cloud" have been widely publicized in a recently released UNEP report. A comparison of several aerosol extensive properties from the regional experiments listed in Table 1 shows that the eastern U.S. plume can be as intense as those downwind of India and Asia (Hegg et al., 1997; Quinn and Bates, 2003).

Figure 1 shows that submicron aerosol mass and nss $SO_4^{=}$ aerosol concentrations observed in the eastern U.S. plume during TARFOX and NEAQS were comparable to or greater than those observed in the Indian and Asian plumes during INDOEX and ACE Asia. The organic carbon (OC) concentrations observed during both TARFOX and NEAQS were higher than those of INDOEX and ACE Asia. In addition, for both surface-measured extinction and aerosol optical depth, the eastern U.S. haze can be as intense as the haze downwind of Asia and the Indian subcontinent (Figure 2). All of these factors, plus the likelihood of intercontinental transport of the U.S. plume, indicate the importance of determining its climate and health impacts.

5. Asian dust is relatively non-absorbing. Prior to ACE Asia, Asian dust was expected to be relatively absorbing due to its mixing with soot aerosol during transport over downwind industrial and urban regions (Huebert et al., 2003). Figure 2 shows regional single scattering albedos (SSA) based on absorption measurements from a particle soot absorption photometer and an integrating nephelometer. All values have been adjusted to ambient RH using appropriate f(RH) values (e.g., Carrico et al., 2003). The mean SSA observed during the ACE Asia Polluted with Dust air masses was 0.94 ± 0.03. A similar mean value of 0.95 ± 0.02 was observed in relatively unpolluted dust layers in the free troposphere (Anderson et al., 2003). Based on these data, soot associated with the dust does not appear to have had a large effect on the SSA of the dust – pollution mixture.

Successes and Areas That Need Improvement

For all of the intensive field experiments discussed here, an over-riding goal has been the collection of data sets needed for reducing uncertainties in estimates of aerosol radiative forcing. Measured aerosol chemical, microphysical, and optical properties are like pieces of a puzzle that must fit together to form an accurate picture of the radiative forcing by the aerosol for a particular region. The collection of an over-determined data set where important aerosol parameters are measured and modeled by multiple independent methods allows for a check on the internal consistency of the data, the identification and quantification of sources of uncertainty, and an assessment of how well the puzzle pieces fit together. Without this approach and the constraints that it offers, it is difficult to determine how well the regional aerosol systems are understood.

As expected, the success of such closure experiments depends on the complexity of the aerosol being considered. Successful closure, defined as agreement within experimental uncertainties, was reported for mass, extinction,

Experiment	Region	Dates	Reference
ACE 1	Southern Ocean south of Australia	Nov. – Dec. 1995	Bates et al., 1998
TARFOX	U.S. eastern seaboard (37˚ to 39˚N)	July 1996	Russell et al., 1999
ACE 2	Sub-tropical northeast Atlantic	June – July 1997	Raes et al., 2000
INDOEX	Indian Ocean	Jan. – Mar. 1999	Ramanathan et al., 2001a
ACE Asia	Western Pacific Ocean	Spring 2001	Huebert et al., 2003
NEAQS	U.S. eastern seaboard (33˚ to 45˚N)	July – Aug. 2002	Quinn and Bates, 2003

Table 1 - Recent field experiments focused on determining the impact of aerosol plumes on regional atmospheric chemistry and climate.

and cloud condensation nuclei (CCN) concentration for ACE 1 (Quinn and Coffman, 1998; Covert et al., 1998). These successes lend confidence in our ability to measure and model the relatively simple marine aerosol of ACE 1. Successful mass and extinction closure also was reported for ACE 2 (Putaud et al., 2000; Neusüb et al., 2000; Collins et al., 2000; Schmid et al., 2000) although the increased complexity of this aerosol relative to that measured in ACE 1 brought several measurement and sampling issues to light. For example, the particle shapes and complex refractive index of Saharan dust were not well- accounted for by satellite retrieval algorithms. Also, changes in particle size and scattering due to changes in RH were not consistently characterized by measurements and models (Russell and Heintzenberg, 2000).

Local (within one platform) mass and extinction closure was achieved for INDOEX in both marine and polluted air masses (Quinn et al., 2002). CCN closure was not achieved, however, as modeled concentrations systematically overpredicted measured values (Cantrell et al. 2001) presumably due to a poor parameterization of the uptake of water by some or all of the organic material. The INDOEX multi-platform Harmony exercise concluded that closure between *in situ* measurements of chemical, microphysical, and optical properties across platforms to better than about 20% will acquire significant improvements in techniques, calibration procedures, and comparison efforts (Clarke et al., 2002).

Perhaps the most difficult aerosol encountered to date in terms of achieving mass and extinction closure is the marine - pollution – dust aerosol mixture measured during ACE Asia. A recently held ACE Asia Harmony workshop as well as papers in press and published have pointed out several aspects of this aerosol system that challenge the capabilities of our state-of-the-art measurement and modeling techniques (e.g., Wang et al., 2002). Difficulties include fundamental measurement questions such as 1) how do particle sizing instruments respond to non-spherical dust particles and 2) can our particle absorption photometers accurately measure absorption in the presence of a large amount of scattering aerosol? Modeling questions include 1) how do we parameterize the many observed forms of soot and soot-dust aggregates and what is their effect on aerosol optics, 2) how can we best estimate the dust density and complex refractive index from the measurements we have, 3) how do we most accurately parameterize the non-sphericity of the dust and dust-pollution particles in order to calculate their extinction, and 4) how well can we estimate the hygroscopic growth and related scattering response of this complex aerosol mixture? To paraphrase Huebert et al. (2003), ACE Asia's success may be judged by the Pandora's Box of measurement and modeling questions that it opened. It most certainly points to the need for instrument development, characterization, and comparisons as well as model development prior to the next field experiment that looks at such complex aerosol.

Summary

In situ measurements are critical for providing information required about aerosol properties for accurate estimates of aerosol radiative forcing. Our understanding of regional aerosols, ranging from remote marine to complex pollution-dust mixtures, and the *in situ* measurement techniques we have for characterizing them have improved tremendously over the past decade. Along with these advances in understanding and technology has come an appreciation for the complexity of that questions that need to be answered to reduce uncertainties in estimates of aerosol radiative forcing. Re-visiting these regions, continuing the approach of collecting over-determined data sets, and emphasizing instrument and model comparisons in the lab and in the field will get us closer to answering these questions over the course of the next decade.

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Announcements

2nd International Workshop on Mineral Dust

The Workshop will be held 10-12 September 2003 in Paris, France. Four years after the first meeting in Boulder, the goal of the Workshop is to evaluate the progress in our knowledge on dust processes and effects, determine the remaining knowledge gaps, and make recommendations for future work. The Workshop will include invited presentations, posters and open discussion.

Deadline for abstract submission for posters is June 20. Further information on abstract submission and registration is available at http://www.lisa.univ-paris12.fr/DUST2003

The 8th Scientific Conference of the International Global Atmospheric Chemistry Project (IGAC)

To be held in September 4-9 2004 in Christchurch, New Zealand

Check the IGAC web site for details.

IGACtivities Newsletter

Editor: Peter Czepiel
Layout and Proofreading: Virginia Moore
IGAC logo: Linda Kubrick

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IGAC was initiated by the Commission on Atmospheric Chemistry and Global Pollution (CACGP) and is a Core Project of the International Geosphere-Biosphere Programme (IGBP). The IGAC Core Project Office is currently supported by the National Science Foundation (NSF), National Aeronautics and Space Administration, and National Oceanic and Atmospheric Administration of the United States of America through NSF Grant No. ATM 99-08980. Any opinions, findings and conclusions, or recommendations expressed in this newsletter are those of the individual author(s) and do not necessarily reflect the views of the NSF or other agencies.

INTERNATIONAL GLOBAL ATMOSPHERIC CHEMISTRY

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