



IGAC **activities**

Newsletter

of the International Global Atmospheric Chemistry Project

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A Note from the IGAC Co-chairs: Phil Rasch and Kathy Law

This issue begins with a summary of three scientific projects presented at last September's IGAC/CACGP/WMO international symposium in Cape Town, South Africa. Four presentations at the meeting received the most votes for "outstanding poster first authored by a young scientist". We asked the authors of these studies to produce a brief article from their posters for IGACactivities, as a way of recognizing the high quality of science done within this context and to let those of you who were not able to attend learn a bit more about some of the interesting work taking place in the IGAC community. Three of the four winners chose to do so. These studies provide a glimpse of the variety of disparate activities in atmospheric chemistry.

The paper by Mills et al, entitled "Monitoring Emissions of Carbon Dioxide, Nitrous Oxide and Methane from an Estuarine Sediment" uses a laboratory study to characterize components of the Carbon and Nitrogen cycles – and the links between them – within the estuarine environment. The processes controlling these species are important to understanding the biogeochemistry of the Earth system and its response to climate change. The study provides a coherent picture of the C-N cycle for the estuarine environment.

Josipovic and colleagues discuss "A Regional-Scale Passive Monitoring Study of SO₂, NO₂, and Ozone in South Africa". The work provides a picture of the anthropogenic sources and transport pathways of some major pollutants in this region of the world, providing a nice opportunity for linking field measurements, model validation and ground truth for satellite retrievals for a region of the world relatively well-separated from other sources of pollution.

The third study, from Mmari and colleagues, on "Corrosive Marine Atmosphere Investigations in Tanzania: Exposure Sites and Preliminary Results" reminds us of the role of pollution on the natural environment and of one of the consequences for society in a developing country.

These articles are followed by a brief report announcing a new initiative within IGAC – the Atmospheric Chemistry and Climate Activity (AC&C), which is being developed in collaboration with the SPARC and WCRP communities. The recent release of the IPCC Fourth Assessment report and its reception by the scientific community and society at large highlight the importance of many aspects of atmospheric chemistry in the climate system. Many of the open issues highlighted in the IPCC report form a part of AC&C. We hope that the results of the project will contribute directly to any future IPCC assessment, as well as to the next WMO Ozone assessment. The project has generated a great deal of interest within the IGBP and WCRP communities, and we invite our readers to get involved in the project soon. You can check on progress on the AC&C initiative at: <http://www.igac.noaa.gov/ACandC.php>

Finally, this issue concludes with an article describing the Network for the Detection of Atmospheric Composition Change, an effort to coordinate studies and produce consistent, coherent datasets that help us understand changes to the atmosphere in the upper troposphere and lower stratosphere. Such efforts are critical to the advancement of atmospheric chemistry research and are of value to the entire community.

We hope that you enjoy all this month's articles. As always, we welcome your feedback and input to IGACactivities.

Monitoring Emissions of Carbon Dioxide, Nitrous Oxide and Methane from an Estuarine Sediment

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Abstract

A system allowing the *ex situ* quantification of the nitrogen cycle and various carbonaceous species (organic carbon, carbon dioxide, methane) in the air, water and sediment has been developed and used to examine changes in the nitrogen and carbon cycles. Marine sediment and water were placed in a chamber where the concentrations of gaseous, dissolved and solid carbon and nitrogen compounds were monitored, and gas fluxes were determined from these data. Clear changes in both carbon and nitrogen species were observed. The methane flux peaked three days after the initial disturbance; nitrous oxide flux peaked after 12 days while carbon dioxide flux varied throughout the experiment. Nitrite and nitrate concentrations in the overlying water peaked at the end of the second and third weeks, respectively. The total quantity of nitrogen within the system was estimated to increase by ~35%.

Introduction

The current focus on quantifying the sources of greenhouse-enhancing gaseous species, along with the adverse effects of eutrophication in nitrogen-limited waterways, has placed a renewed emphasis on the study of nitrogen and carbon cycling within the biosphere (Cook et al. 2004; Arrigo 2005). The carbon and nitrogen cycles are summarized in Figures 1 and 2. These cycles are closely linked, consisting of a series of chemical and microbially-mediated reactions that describe the transformations and physical transportation of carbon and nitrogen compounds within the environment. Links between the cycles include the processes of primary production and remineralization which are common to both cycles. Methanotrophic bacteria have been observed to nitrify ammonia (Dalton 1977; Hanson and Hanson 1996); hence, although an integral part of the carbon cycle, they can also play a significant role in nitrogen cycling. Other nitrogen cycling organisms may not directly cycle carbon yet they still require a carbon source for growth and proliferation. Many of these reactions are also highly sensitive to oxygen availability and hence will occur preferentially in either the upper (oxic) or lower regions (anoxic) of the system.

These carbon and nitrogen processes have been studied individually over many years, but the complexity and interdependent nature of these two

cycles has limited the number of comprehensive studies. As such this study aimed to develop a system capable of monitoring changes in the carbon and nitrogen cycles focusing on:

- the production of C and N greenhouse gases in the estuarine environment
- the transformation and transportation of N compounds between various forms of N including aqueous, gaseous, organically bound and biologically incorporated
- the capabilities of the system were then assessed using sediment collected from a local nutrient contaminated estuarine lake.

Experimental

The System

A looped system for measuring gas concentrations was created consisting of an *ex situ* mesocosm, a gas measurement cell mounted on an FTIR, a flow restrictor, pump, flow meter, computer controlled valves, molecular

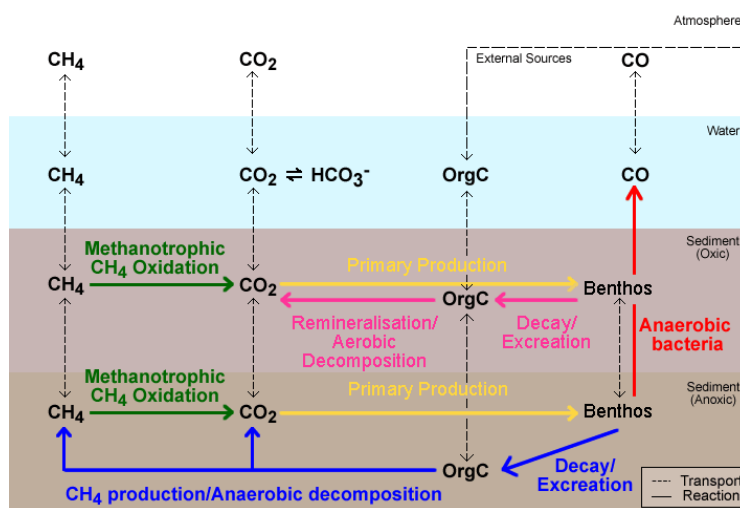


Figure 1. A summary of the major processes of the carbon cycle in the estuarine environment.

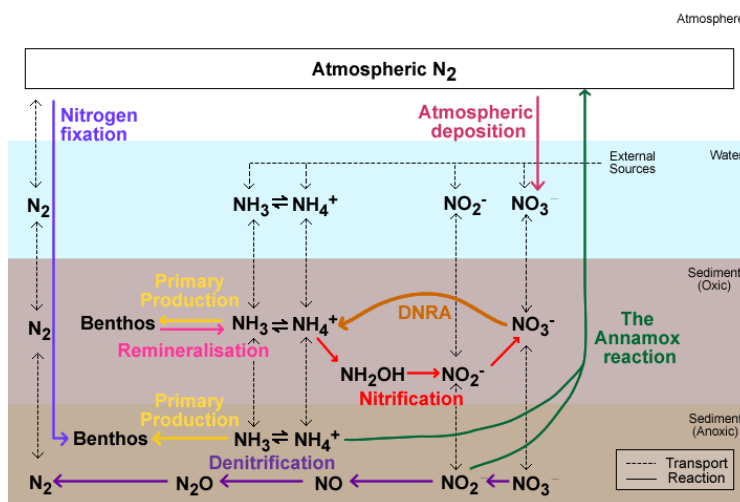


Figure 2. A summary of the major processes of the nitrogen cycle in the estuarine environment. (DNRA – Dissimilatory Nitrate Reduction to Ammonia)

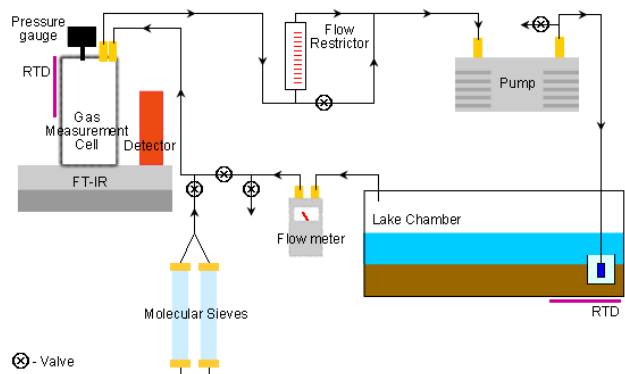


Figure 3. The system consisting of the gas measurement cell (White optics) mounted on a Fourier Transform InfraRed (FTIR) spectrometer, flow restrictor, pump, lake chamber, flow meter, molecular sieves and computer-controlled valves connected by Teflon tubing. The arrows show the direction of air flow. (RTD – Resistance Temperature Detector)

sieves and Teflon tubing (Figure 3).

The mesocosm was housed in a clear polyethylene chamber and consisted of 3 layers:

- sediment from the littoral zone of a known nitrogen nutrient-contaminated, temperate, estuarine lake (Lake Macquarie, New South Wales, Australia), stored frozen until required.
- clean seawater (Fairy Meadow Beach, New South Wales, Australia)
- air

Air was pumped in a loop between the gas cell and the mesocosm chamber. To prevent the build-up of gases that would perturb natural biogeochemical cycles, the system was regularly flushed with external (laboratory) air. As such the air flowed through the system in two modes, flushing and circulating, with the system changing between these modes every 15 minutes. To ensure a consistent composition of the flushing gas the laboratory air was drawn through molecular sieves.

The water was kept in constant motion by sparging the air through the water of the lake chamber.

Sediment and water sub-samples were collected at the commencement and conclusion of the experimental run. In preparation for analysis the collected sediment was thawed, placed in the chamber and physically mixed with the overlying layer of water. The system ran for the next 23 days. Overlying water samples were regularly collected and the gas concentration was determined every two minutes. The experimental run was repeated using fresh sediment and water samples.

Wet chemistry analysis

The concentrations of key carbon and nitrogen species (including: nitrate (NO_3^-), nitrite (NO_2^-), ammonia (NH_3), Total Kjeldahl Nitrogen (TKN = NH_3 + Organic Nitrogen) and Total Organic Carbon were determined in overlying water and sediment samples collected prior to and at the end of the experimental run. The concentrations

of NO_3^- and NO_2^- were monitored in the overlying water throughout the experimental run. Standard wet chemistry techniques were used (Eaton et al. 1998).

Gas flux analysis

Gas concentrations of water, nitrous oxide, carbon dioxide, carbon monoxide and methane were determined using Fourier Transform Infra-red (FTIR) spectroscopy and a non-linear regression (fit) between the measured spectra and calculated spectra (derived using the Multiple Atmospheric Layer program (MALT; Griffith 1996). Gas concentrations showed a distinctive pattern, increasing during the circulating mode and decreasing in the flushing mode. The air flow in the system was modeled, and the flux of each gas species from the water was determined by fitting the model to the measured gas concentrations.

Results and Discussion

Nitrogen Budget

A nitrogen budget (Table 1) was constructed using the N_2O flux and the concentrations of key nitrogen species

Table 1. Nitrogen budget constructed using gas flux data and the concentrations of key N species within the overlying water, sediment and porewater before and after the experimental run. Concentrations are given in ppm-N in terms of milligrams of nitrogen per kilograms of wet sediment or litres of water, ± 1 SD.

| Nitrogen Budget | | |
|--|--------------------------------|--------------------------------|
| | Initial (ppm-N) | Final (ppm-N) |
| Sediment | | |
| Total Kjeldahl Nitrogen | 480 \pm 40 | 580 \pm 40 |
| NH_3 | 6 \pm 3 | 2 \pm 1 |
| Porewater | | |
| Total Kjeldahl Nitrogen | 11 \pm 3 | 1.3 \pm 0.1 |
| NH_3 | 2 \pm 4 | 2 \pm 1 |
| NO_3^- | <0.05 | <0.04 |
| NO_2^- | <0.001 | <0.001 |
| Water | | |
| Total Kjeldahl Nitrogen | 0.048 \pm 0.006 | 0.2 \pm 0.02 |
| NH_3 | <0.03 | 1.4 \pm 0.03 |
| NO_3^- | <0.05 | <0.04 |
| NO_2^- | <0.001 | <0.001 |
| Gaseous | | |
| Mass of N released as N_2O | - | 1.7 \pm 0.1 |
| Mass of N released as N_2^* | - | 85 \pm 5 |
| TOTAL | 500 \pm 40 | 670 \pm 40 |
| Sediment | | |
| | Initial | Final |
| Water Content | 65.50 \pm 0.01 % | 56.45 \pm 0.01 % |
| TOC (mg/kg (Dry)) | 40000 \pm 10000** | 50000 \pm 10000 |
| C:N ratio | >23 | >28 |

* Estimated assuming that N_2O release was approximately 2% of N_2 released

** Estimate based on samples collected from the same site

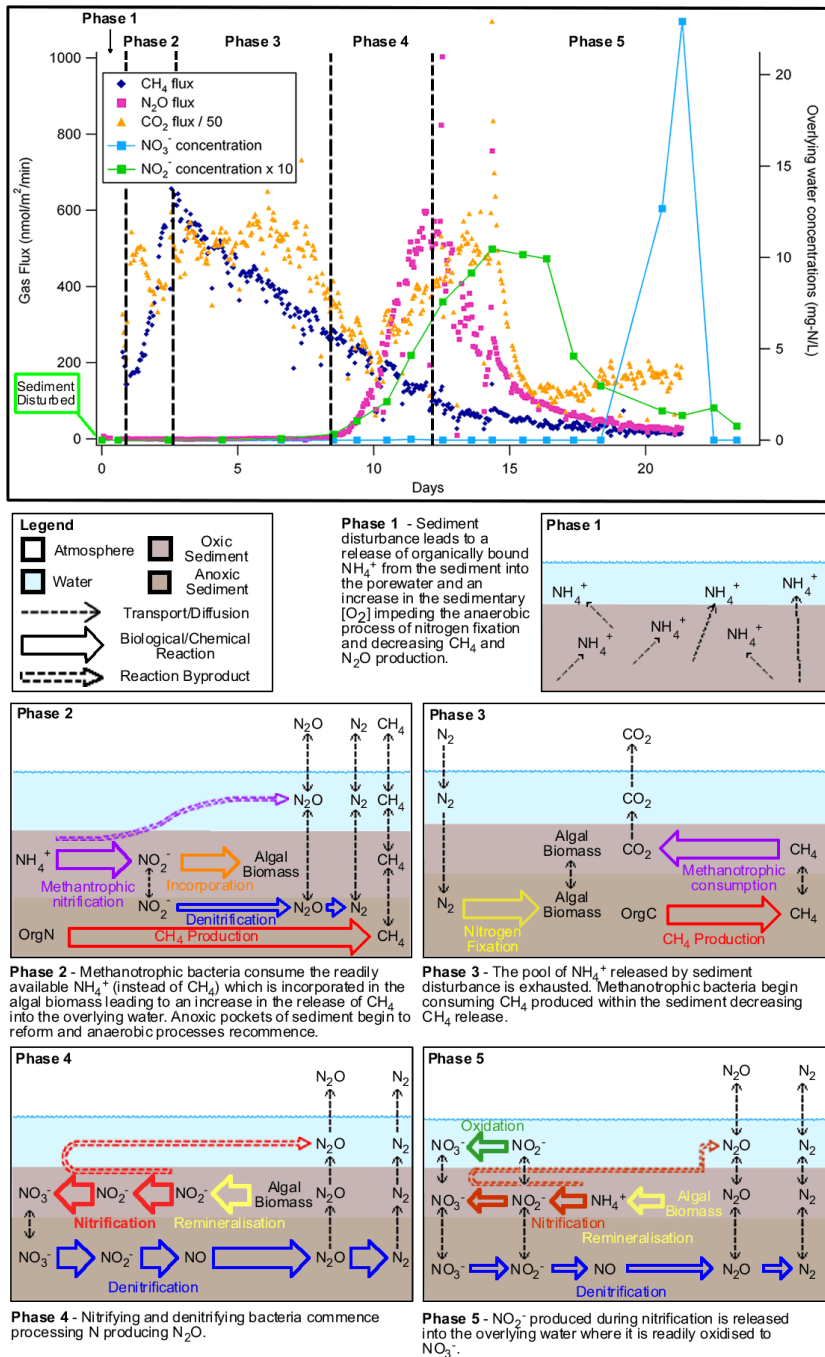


Figure 4. N_2O , CO_2 and CH_4 fluxes from the sediment and NO_3^- and NO_2^- concentrations in the overlying water during the second experimental run, and schematics describing the five phases occurring during the experimental run.

in the overlying water, sediment and porewater. The volume of N_2 produced by the sediment was estimated assuming that the mass of N_2O produced was ~ 2% of the N processed by the system (Robinson et al. 1998; Dong et al. 2002). Using this budget, changes in the total mass of nitrogen within the system, and the portioning of nitrogen between the various pools were evident. Key changes observed in the nitrogen budget include an increase in sedimentary Total Kjeldahl Nitrogen and an increase in the total mass of nitrogen within the system. The only source of nitrogen into the mesocosm was gaseous N_2 , indicating that biological fixation of atmospheric N_2 had

occurred. Increases in sedimentary total organic carbon concentration may also be a sign of biological growth.

Gas Flux and Overlying Water Concentrations

The experiment was conducted twice; the data obtained was consistent for both experimental runs. The data collected from the second 23 day analysis is shown in Figure 4. Five distinctive phases were identified which corresponded to changes in the gas flux and concentrations of nitrogen species in the overlying water (Figure 4).

Phase 1: The first few hours immediately following sediment thawing and disturbance leads to a release of organically bound NH_4^+ from the sediment into the porewater and an increase in the sedimentary $[\text{O}_2]$ impeding the anaerobic process of nitrogen fixation and decreasing CH_4 and N_2O production. Sediment disturbance aerates the sediment, increasing oxygen penetration (Falcao et al. 2003) and inhibiting anoxic processes including denitrification, nitrogen fixation and methane production. This would decrease N_2O and CH_4 production which is consistent with the observed fluxes.

Phase 2: Large increases in CH_4 flux along with the significant production of CO_2 . This clearly shows the changes in the carbon chemistry within the mesocosm. As methane production is an anoxic process, it would have been significantly impeded by the disturbance event in Phase 1. But, as oxygen is progressively consumed in the sediment anoxic regions reform, and methane production would gradually resume, leading to the observed increase in methane flux.

Sediment disturbance is known to lead to the release of NH_4^+ from the sediment surface into the surrounding pore and overlying water (Forja et al. 1994; Falcao et al. 2003; Warnken et al. 2003). Strauss & Lamberti (2000) proposed a critical C:N ratio of 21, above which any ammonia released by sediment disturbance tended to be consumed for microbial growth within the sediment. The C:N ratio for the sediment used in this experiment was found

to be > 23, implying that any ammonia released during the sediment disturbance would have been retained within the sediment.

Methanotrophic bacteria consume methane, oxidizing it to carbon dioxide (Hanson and Hanson 1996). However they preferentially nitrify NH_4^+ to NO_2^- (Dalton 1977). Therefore any ammonia released from the sediment surface would inhibit methane consumption. Hence the large increase in CH_4 flux observed during Phase 2 is probably caused by an increase in CH_4 production, in combination with a decrease in CH_4 consumption.

Phase 3: A decrease in CH₄ flux. As the concentration of organic carbon within the sediment is quite high, it is unlikely that the decrease in CH₄ flux evident in Phase 3 is due to a decrease in CH₄ production. Instead it is more likely that this is an increase in CH₄ consumption; i.e., once the disturbance-released ammonia was consumed the methanotrophic bacteria returned to CH₄ consumption, decreasing CH₄ flux, as observed.

Phase 4: The N₂O flux and water NO₂⁻ concentration increases. During Phase 4 there is an increase in N₂O flux and NO₂⁻ concentration in the overlying water, clearly indicating that nitrogen is cycling within the mesocosm. N₂O is produced as a by-product of nitrification (NH₄⁺ → NO₂⁻) and as an obligatory intermediate of denitrification (NO₂⁻ → N₂ via N₂O) as shown in Figure 2. The increase in N₂O observed during Phase 4 coinciding with an increase in overlying water NO₂⁻ concentration would be consistent with nitrification. However as nitrification and denitrification are often closely coupled it is more likely that the N₂O produced comes from a combination of both processes. In fact, as denitrification is the most prevalent producer of N₂O in nutrient rich estuarine environments (Robinson et al. 1998), it is more probable that the bulk of the N₂O produced was from denitrification.

Phase 5: The N₂O flux decreases and NO₃⁻ concentration rises then falls. These observations appear to indicate a decrease in N₂O production and a slowing of nitrogen cycling. As indicated in Table 1 the sediment is rich in both organic carbon and nitrogen. However it is highly likely that by this stage (Day 12) the labile (easily consumable) carbon pool would have been significantly depleted. Strauss and Lamberti (2000) found that a decrease in labile carbon limited nitrogen cycling, specifically nitrification. A reduction in nitrification would have reduced the available nitrate, decreasing denitrification. The increase in [NO₃⁻] within the sparged overlying water coincides with a decrease in the concentration of NO₂⁻, broadly consistent with the conversion of the released NO₂⁻ to NO₃⁻ within that oxic environment.

Conclusion

The system was found to be capable of monitoring changes in the carbon and nitrogen cycles. Clear variations in the production of carbon- and nitrogen-containing greenhouse gases were observed during the 23 day analysis. The transformation and transportation of nitrogen compounds

between various forms including aqueous, gaseous, organically bound and biologically incorporated was also successfully monitored. Key changes observed included:

- the production of significant quantities of CH₄ and N₂O from sedimentary phase carbon and nitrogen cycling; and
- an increase in the concentration of organically bound N within the sediment phase over the experimental run.

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A Regional-Scale Passive Monitoring Study of SO₂, NO₂ and Ozone in South Africa

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Introduction

South African Situation

Pollutant trace gas generation

South Africa has one of the largest industrialized economies in the southern hemisphere and is the only industrialized regional energy producer on the African continent (Sivertsen *et al.*, 1995; Rorich and Galpin, 1998). A large proportion of this industrial infrastructure is concentrated on the Highveld plateau. The industrial Highveld plateau (~1 700 masl, ~30 000 km²) accounts for approximately 90% of South Africa's scheduled emissions of industrial dust, sulphur dioxide and nitrogen oxides (Wells *et al.*, 1996).

Table 1. Scheduled emissions from South Africa and the industrial Highveld region, metric tonnes per year (1993) (Source: Wells *et al.*, 1996)

| | South Africa | Industrial Highveld Region | % of total |
|-----------------|--------------|----------------------------|------------|
| Particulates | 331 399 | 285 405 | 86 |
| SO ₂ | 2 120 452 | 1 986 193 | 94 |
| NO _x | 1 004 716 | 913 486 | 91 |

In addition to primary pollutants, ozone formation is enhanced due to naturally occurring and extensive anthropogenic chemical precursors.

Importantly, the role of biomass burning emissions in contributing to tropospheric trace gas loads cannot be underestimated. South Africa, in common with the rest of sub-Saharan Africa, is prone to large scale savannah and bush fires during dry seasons. Also fire wood forms the basis of the domestic energy economy for a large fraction of South African rural populations (Helas and Pienaar, 1996) while on the Highveld, the urbanized lower income population burn coal as a domestic energy source. All of these sources contribute to the overall load of trace gas and aerosol pollution across the entire region.

Table 2. Comparison of strengths of different combustion sources for two gaseous species in South Africa, per annum (extracted from Helas and Pienaar, 1996)

| Activity | NO _x (Gg) | N ₂ O (Gg) |
|------------------------|----------------------|-----------------------|
| Industrial coal use | 1359 | 1.9 |
| Domestic coal fires | 13.1 | ? |
| Domestic wood fires | 49.3 | ? |
| All types of vehicles | 519 | 0.82 |
| Veld and bush fires # | 30.9 | 1.32 |
| *Veld and bush fires # | 122 (⊕38) | --- |
| Sugar cane burning | 1.88 | 0.09 |

?= value not known;

based on an estimated total of 44.3Tg dry mass burnt per annum;

* using averaged emission ratios as reported by Helas and Pienaar (1995);

⊕ for emission ratios measured during Safari'92 (Helas & Pienaar, 1995)

Air pollution transport

In addition to there being substantial air pollution generation in this region, it is important to note the role of air pollution transport. The prevailing synoptic condition is a recirculation associated with an anti-cyclonic circulation. The strength and the stability of this synoptic-scale recirculation governs the accumulation and dispersion of atmospheric pollutants over the whole sub-continent.

In essence there are two main transport modes of air masses, aerosols and trace gases out of industrial Highveld region. The first is direct transport, in which material is advected in various directions directly, with little delay. The second is re-circulated transport, in which material re-circulates towards the point of origin on a regional or sub-continental scale, before finally exiting the region (Figure 1).

The long-range atmospheric transport and recirculation of anthropogenic trace gases over southern Africa affects the photochemistry and biochemistry of the whole region (Freiman and Piketh, 2003). Given the relatively high emissions of pollutant trace gases from the source region

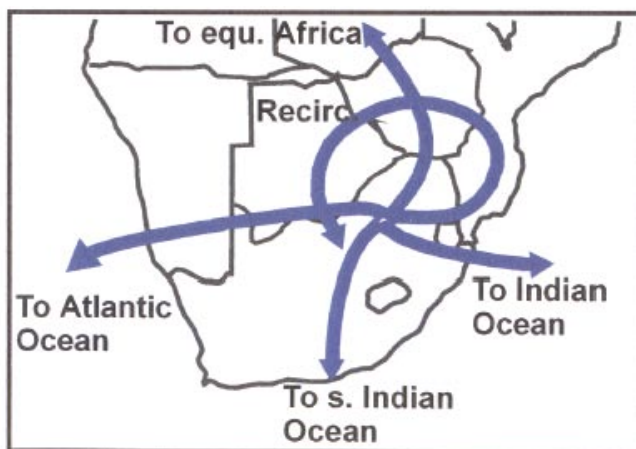


Figure 1. The main air transport pathways out of the Highveld (Freiman and Piketh, 2003).

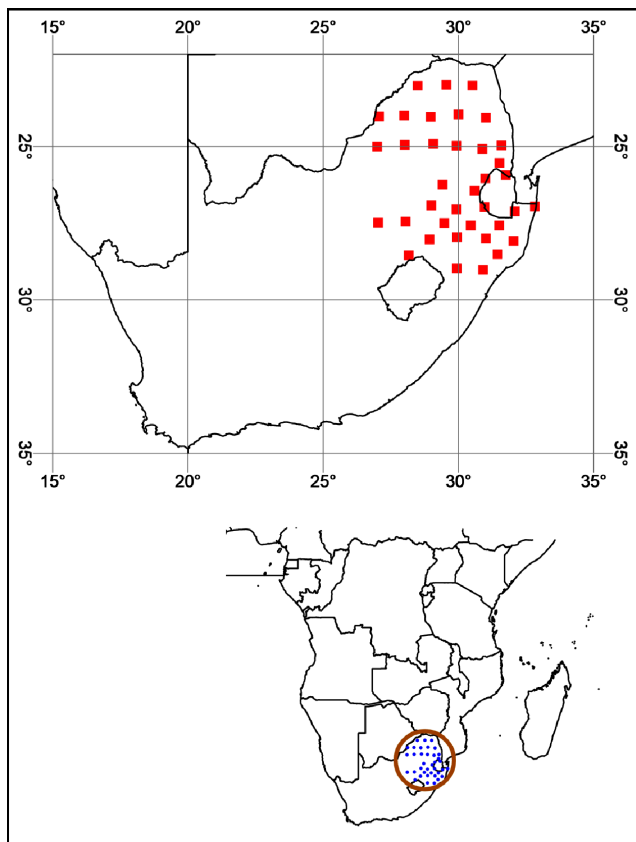


Figure 2. Extent of the study area within South Africa and sub-Saharan Africa.

and the inhibiting dispersion climatology, it is important to quantify the deposition of these pollutants on a regional scale in order to address impacts.

Air quality legal environment

Recently, a new air quality act (NEMA: Air Quality Act 39 of 2004) has been promulgated in South Africa, repealing the outdated Air Pollution Prevention Act 45 of 1965. This new Act embodies a paradigm shift in the domain of air quality regulation, from end-of-pipe air pollution control measures to effects-based air quality management. This is accomplished using proactive, more flexible, varied and fairer measures under the new Act.

The research presented herein will support the new law's requirements by providing measurements for an effect-based impact assessment of three important tropospheric trace gas pollutants.

Research Rationale

While the transport of atmospheric pollutants from the Highveld area is a known phenomenon and has been measured in various studies, the implications of these pollutants and the regional integration of their impacts has not yet been addressed. Many studies have shown that remote sites in the South receive trace gases from the Highveld (Bluff *et al.*, 1991; Snyman *et al.*, 1991; Turner *et al.*, 1996; Galpin and Turner, 1999; Zunckel *et al.*, 2000). Among the questions that remain unanswered are trace gases concentrations and deposition rates in

areas further from the “epicentre” of South African trace gas emissions. Ambient trace gas sampling further from the industrial Highveld needs to be done in order to provide initial data for the methodology to follow – i.e. determination of ecosystems exposure and cumulative loads and potential sensitivity to acidic deposition.

Regional Scale

The novel aspect of this study is that it comprises an empirical survey of a relatively massive ~600 x 600 km array, allowing us to generate a regional scale dispersion field of key pollutants. The study area for the current project is set to include major parts of five of South Africa's nine provinces.

Aim and Objectives

This research aims to determine critical concentration levels of sulphur dioxide (SO₂) and nitrogen oxides (NO₂) emanating from various sources, and to measure ozone (O₃) concentrations in areas surrounding and downwind of the industrial Highveld. Temporal – including seasonal and annual averages – and any recognizable trends related to the concentrations and deposition will be identified. The integral tasks and objectives are:

- Monitoring of concentrations and distribution of SO₂, NO₂, O₃
- Determining whether critical concentration levels of O₃, SO₂, NO₂ are exceeded
- Computing dry and wet deposition of SO₂, NO₂, and estimating base cation deposition
- Validation of regional dispersion modelling outputs
- Further comparison and correlation with spatial investigations of trace gases concentrations by remote sensing
- Comparison and correlation with NO₂ generation by lightning within the study region

Research Methodology and Data

Taking into account a number of the objectives several consecutive methodologies related to each objective have been envisaged.

Passive Sampling

The chosen methodology of measuring gaseous concentration and distribution is *passive diffusive* sampling. This methodology was chosen for its many advantages in the field such as no need for calibration or a power supply. The sampler is small, light, re-usable, cost-efficient and soundless. Applying this methodology was essentially a necessity due to the large regional scale of the study field.

This project uses the passive sampling technology applied for the IDAF (IGBP/IGAC/DEBITS in AFRICA) network. The IDAF programme is an initiative to determine atmospheric depositions. For the IDAF project, a set of passive samplers was developed at the laboratory of Aerology in Toulouse, France (European Union). These samplers have been developed according to the DEBITS

procedures based on the work of Ferm (1991, 1994). Passive samplers have been tested and validated since the beginning of 1998 in the IDAF network in 6 African stations (Al Ourabi and Lacaux, 1999). This technique has also been tested in different tropical and subtropical regions (Ferm and Rodhe, 1997). Such measurements are based on the property of molecular diffusion of gases and species-specific collection on an impregnated filter specific to each pollutant measured.

Table 3. Chemical reactions used in passive sampling for NO₂, SO₂ and O₃ (source: <http://medias.obs-mip.fr/idaf>)

| Color of sampler | Gas | Chemical reaction on the filter |
|------------------|-----------------|--|
| Grey | NO ₂ | 2 NO ₂ (g)+3 I ⁻ => 2 NO ₂ ⁻ + I ₃ ⁻ |
| Black | SO ₂ | 2 SO ₂ (g)+4 OH ⁻ => 2 SO ₃ ²⁻ + 2 H ₂ O |
| Grey & black | O ₃ | O ₃ (g) + NO ₂ ⁻ => NO ₃ ⁻ + O ₂ |

All the samplers are exposed in pairs to ensure the reproducibility of the results and to reduce data loss if a sampler suffers interference. In the monitoring sites, samplers are installed (slid) mesh side down in the underside of a metal rain shelter which is screwed or welded to the top of a metal pole and left in position for one month.

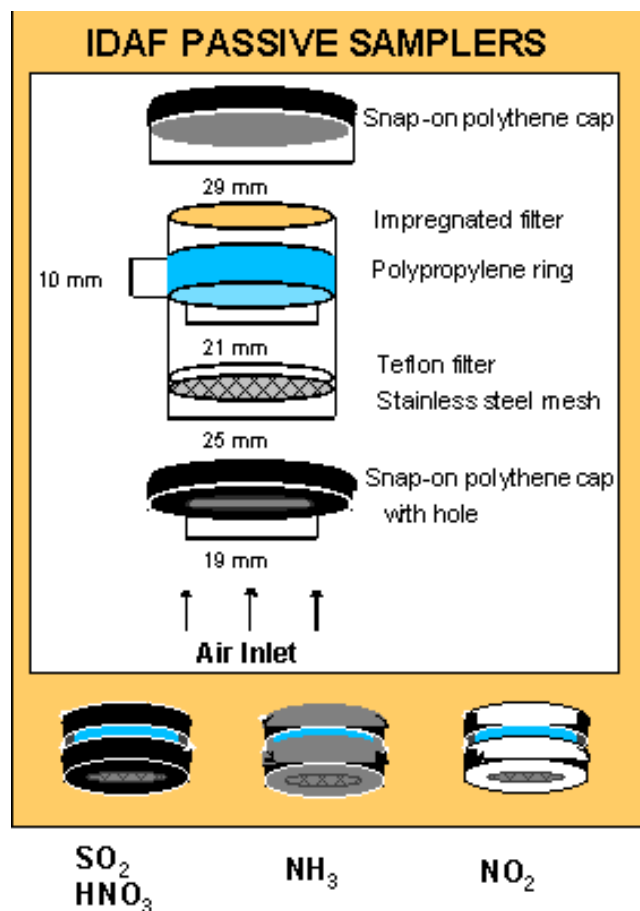


Figure 3. IDAF passive sampler design (source: <http://medias.obs-mip.fr/idaf>)

In the IDAF network three kinds of samplers are used which differ only by their color (important for the exposed samplers processing) and their coating solutions. The different parts are assembled under a hood. In both cases, 50 µl of coating solution (see Table 4) are added by pipette to a paper filter which is placed directly into a sampler body.

Table 4. The different samplers' coating solutions (source: <http://medias.obs-mip.fr/idaf>)

| Color of the sampler | Sampled species | Coating solution |
|----------------------|--|---|
| Black | SO ₂ (and HNO ₃) | 0.5 g NaOH in 50 ml methanol (pH>12) |
| Grey | NO ₂ | 0.44 g NaOH + 3.95 g NaI in 50 ml methanol (pH>12) |
| Grey & black | O ₃ | 0.25g NONO ₂ + 0.25g K ₂ CO ₃ + 0.5 ml redistilled glycerol in 50 ml water |

The Laboratory of the School for Chemistry and Biochemistry of North-West University (Potchefstroom campus) in South Africa is tasked with the preparation and analysis of passive samplers for this research. The passive samplers are supplied ready for use in sealed containers, loaded with a filter treated for a nominated pollutant gas; it is sent to the station with a technical log sheet (requiring the input of dates of insertion/removal, temperatures, rainfall and local fires during exposure). Upon receipt of an exposed sampler, impregnated filters are analyzed for pollutant concentrations in the laboratory through *Ion Chromatography* (SO₂ and O₃) or *Spectrophotometry* (NO₂). Samplers are reloaded with a freshly impregnated filter, resealed and returned by courier to the site operators.

Table 5. Different samplers' detection limits (source: <http://medias.obs-mip.fr/idaf>)

| Gas | Reproducibility (%) | Detection Limit (ppbv) |
|-----------------|---------------------|------------------------|
| NO ₂ | 3.7% | 0.3 |
| SO ₂ | 17.4% | 0.1 |
| O ₃ | 7.9% | 0.1 |

The passive sampling monitoring network

The air concentration data network for this research is designed to measure – at remote sites – the pollution originating from the main pollution centre in South Africa, the industrial Highveld area of Mpumalanga Province. Geographically, the industrial Highveld is centered on the Mpumalanga Highveld. Additional areas included in the project measurement zone besides the entire Mpumalanga Province are the upwind and downwind areas indicated in Figure 1.

The area of concern comprises a square, with a gridded network chosen to give appropriate and equal coverage by the monitoring sites. The meridians and parallels crossing within the study square are used to determine the posi-

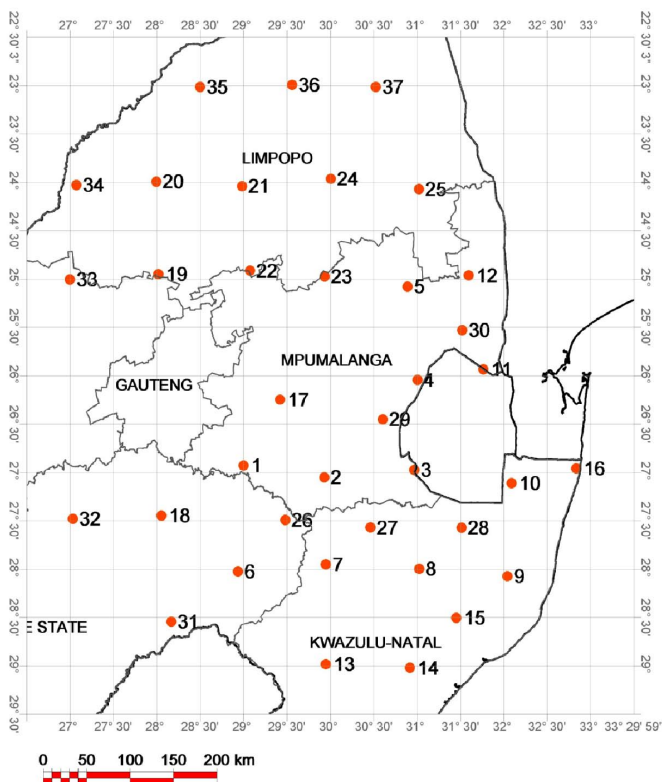


Figure 4. Location map of all 37 sites for passive monitoring network, with site reference numbers.

tion of most of the monitoring sites. The distance between each site within the grid is usually one degree of latitude/longitude, and in several instances a half a degree. It is critical that the study measurements not be influenced by major local air pollution sources, and so care is taken to position the sites outside of urban centers, industrial areas and any other local point sources. Leeway for setting sites in the field is maximized at 10 minutes of latitude/longitude away from the nominal geo-position (Figure 4).



Figure 5. One of the research project sites in its natural setting (Site # 24, Summerlane Farm, Near Hanearsburg, Limpopo Province).

Servicing of monitoring stations in the field is done by local volunteers who are considered as partners in the project. The effectiveness of the network is dependant on the performance of volunteers and the logistics arrangements for delivering to and returning samples from site operators.

A network of 30 monitoring sites was established and has been operating since January 2005, initially collecting SO₂ data only. This net-

work was extended to include measurements of O₃ and NO₂, starting in August and September 2005 respectively. Seven more inland sites have been added to the network as well.

Critical Concentration Levels

In this study critical concentrations levels of acidic compounds of S and N will be primarily determined as will ground level O₃ in light of its close relationship with its NO_x precursor.

Once the concentration values are obtained and plotted, an interpreted layer is created showing regions of exceedance and those approaching exceedance of current local and internationally recognized standards. The critical gas concentration levels maps will be based on the exceedance of the South African standards (NEMA: AQA 39, 2004), World Health Organisation guidelines (2005) and UN Economic Commission for Europe's Convention on Long-Range Trans-Boundary Air Pollution (CLRTAP, 2004) limits.

Remote Sensing

Remote sensing of tropospheric constituents (trace gases, aerosol and cloud) is a relatively new area of research. The unique location of South African trace gas sources (well separated from any other major regional and global sources) bodes well for the comparison and eventual validation of the trace gas measurements by instruments on-board satellites (Annegarn, pers. com., 2005). This research proposes to utilize available SCIAMACHY images for the study region for comparison and validation of those images against the ground level concentration measurements.

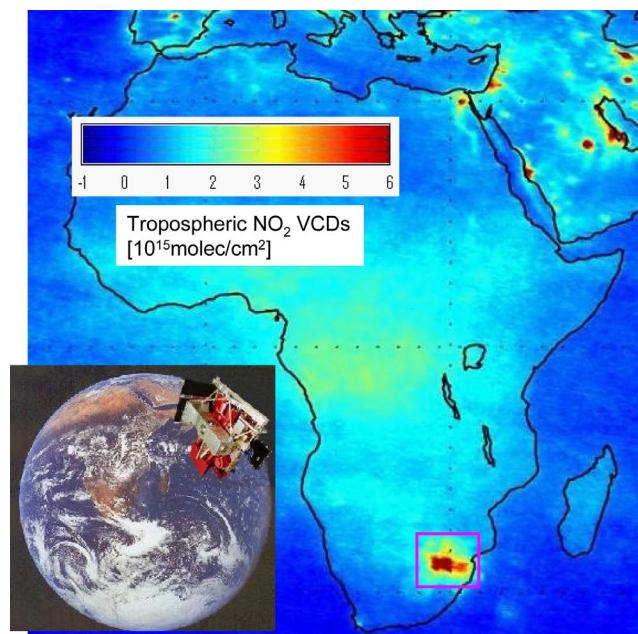


Figure 6. Integrated column NO₂ concentrations over Africa as seen by SCIAMACHY [source: Institute of Environmental Physics, University of Heidelberg, Germany, http://satellite.iup.uni-heidelberg.de/index.php/Data_Products/23/0].

Air Dispersion Model Validation

The measured gaseous concentration fields also provide a unique data set to validate recently available regional scale dispersion models (Figure 7). This will be done either in an electronic form (GIS) subject to the availability of such dispersion modelling results and/or by comparison of tabular and spatial data. Possible significant differences and digression of the results will be recorded and characterized.

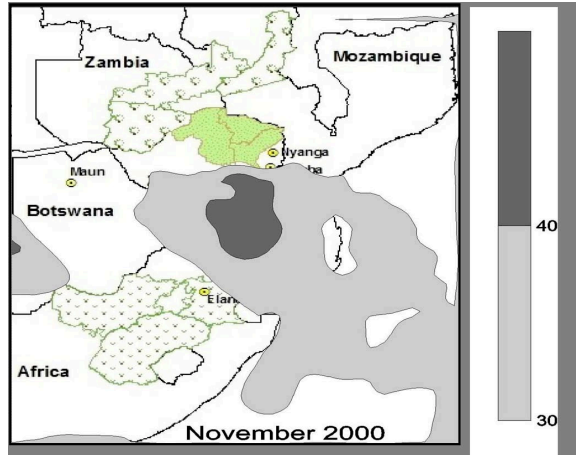


Figure 7. Average daylight concentrations of O_3 (ppb) over CAPIA study region for November 2000 (Source: Van Tienhoven *et al.*, 2006)

Lightning NO_x

Lightning generated NO_x (LNO_x) has been estimated for the year 2002 (Figures 8-9) (Ojelede, 2004). This research will compare its overall cumulative and seasonal levels

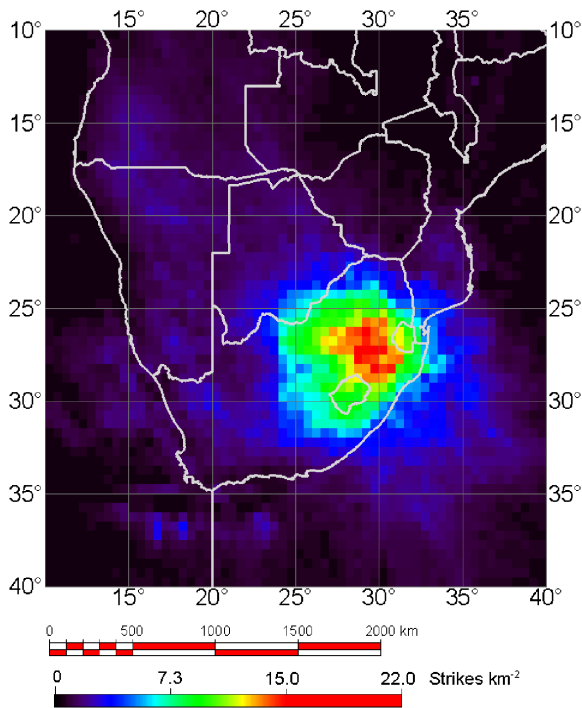


Figure 8. Annual LPATS strike frequencies per km^2 for 2002 (Source: Ojelede, 2004)

with those LNO_x estimates. The concentration levels and deposition loads over both the wet and dry season will be assessed. This in turn will attempt to answer if there are any seasonal maxima, through natural contributions to the regional load of nitrogen oxides. The results will be presented in both numerical and spatial formats.

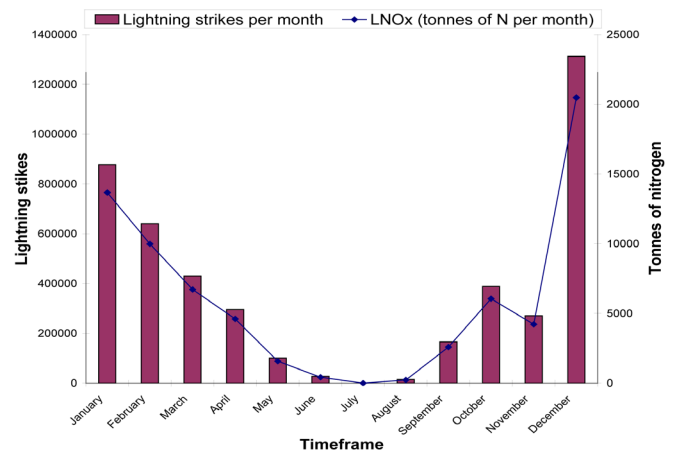


Figure 9. LPATS monthly lightning statistic/ LNO_x monthly budget for 2002 (Ojelede, 2004).

Current Research Status

Samplers providing SO_2 concentration data have been collected and analyzed for the first 21 months of the campaign. The samplers providing O_3 and NO_2 concentrations have been collected and analyzed for a full year. During this project period three field campaigns have been undertaken (January 2005, July and August 2005, and February and March 2006). All sites were visited and the monitors and the samplers within were checked. The field trip team talked to all site volunteer operators in addition to collecting summer grab samples of soils and leaves from all 37 sites.

Soil and Leaf Sampling

This sampling is intended to reveal any increased intake (uptake) of the study gases compounds and would help with determining seasonal as well as spatial variations within local ecosystems. Winter soil and leaf sampling was done during July and August 2005, and summer samples were collected during site visits in February and March 2006. Seventy four soil samples (two per site) and 111 leaf samples (three per site) were collected. Currently those samples are safely stored and still awaiting analysis due to budgetary constraints.

Operational Challenges

During the project, loss of some samplers was expected. Losses due to postal items being lost and due to volunteers not performing were identified as operational weaknesses. The project was designed to allow for some loss. However, as the project has progressed it became clear that the level of these losses was unacceptable.

During the summer field trip (February and March 2006) the project team analyzed all the operational arrangements

and systems. The summer field campaign provided an opportunity to interview all participants in the project in order to establish their views and identify difficulties. It was the project team's assessment that the majority of volunteer operators had performed successfully the assigned field tasks and have embraced their part in the project. Sites where support was sporadic or weak were relocated. Relying essentially on the voluntary participation of people in the study field as community participants, in a partnership with the project team, this project is effectively a private-public partnership, which in more cases than expected is proving successful. Contact with the volunteer participants is now principally by telephone and further communication is maintained through newsletters, emailed or snail mailed as appropriate.

Losses in the postal system were addressed by changing from normal parcel delivery services to registered parcel delivery, and finally to courier service. The considerable increase in costs was justified by reducing sample losses in transit from >40% to less than 10%, which is still not ideal but is tolerable.

Project Expansion

There is an agreement from all project partners to extend the current project into a longer term (two to five years) operation of the observation network. The nature of the research and the size of the study area warrant this extension and there is a proposal to later hand over the operational network from the current university-based project management to the National Research Foundation *South African Environmental Observation Network* (SAEON) for a long-term observation period (five to ten years). It is hoped that ten suitable sites within territories of our southern African neighbours will also be possible to set in the near future.

Results

The samplers received back from 21 (SO₂), 13 (O₃) and 12 (NO₂) month exposures were chemically analyzed [School of Chemistry, North-West University (Potchefstroom Campus)]. Results are reported here in the form of spatial and temporal average isopleths maps for each monitored gaseous species, from the start of monitoring up to and including May 2006 (Figures 10-12).

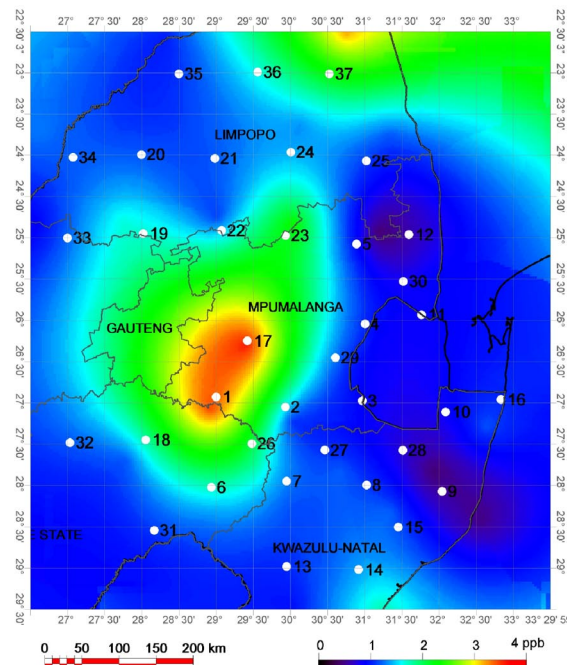


Figure 11. Average concentration isopleths of NO₂ (ppb) from September 2005 to May 2006.

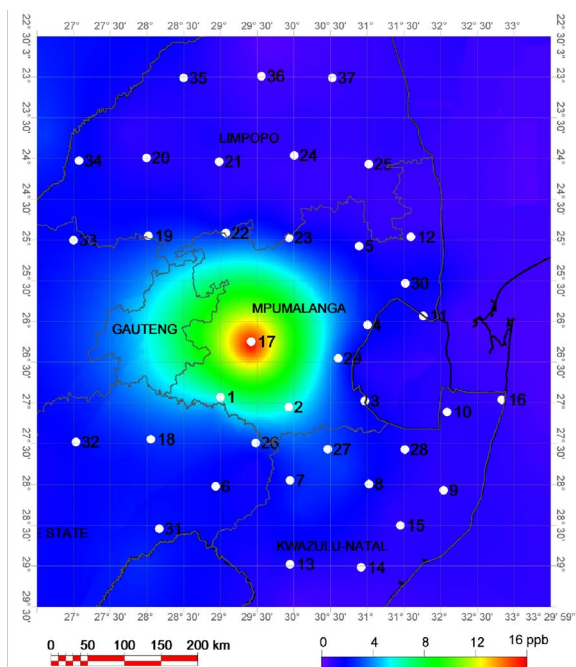


Figure 10. Average concentration isopleths of SO₂ (ppb) from January 2005 to May 2006.

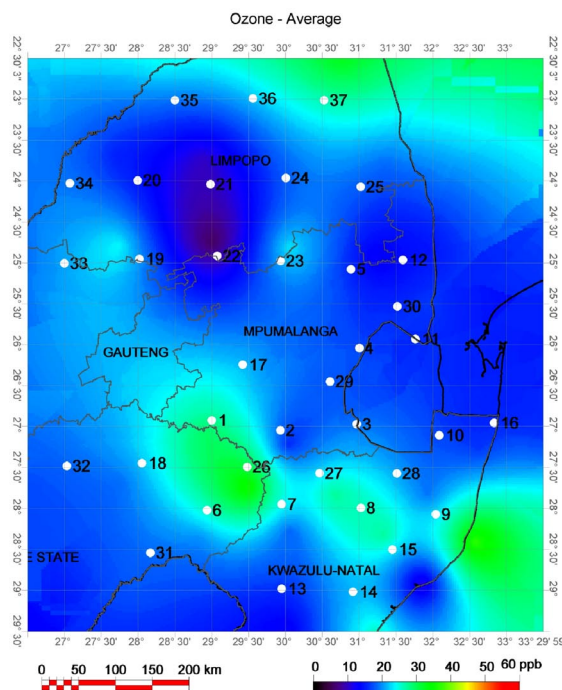


Figure 12. Average concentration isopleths of O₃ (ppb) from August 2005 to May 2006.

Current Assessment

Our overall assessment is that the research had a successful first phase and is on track for the medium- to long-term future phases. Considering the dependence on external factors and circumstances, the project design has proven viable. Data collected up to now are sufficient to perform short-term analyses. From the above plots, several patterns become distinguishable from the visual observation of the concentration distributions for each species.

As expected, a well-concentrated sulphur epicentre coincides with the area of major emission sources on the industrial Highveld area of South Africa (Figure 10). However, the NO₂ spatial distribution field differs by appearing in a broader maximum extending also over the Witwatersrand and Vaal Triangle urban-industrial areas (Figure 11). Conversely, ozone maxima occur to the south and south east of the pollutant source regions (Figure 12). Considering the rather low wind speed regimes prevalent over the Highveld for most of the year and the time-constants for in-atmosphere processing along transport pathways, the observed zones of enhanced ozone are plausible. Further analysis using extended data sets and dispersion models with embedded chemical reactions are needed to interpret these patterns.

It is envisaged that analysis of monthly and annual-average concentration distributions plots in conjunction with a review of synoptic charts over the study region for the studied period will give more understanding of the measured ground level distributions. This distribution analysis is the next step for the project team and will be reported in the following period. This will build a firm foundation for the project, in conjunction with continuous monitoring for the medium and long term data collection and their subsequent analyses.

Expected Results of the Research

It is anticipated that the study will contribute to the assessment of the background and cumulative levels of the specific gaseous industrial pollution from the Highveld. Products will include concentration and spatial distribution maps of acid precursors. Quantitative maps of interpolated near-surface concentrations of trace gas pollutant species (SO₂, NO₂, O₃) over the industrial Highveld and downwind over potentially sensitive residential, agricultural, forestry and tourist regions of South Africa will be produced. These results will specifically allow for definitive quantitative answers regarding the potential risks to the environment posed by the emissions of acid precursors from coal-fired power plants.

Further insights will result from sharing these data through the regional air pollution network (APINA), contributing to our understanding of trans-boundary transport of air pollution.

Scientific Relevance and Contribution of the Research

Previous spatial concentration and assessments of critical levels have not been attempted on this scale in South Africa. The past and recent modelling for the acid precursor gases and ozone can be validated using these data.

This could go some way in supporting the regional policies and environmental management planning in both the public and private domain for mitigation and control measures related to the study region.

Acknowledgments

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Corrosive Marine Atmosphere Investigations in Tanzania

Exposure Sites and Preliminary Results

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Comprehensive gaseous and particulate air pollution studies in Africa are limited and the influence of ambient

air quality on buildings and constructions have not been investigated in the larger part of Africa. The increasing burden of emissions from industry, traffic and coal power plants on ambient air pollution in Africa necessitates a review of previous and current studies of the impacts of air quality in this region. In South Africa a 20-year exposure program focussing on the effect of ambient exposure on various metals and alloys showed that the amount of rainfall, relative humidity, atmospheric pollution, wind speed, solar radiation and the structural design are some of the factors controlling atmospheric corrosion (Callaghan, 1991).

For the study herein, in accordance with aims and guidelines set by RAPIDC¹ and APINA², three different exposure sites were selected in and around Dar-es-Salaam, Tanzania to conduct an investigation on the effects of the marine atmosphere on metal roofing sheets and cement mortar blocks as well as to use the rural and urban data to compare with that of the marine data so as to establish if the air quality is significantly different. Secondly, the data will be used to identify and quantify tracers present in the marine air that could be responsible for the severe degradation observed at the coast. The sites (0, 15 and 40 km from the coastline) represent

¹ RAPIDC=Regional Air Pollution in Developing Countries (<http://www.york.ac.uk/inst/sei/rapidc2/rapidc.html>)

² APINA=Air Pollution Information Network Africa (<http://www.york.ac.uk/inst/sei/rapidc2/apina/apina.html>)

exposure to air influenced by the marine environment, urban and rural areas, respectively. Materials were analyzed for surface changes by means of SEM/EDX³, XRD⁴, micro-Raman spectroscopy, polarised light microscopy, visual inspection and digital imaging. The ambient air quality was determined by bulk elemental analysis of particulate matter (PM) and NO₂, SO₂ and O₃ gaseous concentrations. This article describes the exposure sites' set-up, and it reports some preliminary results showing the air quality and its relation with the meteorological conditions as well as the observed change to the materials' surface in the first two years of exposure.

Background

Atmospheric corrosion of metal and cementitious materials has been known for more than a decade, especially in North America, Europe and parts of Asia (Fuente et al, 2007; Natesan et al, 2006; González et al, 2002; Robergea et al, 2002; Kucera et al., 1993). Atmospheric corrosion which is linked to atmospheric pollution is considered a global environmental problem, especially when incorporating its effects, atmospheric transportation and chemical transformation, from emission sources to deposition many miles away from its source (RAPIDC, 2003).

Natesan et al., 2006, report global studies showing the overall cost of corrosion amounts to at least 4-5 % of the Gross National Product (GNP); they further show that, 20-25 % of this cost could be avoided by using appropriate corrosion control technology, with atmospheric corrosion making the major contribution to this problem.

In Sub-Saharan Africa some individual countries have initiated air pollution monitoring and mitigation efforts. An overarching activity, the Air Pollution Information

Network Africa (APINA), aims to link scientists and policy-makers on issues relating to air pollution. They have, among other things, investigated the effect of atmospheric corrosion on materials such as carbon-steel, painted steel, copper and zinc. Participating countries (number of exposure sites in brackets) include Mozambique (1), Republic of South Africa (2), Tanzania (1), Zambia(2) and Zimbabwe (2). Findings from year one's material evaluations are in the compilation stage in preparation for publication. Levels of the pollutants NO₂, SO₂, NH₃ and of particulate matter (PM) have also been established under the UN/ECE⁵, ICP 8 year's project.

In the past decade, only a limited number of environmental studies have been conducted in Tanzania. Most of these studies have focused on establishing the air pollution levels within the city of Dar es Salaam. However, these studies did not include investigations of the effects of atmospheric composition and/or pollutant levels on building materials in Dar es Salaam and its coastal regions. Rusting of galvanized corrugated iron and aluminum sheets, which are used ubiquitously along the coast of Dar es Salaam, is a major problem. It was not an anticipated problem because metallic coating by Zn and the use of Al are among corrosion control methods. The degradation of the material is probably accelerated by the high relative humidity (67-96 %), high temperature (mean of 26°C), annual rainfall of 1100 mm and the saline atmosphere of the area.

It is envisaged that the findings of this project will not only be of benefit for the local people with regards to suitable materials for construction purposes but will also contribute on a global level towards the monitoring of air pollution and its potential degradation to the environment.



Figure 1. (left to right) Dar es Salaam City centre, Mbezi beach and Magomeni residential areas.

³ SEM/EDX = Scanning Electron Microscope/ Energy Dispersive X-ray

⁴ XRD = X - Ray Diffraction

⁵ UN/ECE, ICP = United Nations / Economic Commission for Europe, International Cooperative Programme

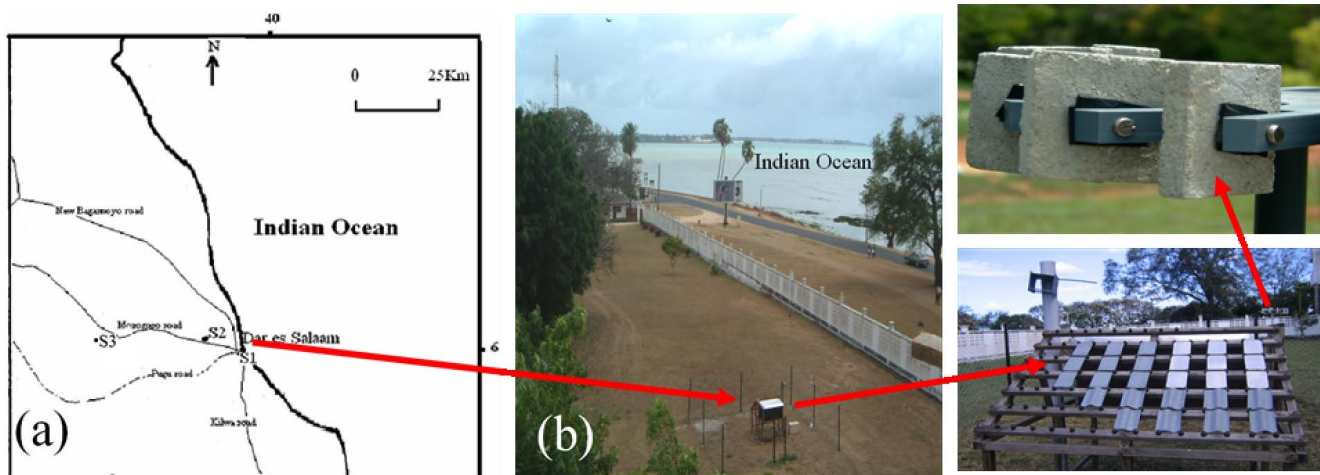


Figure 2. (a) Geographical map of S1, S2 and S3, (b) At site S1, on the coast of the Indian Ocean.

Materials and Method

Galvanized corrugated iron sheets (gauge ≤ 30), aluminum sheets and cement-based blocks, are commonly available, are affordable, are widely used and are recommended by the Tanzania Bureau of Standards (TBS) as building materials in Tanzania. The impact of atmospheric chemistry on each of these materials was investigated as part of our study.

Exposure sites

A preliminary random visual study of different community areas (mostly residential areas and offices within Dar es Salaam and the surrounding coastal regions) was made to assess the viability of the study. Based on this initial survey, the following community areas were short-listed for the study (Figure 1): Dar es Salaam city centre, Mbezi beach (along the coastline), Magomeni, Ubungo and Kibaha (inland from the coast). These were chosen on the basis of their respective building and human populations, and to have a set of sites a range of distances from the Indian Ocean. In the city centre, which is located just offshore, most of the construction comprises cement blocks for superstructures roofed by tiles commonly known as Mangalore Indian red tiles or concrete slabs. The residential areas in and around Mbezi beach are mostly characterized by tiled roofs with metal security bars in front of the windows, as well as metal fences. In Kibaha, houses roofed by tiles are rare since roofing is mostly galvanized corrugated iron sheets. The same applies to Ubungo and Magomeni, where mud houses thatched with grass have been replaced by modern block houses built with cement blocks and roofed by galvanized corrugated iron sheets.

To investigate the influence of the marine environment on the degradation of building materials typically used in the area, three exposure sites were selected: one at the coast (S1) and two located inland, one representing a rural area (S3) and the other an urban area (S2). The areas had different population densities and in all areas a high number of buildings contained the building materials of interest. These were all in a 40 km radius of Dar es Salaam. The sites' selection was based on visual observations indicating the occurrence of corroded rooftops and deteriorated cement-

based walls.

Specimen set-up and exposure rack

Wooden exposure racks of dimensions 1150 x 720 x 1650 mm for the exposure of unsheltered and sheltered samples respectively, were locally constructed. Galvanized corrugated Fe and plain Al sheet samples (15 cm x 10 cm) representing commonly used roofing materials were mounted on a wooden exposure rack with an inclination of 30°, to imitate a typical house roofing design. The cement mortar block samples representing building blocks were mounted vertically to imitate a typical house wall (Figure 2b). These samples were exposed, as prescribed by RAPIDC, in unsheltered conditions, as well as in sheltered conditions, as prescribed by ICP Materials projects. This is to ensure that the contributions of both dry and wet deposition on the various materials are investigated.

Experimental

Metals materials

Galvanized corrugated iron (> 99%) sheet of gauge 30 (thickness 0.2 – 0.3 mm) and flat aluminum (> 99%) all commercially manufactured by Aluminium Africa (Tanzania) were purchased from a hardware store. Representative roofing samples were then cut into 100 x 150 mm sheets and mounted as described previously.

Cement mortar blocks

Fabrication of cement mortar cubes (50x50x10mm) was made possible using Ordinary Portland Cement (OPC) (Table 1), type II, at normal standard Water:Cement:Sand (W:C:S) ratio of 0.4:1:3. The casted cement mortar blocks were then cured for 28 days.

Table 1. Chemical composition of the Ordinary Portland Cement (OPC) used in this study to form cement building blocks.

| SiO ₂ | Al ₂ O ₃ | MgO | Alkali Oxide | CaO | SO ₃ | Fe ₂ O ₃ |
|------------------|--------------------------------|------|--------------|-------|-----------------|--------------------------------|
| 21.1% | 5.8% | 2.5% | 1.4% | 63.9% | 1.7% | 2.9% |



Figure 3. A photo showing a rack of the exposed roof tiles and the PM sampling unit, at site S2.



Figure 4. A photo of the filter unit used in sampling.



Figure 5. The passive sampler configuration used in this study.

Sampling and Analysis of Particulate Matter (PM)

Sampling campaigns for PM were set up as indicated in Figure 3. A filter unit (Figure 4) was used for bulk collection at an air flow rate of 20 l/min for 24 h on nuclepore membrane filters of 0.4 μm pore size and 47 mm diameter. Sampling frequency was twice per season (dry and wet) at 2 m above the mean ground level. PM was analyzed for bulk elemental content.

The calculation of enrichment factors is a commonly used tool that is applied in studies involving elemental bulk analysis of atmospheric aerosols. Enrichment factors indicate whether the observed concentration of a specific element is enriched in comparison to the concentration which would be expected if the element was sampled directly from its natural source. Enrichment Factors (EF) were calculated from the elemental concentrations from sampled particulates with Fe as a reference element based on reported soil analysis results from samples collected in the neighborhood area [Kahebo and Rutabingwa, 2005].

SO₂, NO₂ and O₃ Passive Sampling and Analysis

The gaseous pollutants NO₂, SO₂ and O₃ were sampled with compound-specific radial passive samplers with an exposure time of 14 days at a height of 2m above the ground level. Sampling campaigns were twice per season (dry and wet) and run concurrently with PM sampling. For protection from direct sunlight and rain, the passive samplers were sheltered throughout the sampling duration (Figure 5). Aqueous extracts were analyzed by means of UV-VIS spectrophotometry and Ion Chromatography.

Weather parameters

Meteorological parameters, such as precipitation, temperature, relative humidity and wind (speed and direction) were recorded from the respective nearest weather stations belonging to the Tanzania Meteorological Agency (TMA).

Results and discussions

SURFACE CHARACTERIZATION: After the 1st year's exposure the metal roofing samples showed visible signs of deterioration. The metal surface tarnished progressively from S1 to S3, indicating a more aggressive attack by the marine atmosphere (Figure 6). Signs of pitting corrosion and rust at the lower edges of the metal samples were also observed, and are illustrated in the SEM photo in Figure 7. The mortar blocks did not show any visible deterioration but with micro-Raman spectroscopy it was observed that there was a significant increase in CaCO₃ (Figure 8). This is an indicative of accelerated carbonation in the humid environment, as would be expected.

Particulate Matter

Bulk elemental content was analyzed by means of high energy polarized EDXRF. Concentration profiles are illustrated in Figure 9. The EF values from the detected elements are calculated as: Enrichment factor, $EF = \frac{C(x)/C(\text{ref})}{C_c(x)/C_c(\text{ref})}$

where $C(x)$ is the concentration of an element in the sample, $C(\text{ref})$ is the concentration of reference element in the sample, $C_c(x)$ is the concentration of an element in the crust and $C_c(\text{ref})$ is the concentration of reference element in the crust. These are categorized (Chimidza., 2001; El-Tahir et al., 2005) so that those samples with $EF > 10$ for Cl, Zn, Ca and Pb are of non-crustal origin those with $EF > 10$ for Al, Si, K and Ti are of crustal origin, as illustrated in Figure 10. EF_{Cl} shows a significant decline (8500-4000), illustrating the marine input close to the sea shore, consistent with air mass trajectories for that period, as illustrated in Figure 11. It appears that the PM is more Zn and Pb-enriched closer to urban activities and indicative of increased anthropogenic activities.

Conclusions

The physical set-up seems to be suitable and appropriate for the proposed investigation. Changes in the material's condition and appearances could be detected



Figure 6. Galvanized Fe sample at site S1.

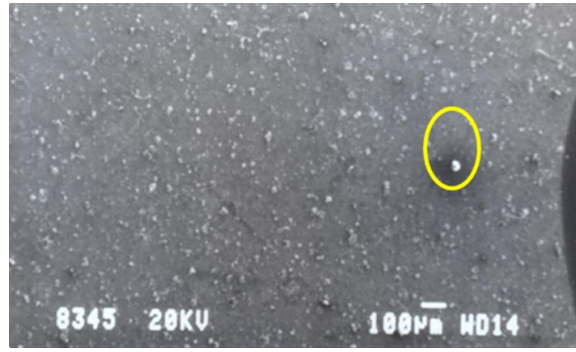


Figure 7. SEM image indicating corrosion products and pit corrosion on the surface of the Galvanized Fe sheet.

from both visual observations as well as by instrumental analysis.

It is also observed that there is a correlation between the elemental concentration distribution and environmental factors, for example, higher concentration of chlorides at coastal site is observed with Indian Ocean considered as its potential source. Furthermore, variation of elemental concentration levels towards inland may as well be accounted to the climatic factors such as, wind velocity, or wet/dry cycles. Also, other elemental concentration variations are linked to the introduction of other emission sources, for instance, anthropogenic activities.

To a certain extent, this allows for comparison to other studies' findings where urban and rural test sites are away from the direct marine atmosphere influence, as relates to the RAPIDC test sites selection guideline.

Thus, the results obtained contributed new data regarding atmospheric corrosion in an area of Africa where no or little data was collected previously and extends current knowledge of this phenomenon. Furthermore, it can form the basis of more extensive studies in the future to establish a database of atmospheric conditions and its subsequent influence on materials' deterioration in previously uninvestigated areas of the world. Value can also be added to the APINA project investigations, currently ongoing in Africa.

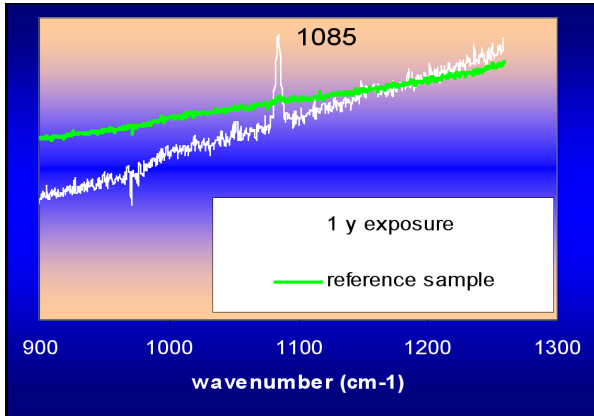


Figure 8. Raman spectra of CaCO₃ in the cement mortar block.

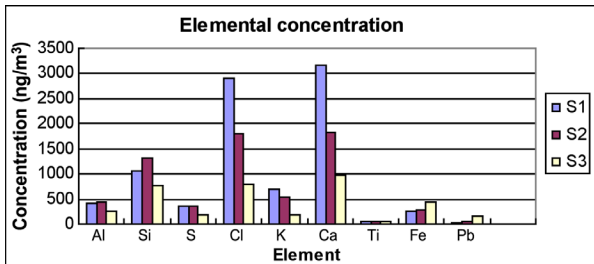


Figure 9: Elemental concentrations of atmospheric particles sampled at sites S1, S2 and S3.

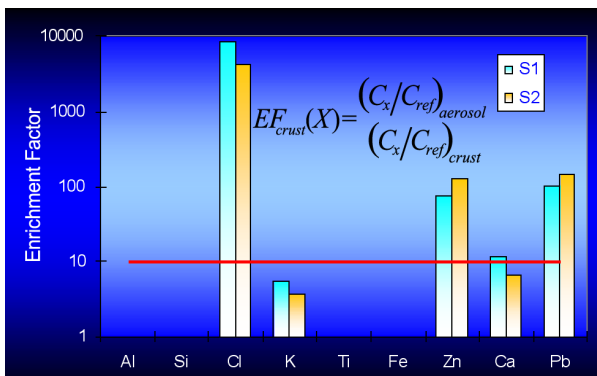


Figure 10. Enrichment Factors for sites S1 and S2, during the dry season.

Acknowledgments

We thank the management of the Ocean Road Cancer Institute, the University of Dar es Salaam and the Kibaha Secondary School for exposure sites provision, and the Universities of Antwerp (Chemistry Department) and Witwatersrand (SEM

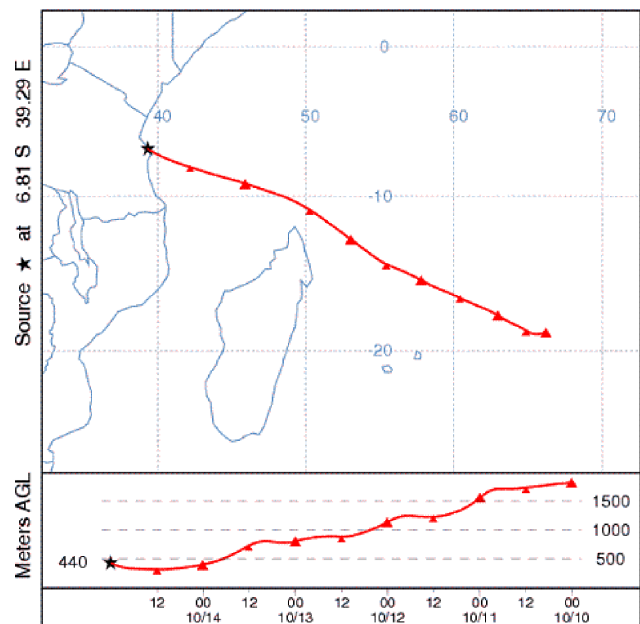


Figure 11. Backward air masses trajectory models for site S1. In October, the wind is typically from the South/South-East, originating over the Indian Ocean.

unit) for the material analyses.

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Atmospheric Chemistry and Climate

A New IGBP-IGAC/WCRP-SPARC Initiative

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Background

A significant part of the current human-induced climate forcing occurs through chemically active species. Changes in climate can lead to changes in the chemical composition of the atmosphere both by altering emissions and through changes in the chemical processes that occur in the atmosphere. The study of climate-chemistry interactions represents one of the most important and, at the same time, most difficult foci of global change research. Further, chemically active species are more amenable to short term manipulations through changes in emissions and are therefore of major policy relevance. Changes in emissions themselves can be brought on by climate trends or a change in climate variability. These factors also feed into the emerging issue of the coupling of climate and air quality, from both scientific and policy perspectives. Provision of high-quality, policy-relevant information on the current state of climate and its possible future states, as well as options for mitigation / control / change / adaptation are strongly dependent on the progress in studies in this area.

In addition, at least two major assessments – The World Meteorological Organization (WMO) Ozone Assessment and the Intergovernmental Panel on Climate Change (IPCC) climate change Assessment – would benefit by

improved understanding of chemistry-climate interactions; such improvements would help society through better information and policy. Significant progress to this end has been made through SPARC's Chemistry Climate Model Validation (CCMVal) effort, which has focused specifically on stratospheric chemistry-climate models and has fed directly into the latest WMO/UNEP International Ozone Assessment. Additional progress can be made by coupling this effort with studies using tropospheric chemistry-climate models and through coordinated studies with tropospheric chemistry-climate and aerosol models. The next IPCC assessment needs better information on emissions and abundances of chemically active constituents to address not only global climate change attribution but also the needed regional emphases for attribution and predictions. Improvements to the representation of these species in chemistry-climate models will also allow for better representation of the climate system in global models.

Because of the importance of chemistry-climate interactions, much work is already going on in this area. Modeling centers are rapidly expanding the scope of their modeling efforts (for example, to include biogeochemical processes at the surface, chemical processes in the troposphere and middle atmosphere, and the impact of each of these on climate). Within IGAC, efforts to date have focused primarily on constraining atmospheric chemistry components and processes through measurements. Within WCRP's SPARC¹ project, the focus has been on modeling activities in the middle atmosphere, with less emphasis on field experiments of chemistry and chemical processes and the troposphere. The steering groups of SPARC and IGAC and their parent organizations, WCRP and IGBP, believe that a synergy would result from a coordinated effort by the SPARC and IGAC communities that focuses specifically on the representation of chemistry-climate interactions in earth system models. This effort would both be informed by inputs from the observational community (in-situ and

¹Stratospheric Processes and their Role in Climate

remote sensing) and would help inform decisions about how to optimize future measurement campaigns.

AC&C Goals

The “Atmospheric Chemistry and Climate Initiative” (AC&C) was endorsed in March 2006 as a joint effort of WCRP and IGBP, with the SPARC and IGAC projects tasked to take the lead in its implementation. An initial scoping meeting for the Atmospheric Chemistry and Climate Initiative (Boulder, Colorado; August, 2006) laid the groundwork for the basic structure and goals of the Initiative. Using this as a starting point, a first set of AC&C activities, more specific goals, and a time-line were set at the 1st AC&C Workshop, which was held in January 2007 in Geneva, Switzerland.

AC&C will be implemented in phases, with the first phase planned to end in 2009. In Phase I, the primary focus will be on improving process representation in chemistry-climate models but the effort will also be useful for Earth system and regional/global air quality models. The role of the AC&C project is coordination, in that it is not an independently funded effort. The mission of AC&C is to help the scientific community to define a common set of scientific themes and facilitate their execution once defined. Some of this coordination will involve defining new activities. Other advances on aspects of this problem will be made by connecting to and influencing the direction of several existing activities linked to AC&C – e.g. the Chemistry-Climate Model Validation activity of SPARC (CCMVal), the global Aerosol model inter-Comparison (AeroCom), the European ACCENT project Model Inter-comParison (ACCENT-MIP), and the Task Force on Hemispheric Transport of Atmospheric Pollutants² (TF HTAP). CCMVal is a model inter-comparison and validation effort for stratospheric chemistry-climate models. Under AeroCom, global tropospheric aerosol models were compared and tested against satellite, lidar, and sun photometer measurements. The ACCENT-MIP effort previously focused on coordinating and comparing IPCC scenarios, contrasting the climate between 2030 vs. 2000 across a suite of tropospheric chemistry-climate models, with an eye toward capturing how climate change might affect air quality (gas species only). This effort has now been extended to encompass the activities of the Task Force on Hemispheric Transport of Atmospheric Pollutants (TF HTAP). The TF HTAP activities focus on understanding and quantifying northern hemispheric transport of gaseous and particulate air pollutants and their precursors from source to receptor region.

For all of these activities and for the AC&C objectives in general, emissions characterization (time-history, uncertainty, etc.) are of critical importance. Therefore, the IGBP-AIMES Global Emission Inventory Activity (GEIA) and other emissions activities will also be associated with the AC&C.

AC&C activities involve:

- identifying a set of science questions around atmospheric chemistry and climate that require integration and synthesis across the projects;
- identifying atmospheric processes that are both important to addressing key science questions and yet which remain poorly understood;
- identifying a set of common diagnostics that can be used to address these uncertainties;
- coordinating the modeling and measurement communities so that the measurements can be used more effectively to constrain the models and so that models can be used to inform measurement planning;
- facilitating the development of improved representations for critical processes; and
- helping to define common model output and data conventions, file formats, and perhaps the establishment of data portals or data centers for model outputs and observations.

At the first workshop in Geneva, leaders from CCMVal, AeroCom, ACCENT-MIP, TF HTAP and GEIA were asked to give overviews of their project, with an emphasis on how the activity relates to the goals of AC&C and on how the AC&C initiative might benefit that activity. There were several resounding messages on this latter point:

1) *Physical system interdependencies*

The science within each project would benefit through cross-fertilization with related projects, given the interdependencies of the different components of the system – for example, the physical connections between the troposphere and stratosphere and between the aerosol and gas phases of atmospheric chemistry. To date, there have been largely separate efforts addressing stratospheric chemistry, tropospheric gas phase chemistry, and tropospheric aerosols. The science and models have recently become sufficiently advanced to address these “compartments” as a single system.

2) *Emissions inventories*

An overarching activity such as AC&C could be used to promote an expansion and a thorough evaluation of emissions inventories. Current emissions inventories are effectively a database, with little or no accompanying meta-data and with little effort toward assessing the characteristics of the inventories for any given application. GEIA has a strong activity in assembling emission inventories relevant to atmospheric chemistry and climate. There are also efforts (e.g. within the TF HTAP community) that focus on emissions for air quality research, and efforts from the socio-economic scenarios community to produce future emissions scenarios. A systematic assessment of uncertainties, harmonization of the emissions data bases, and the addition of meta-data about how the inventory was derived, what applications it is useful for, etc., would be highly beneficial to this community and for the other communities, such as for model evaluation and for process-related field studies. Furthermore by helping to define the criteria by which the modeling community judges these inventories we might influence the methodologies used to produce next generation inventories.

²The Task Force on Hemispheric Transport of Air Pollution is set up under the auspices of the Convention on Long-range Transboundary Air Pollution. More information is available on www.htap.org

3) Common database and tools for model output

Within each of the existing projects (CCMVal, AeroCom, ACCENT-MIP, TF-HTAP) a common data format has been established; however, the chosen data format differs *between* some of these projects. It would be beneficial to have a common data center (even if it were only a “virtual” link), a single formatting standard, a set of visualization tools that could be utilized across the whole community, and a single meta-database with information on the models themselves.

4) Observational/Laboratory data sets

First steps have been made within the existing projects to go beyond model inter-comparisons, e.g. to model evaluation via comparison with observations/measurements. However, in many cases the comparisons help reveal which models might be in error but do not provide information on which model processes are causing the error. In addition, the observations themselves might be biased, making results sometimes inconclusive. Therefore a comprehensive comparison to multiple types of observations/measurements is needed, and these comparisons should be crafted wherever possible to reveal information about the performance of processes in models. Barriers to achieving this include a lack of understanding within each community of what the other needs or can provide and where to go for information; the lack of a centralized, standardized observational database that includes information on data quality/uncertainties and other meta-data; difficulties around mis-matches in the scales (spatial and temporal) of model output vs. measurements; and differences in the model input and output parameters versus those physical parameters that are measured. Under AC&C, some of these barriers could be overcome through coordination of the relevant communities.

5) Need for advanced planning and “legwork” to meet assessment demands

It was clear to the participants that advanced planning, preparation, and initiation of activities help a better assessment and are essential for the science community. There is very little time between assessments and there is a serial nature to the sequence of events that lead to the assessments, so that any planning and preparation is greatly helpful. In some cases, chemistry model runs have to be done even before climate runs are carried out. AC&C provides a pathway for the international scientific community to carry out this early work.

Phase I Activities & Structure

The activities of AC&C will be pursued under the organizational framework given in Figure 1. This framework has been presented to the governing bodies of both IGBP and WCRP; they have both accepted and endorsed this approach. Two existing activities – CCMVal and AeroCom – cover two of the areas of interest under AC&C: stratospheric chemistry and tropospheric aerosols. A third area of interest, tropospheric gas phase chemistry, is covered only in part by other activities (e.g. ACCENT-MIP/TF-HTAP). Thus a new group, dubbed “TropChem”, will act as a liaison to the gas-phase tropospheric chemistry/climate modeling community and will build on existing activities

such as under TF-HTAP and ACCENT-MIP. These three groups will act as the Research Implementation Bodies for AC&C activities. It should be emphasized that the activities of AC&C will comprise *components* of the science pursued by CCMVal and AeroCom and will require buy-in from these projects’ communities. As discussed below, AC&C activities were selected with this in mind.

In Boulder, three thematic areas were decided on for AC&C: the impacts of climate on atmospheric chemistry; the impact of atmospheric chemistry on climate; the impact of climate on air quality. As AC&C is an unfunded activity, improvements in each of these areas will only be made through the efforts of independently funded research groups. Thus its success is contingent on buy-in from the scientific community and on being able to take advantage of already-planned or existing activities/model runs. Given limited time and financial resources, not all aspects of these thematic areas can be addressed simultaneously. Conversely, activities under AC&C – which is by definition a coordination activity – should require the participation of three or more modeling groups and two or more of the Research Implementation Bodies. Thus, discussions in Boulder and at the 1st AC&C Workshop focused on selecting a set of activities based on scientific questions that:

- have a high scientific priority;
- are likely to be tractable;
- are likely to be of interest to/addressed by a large number of research groups;
- as a collection, address a breadth of tropospheric and stratospheric processes critical to chemistry/climate interactions;

Additionally, the policy-relevance of AC&C is recognized. In particular, activities were chosen in consideration of the upcoming WMO Ozone Assessment and recognizing the likelihood of another IPCC assessment, with the desire for the activities of AC&C to inform these assessments.

Using the above criteria, four projects were selected in Geneva for pursuit under AC&C in Phase I of the project (nominally to end in 2009):

Activity 1: A 20-25 year hindcast of tropospheric ozone and aerosols.

Activity 2: Defining what controls the distribution of aerosols/gases in the atmosphere, initially focusing on distributions in the troposphere between 5km and the tropopause.

Activity 3: Better representation of cloud, aerosol, and chemical interactions.

Activity 4: Analyses of sensitivities and uncertainties in the future scenarios for climate models.

In addition, a Data Center Committee was formed to explore issues/options for having a centralized data center/tools under AC&C and an Emissions Harmonization Committee was formed to work with GEIA and HTAP to try and improve the utility of emissions databases for use by models.

It was decided that there would *not* be a centralized effort to consolidate observational data sets as a general task of

AC&C, as this is beyond the scope, capability, and resources of the initiative. Instead, observations and laboratory data will be utilized within each of the four AC&C activities as appropriate for validating and understanding model processes and output and as a way of increasing our ability to represent processes in models. The observational and laboratory community will be engaged in each of the AC&C activities for this purpose.

In Geneva, broad outlines were drawn up for each of the AC&C Activities, and draft steering committees were established. These committees are currently working on the details of how each activity will proceed. Below, brief descriptions of each, as defined at the 1st AC&C Workshop, are given.

ACTIVITY 1: 20 Year Hindcast Simulation

Five or more models would do a 20-25 year “hindcast” to address the questions:

- Can we replicate the observed changes in chemical composition over the past 20 years?
- Can we understand what processes have acted to change the tropospheric chemistry of the atmosphere, particularly ozone and aerosols?

Model results would be compared with each other and with available observations to assess them for where uncertainties lie. The 20 year runs might be designed to incorporate special “focus” or “snapshot” periods; e.g. El Nino vs. La Nina years, periods when field campaign data are available as ground-truth, etc. To the best degree possible, everyone would run with the same anthropogenic emissions. Diagnostics would be designed to reveal information on model processes. Such an experiment can be based on experiences gained from the European RETRO project, in which 3 global models have simulated the period 1960-2000 and investigated changes in tropospheric ozone and its precursors.

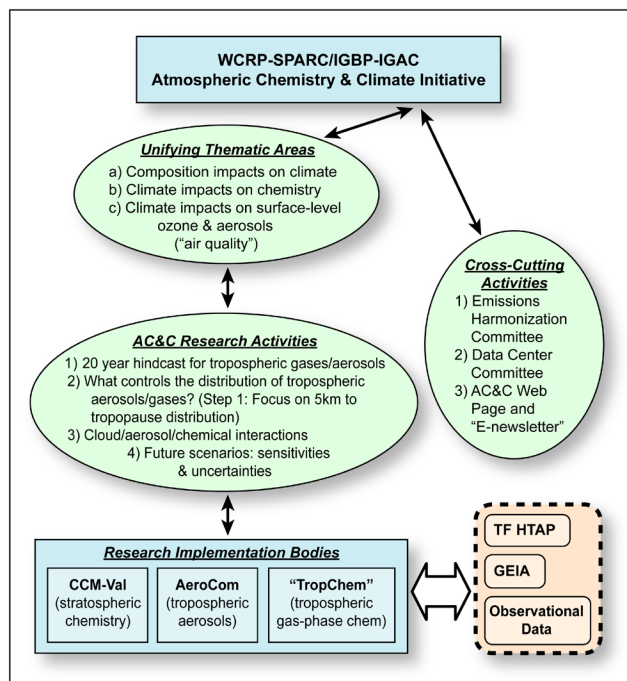
ACTIVITY 2: What controls the distribution of aerosols/gases in the troposphere?

Step #1: Investigate what controls the distribution 5km->tropopause.

This activity would contribute to the next WMO Ozone Assessment. The upper troposphere was chosen as an area of interest because a) the processes that control trace constituents in this region differ from model to model, and this results in dramatic difference in the distributions themselves from model to model; b) species in this altitude range (e.g. ozone, dust, black carbon) can have a significant radiative impact, and may affect other components of the climate system (like cirrus clouds); c) the processes that control the distribution of species in this altitude range (e.g. vertical lofting; wet deposition; cloud processing) also control the long-range transport of these species; and d) the distribution of species in this region depends on and influences processes in the upper troposphere/lower stratosphere.

ACTIVITY 3: Cloud, Aerosol, Chemical Interactions

This activity will address the question: How well can we characterize warm cloud / aerosol interactions in global models, with a specific focus on the interactions with



gas chemistry photochemistry? It will explore the impact of aerosols on atmospheric chemistry through their modification on clouds. This would be done employing a paradigm of controlling iterative sets of parameters (cloud droplet number, etc.) during model runs, slowly adding in links to aerosols and investigating the impacts on chemistry in clouds.

ACTIVITY 4: Future scenarios: Sensitivities & Uncertainties

This activity would contribute to the next IPCC Assessment. The goal here would be specifically to have a better representation of aerosol and chemistry in the next IPCC Assessment Report 5 (AR5; should there be one). This group could define the pre-industrial to present to future scenarios, based on emissions that are consistent with other AR5 runs (to the best degree possible). By running multiple models with constrained emissions, it would be possible to define a “best guess” and uncertainties. The model runs would further be designed to explore sensitivities to model processes.

More details on these activities will be given in a future journal article. A web page for AC&C will also provide updates on progress on the initiative:

<http://www.igac.noaa.gov/ACandC.php>

If you are interested in participating in one of the AC&C activities described above or have other input, please contact Sarah Doherty of the IGAC Seattle Core Project Office (igac.seattle@noaa.gov).

Boulder AC&C Initial Planning Meeting Attendees:

Mary Barth (NCAR-ACD), Guy Brasseur (NCAR-ACD), William Collins (U.K. Met Office), Sarah Doherty, (IGAC Core Project Office), Anne Douglass (NASA Goddard), Veronika Eyring (DLR), Andrew Gettelman (NCAR-ACD), Claire Granier (Service d'Aeronomie CNRS), Didier Hauglustaine (LSCE, CEA-CNRS), Peter Hess (NCAR-

ACD), Kathy Hibbard (*AIMES Core Project Office*), Larry Horowitz (*NOAA-GFDL*), Ivar Isaksen (*Univ. Oslo*), Jean Francois (J.F.) Lamarque, (*NCAR-ACD*), Phil Rasch (*NCAR-ACD & IGAC co-chair*), A. R. Ravishankara, (*NOAA-ESRL & SPARC co-chair*), Michael Schulz (*LSCE, CEA-CNRS-IPSL*), Ted Shepherd (*Univ. Toronto*), Drew Shindell (*NASA-Goddard*)

1st AC&C Workshop Attendees:

Yves Balkanski, Gufran Beig, Isabelle Bey, Bill Brune, Philip Cameron-Smith, Mian Chin, Martyn Chipperfield, Bill Collins, Frank Dentener, Sarah Doherty, Veronika

Eyring, Arlene Fiore, Savitri Garavait, Claire Granier, Volker Grewe, Ann Henderson-Sellers, Peter Hess, Hans-Werner Jacobi, Terry Keating, Jean Francois Lamarque, Kathy Law, Mark Lawrence, Hong Liao, Jennifer Logan, Tatsuya Nagashima, Thanos Nenes, David Parrish, Vincent-Henri Peuch, Joyce Penner, David Plummer, Michael Prather, Phil Rasch, Sebastian Rast, A. R. Ravishankara, Andreas Richter, Jose Rodriguez, Vladimir Ryabinin, Martin Schultz, Drew Shindell, David Stevenson, Kengo Sudo, Christiane Textor, Michiel van Weele, Oliver Wild, André Zuber.



Network for the Detection of Atmospheric Composition Change

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Introduction

The Network for the Detection of Atmospheric Composition Change (NDACC) is a set of more than 70 high-quality, remote-sensing research stations for observing and understanding the physical and chemical state of the stratosphere and upper troposphere. NDACC data is also aimed at assessing the impact of stratosphere changes on the underlying troposphere and on global climate. NDACC was formerly known as the Network for the Detection of Stratospheric Change (NDSC) which commenced observations in 1991 with the aim of monitoring changes in stratospheric ozone and the substances which lead to its depletion. The recent change of name reflects the considerable widening of the network's aims to the detection of trends in overall atmospheric composition and to understanding their impacts on the troposphere and establishing links between climate change and atmospheric composition.

Information on the NDACC can be obtained from the NDACC home page (www.ndacc.org). This site provides a link to the public ftp database and also includes maps of the NDACC sites, instrument information, available data sets, and contact information. This short article is to help inform IGAC scientists of the existence of NDACC and the availability of data.

The principal goals of NDACC are:

- To study the temporal and spatial variability of atmospheric composition and structure in order to provide early detection and subsequent long-term monitoring of changes in the physical and chemical state of the stratosphere and upper troposphere; in particular to provide the means to discern and understand the causes of such changes.
- To establish the links between changes in stratospheric ozone, UV radiation at the ground, tropospheric chemistry, and climate.

- To provide independent calibrations and validations of space-based sensors of the atmosphere and to make complementary measurements.
- To support field campaigns focusing on specific processes occurring at various latitudes and seasons.
- To produce verified data sets for testing and improving multidimensional models of the stratosphere and the troposphere.

These aims require high quality data and, accordingly, since the inception of the NDSC, much effort has been invested into instrument inter-comparison, calibration, and software validation. The result is a self-consistent data set suitable for addressing the above aims. In order to permit the widest possible usage, all data over two years old is made publicly available.

Example Data

The NDACC database consists of ground-based and sonde observations of ozone and other key species in atmospheric chemistry and climate. Ground-based column observations are obtained with Dobson, UV-visible, microwave, and Fourier Transform infrared (FTIR) spectrometers. The list of species observed includes not only typical 'stratospheric' species such as O₃, HCl, ClONO₂, ClO, NO, NO₂, HNO₃, HF etc. but also species of tropospheric relevance such as CO, OCS, HCN and CH₄ and other hydrocarbons. Ozone and temperature profiles are also obtained using lidar and sondes. In addition to these chemical measurements, the NDACC database includes observations of UV flux at the ground and supporting meteorological data.

An example use of NDACC data of relevance to both the troposphere and stratosphere is shown in Figure 1. This shows ship-based FTIR profile observations of COS and CO. These cruise data are also part of the NDACC database. The observations revealed large COS mixing ratios near the tropical tropopause, which correlated with, for example, high CO (Notholt et al, 2003). Many other studies are starting to apply NDACC data to tropospheric issues.

Accessing the Data

NDACC data over 2 years old is publicly available. Access to this data is available through an anonymous ftp server (details on www.ndacc.org). Users of these NDACC data

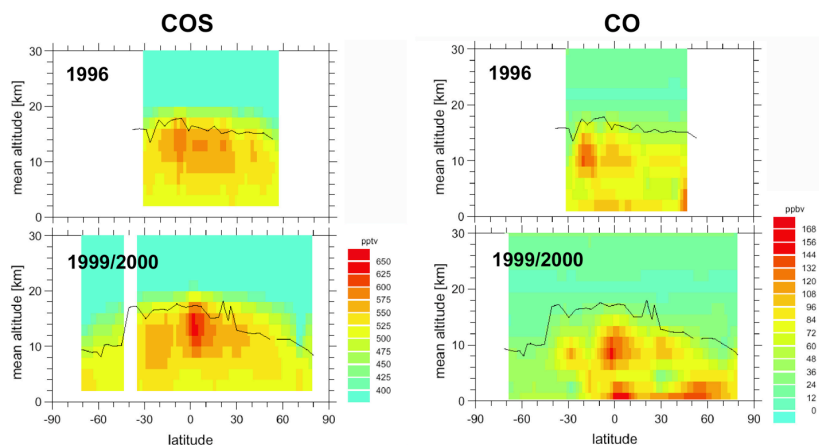


Figure 1. Latitude cross-sections of retrieved volume mixing ratios of COS and CO from cruises using ship-borne FTIR solar absorption spectrometry. The FTIR retrievals allow observations of the trace gas profiles with a vertical resolution of ~4 km. See Notholt et al., (2003) for details.

should consult the on-line documentation and reference articles to fully understand the scope and limitations of the instruments and resulting data. Scientific users of the data are encouraged to contact directly the appropriate NDACC Principal Investigator (listed in the data documentation on the web page) to ensure the proper use of specific data sets.

The PI can also be contacted if you wish to use data less than 2 years old.

Acknowledgments

Because of its worldwide dimension, the NDACC has been recognized as a major component of the international atmosphere research program. As such, it has been endorsed by national and international scientific agencies, including the United Nations Environmental Programme (UNEP) and the International Ozone Commission (IOC) of the International Association of Meteorology and Atmospheric Physics (IAMAP). It has also been recognized by the World Meteorological Organization (WMO) as a major contributor to WMO's Global Ozone Observing System (GO3OS) within the frame of its Global Atmosphere Watch (GAW) Programme.

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Notholt, J., et al., Enhanced upper tropical tropospheric COS: Impact on the stratospheric aerosol layer, *Science*, 300, 307-310, 2003.

Announcements



10th IGAC 2008 Conference:

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Bridging the Scale in Atmospheric Chemistry: Local to Global





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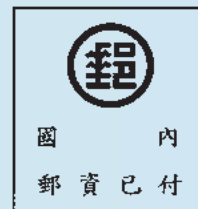
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