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## Non-Linear responses and surprises: A new Earth System Science initiative

by Pep Canadell

We live in a world where rapid and unpredicted system responses can result from even very small changes in forcing conditions or from gradual and continuous environmental change. Such nonlinear dynamics is the product of complex interactions and feedbacks and/or from simple biochemical and structural threshold-like responses that cascade throughout a system. This type of nonlinear behavior is characteristic of the way ecological systems function, yet, tremendous effort has been geared towards describing complex nonlinear responses as more readily tractable linear ones. Linear thinking is very much entrenched in the way policy-makers perceive environmental change and, consequently, ways to manage it (e.g., climate change will alter production of terrestrial ecosystems in a proportional manner).

A deeper understanding of the nonlinear nature of systems will contribute to increasing our capacity to predict future ecosystem behavior under novel combinations of resources and forcings that brought about environmental change, and to detect early in advance low-probability/high-catastrophe events, such as the terrestrial biosphere's flip from C sink to C source or the collapse of production systems.

IGBP, building upon an early initiative from GCTE (Global

Change and Terrestrial Ecosystems), has initiated a new research focus to study biospheric responses to global change that involve rapid nonlinear changes and thresholds. The initiative is very much in its early stages of development but some of the emerging objectives are:

- To identify processes and resource gradients prone to generate nonlinear responses, and therefore, unexpected system behavior under future

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environmental change.

- To understand when nonlinear responses are important to scaling issues in time and space.
- To quantify transfer functions between forcings and responses for verifying and parameterizing predictive process models.
- To develop new numerical tools and experiments to study nonlinear responses (e.g., thresholds).
- To formulate new hypotheses derived from math-

ematical treatment of model systems (e.g., spatial scale-dependent effects of perturbations) that may be tested using reconstruction methods.

- To use knowledge of nonlinear phenomena to better guide policy development for adaptation strategies and mitigation to environmental change.

A scientific committee has been assembled to prepare a first workshop that will bring together relevant research on this

field from various core projects of IGBP. The committee is made up of Ian Noble (GCTE), Jim Reynolds (GCTE), John Dearing (PAGES), John Schellnhuber (GAIM), Paul Crutzen (IGBP-SC, IGAC), Roger Pielke (BAHC), TBA (JGOFS), and Pep Canadell (coordinator). Inquiries about this new activity can be sent to Pep Canadell.

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## BIOME 300: Understanding the impacts of human activities on land cover over the past 300 years

by Robert S. Thompson

**Although land clearance and anthropogenic increases in greenhouse gases have drawn much attention during the past decades, few people are aware of the significant impacts of humans on landscapes prior to the 1900s.**

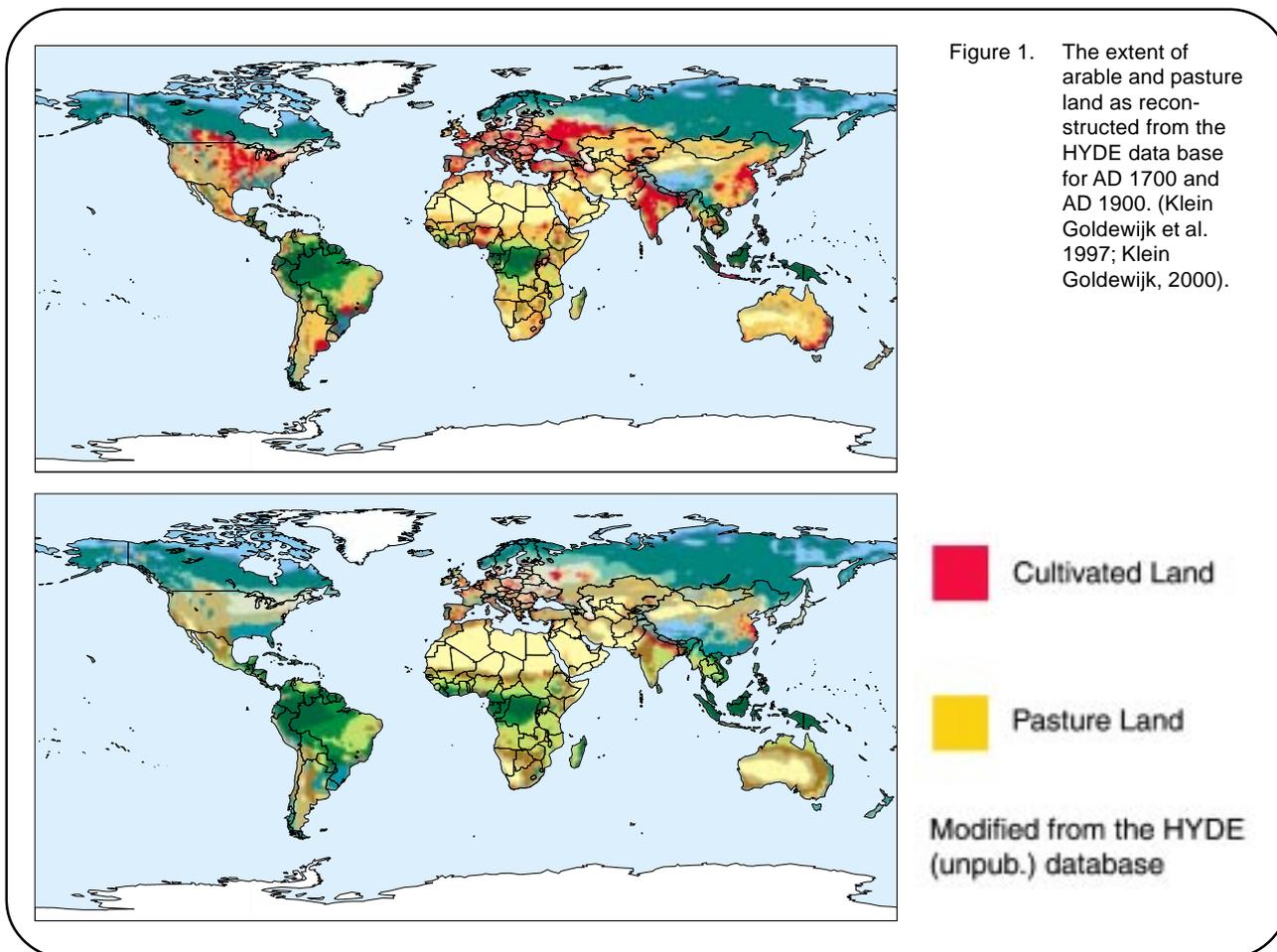
In areas with long-standing agricultural civilizations, such as China, India, the Middle East, Europe, parts of Africa and the Americas, much of the arable land has been modified/controlled by humans for centuries or millennia. Even in areas without large agricultural populations, humans used fire to modify vegetation. The spread of Europeans and their land use practices in the last several hundred years significantly impacted the landscapes around the world, as concurrent population increases and population movements (due to colonization and the slave trade) brought much more of the world under human management. Human impacts accelerated with the coming of the

industrial revolution, but were significant in many parts of the world prior to the 1800s.

These land use and land cover changes affected many aspects of the Earth surface-atmosphere system, including the carbon budget, ecosystems, and hydrology. However, these factors are poorly understood within the current IGBP framework. PAGES has focused on long-term climatic changes and their associated impacts, whereas LUCC has focused largely on landscape impacts of human activities during the last few decades. To address this shortfall, PAGES and LUCC, in collaboration with GAIM have initiated BIOME 300, a joint effort to reconstruct global patterns of land use and associ-

ated land cover changes since A.D. 1700. This work will involve a unique intersection of the interests and skills of archaeologists, historians, economists, demographers, ecologists, paleoecologists, palynologists, as well as ecological, climatic, and carbon-cycle modelers.

An organizational workshop for BIOME 300 was held in Bern, Switzerland from the 5th through the 7th of March, 2000, under the auspices of PAGES, LUCC, and the Bern Geobotanical Institute. This meeting brought together over 40 researchers from nearly 20 countries in Europe, Asia, and the Americas to discuss which methods and data are most appropriate to the detailed reconstruction of past land-cover changes. Under the leadership of Frank Oldfield (PAGES), Emilio Moran (LUCC Focus Group 1), Rik Leemans (GAIM/LUCC), Andre Lotter (Switzerland), and



Marie-Jose Gaillard (Sweden), this group has two primary objectives. The first is to devise a plan for the production by June of 2001 of revised maps at 50 year intervals since A.D. 1700 showing the global and regional coverage of areas of major human activities, including estimates of population size, degree of land clearance, and areas of croplands, orchards, pastures, etc. The HYDE database (ref.) provided the starting point of this effort.

The second objective is to begin the task of building a community for a longer-term effort to reconstruct and understand human impacts on the landscape over the past several millennia. This effort includes discussions of the methods that should be included, the data sources available in the various regions, and the perceived gaps in data coverage and interpretive methods.

A steering committee for this longer term research agenda growing out of the BIOME 300 meeting was established at the end of the workshop, that includes: Frank Oldfield (PAGES, Switzerland), Emilio Moran (LUCC, USA), Carol Crumley (USA), Marie-Jose Gaillard (Sweden), Rik Leemans (GAIM/LUCC, the Netherlands), Charles Redman (USA), Shinya Sugita (Japan), and Bob Thompson (USA). This committee established targets for the initial phase, including a Symposium session at the Fall Meeting of the American Geophysical Union entitled: "*Past land cover, human activities and climate variability: future implications*". Most of the members of this group will also hold a steering meeting at the fall AGU and give further momentum to the next stages of the initiative which, in the short term, will focus on the prepara-

tion of a 'fast track' product in time for the Amsterdam Congress, as reported in the upcoming LUCC and IHDP Newsletters.

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# Last Ice Age global ocean and land surface temperatures: The EPILOG initiative

by R.R. Schneider, E. Bard and A.C. Mix

The IMAGES EPILOG working group (<http://www.images.cnrs-gif.fr/wgroups.html>) was formed in December 1997 in order to establish a new and comprehensive look at the paleoenvironments of the last Ice Age. The major aim of this working group is to foster a revision of global reconstructions of the Ice Age Earth. This will be carried out by assembling international groups of paleoclimatologists to discuss and review the progress made for paleoenvironmental reconstructions for the last Ice Age during the last two decades since the completion of the CLIMAP (1981) LGM project.

Following this premise, an international workshop was held at the HANSE Institute for Advanced Studies, Delmenhorst, Germany, May 3-6, 1999, entitled "Global Ocean and Land Surface Temperatures during the last Ice

Age". The workshop focused on the presentation and discussion of oceanic and continental temperature compilations using new or improved techniques for the estimation of absolute surface temperature values around

20,000 years before present. By bringing together marine and terrestrial paleoclimatologists, as well as paleoclimate modelers, the workshop provided an important step forward in our assessment of Last Ice Age climate. Discussion centered on glacial temperature data which have evolved significantly based on a suite of investigations over the past two decades since the presentation of CLIMAP (1981) paleotemperature maps. A new and comprehensive synthesis is essential both in its own right and in order to provide boundary conditions for climate models. Evaluation of the sensitivity of these climate models to changing

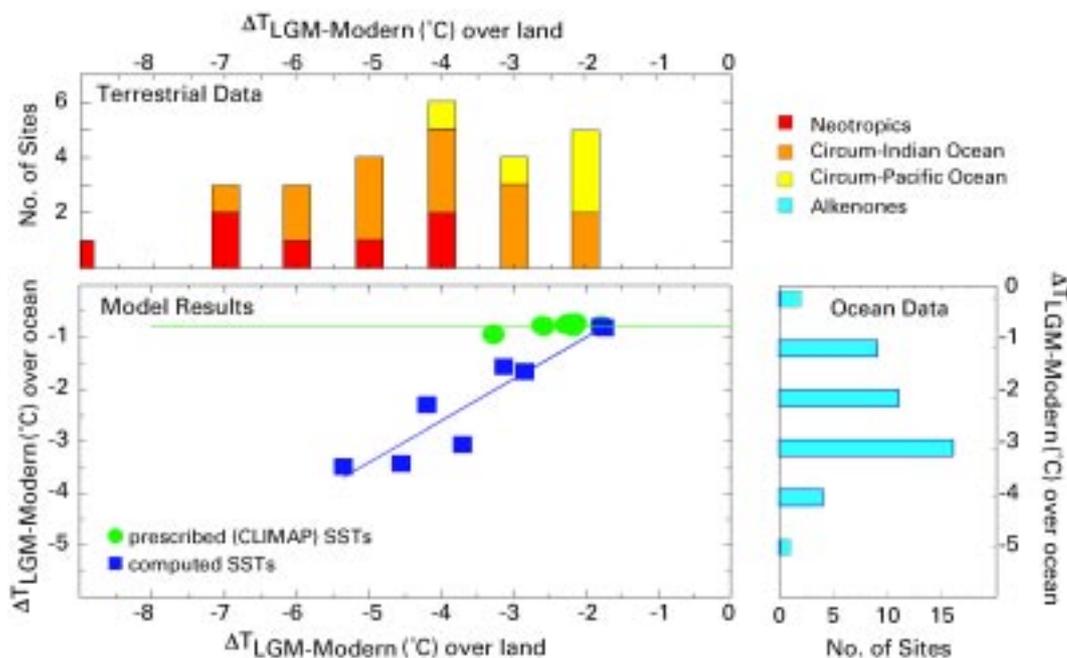


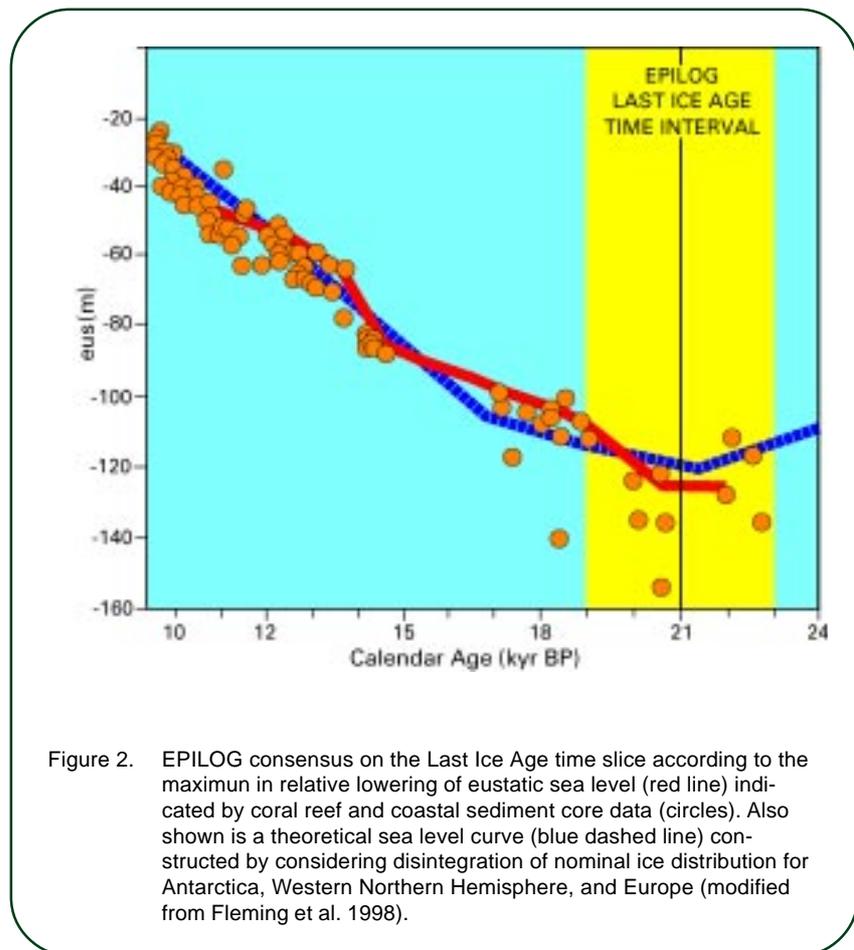
Figure 1. Comparison of Last Ice Age tropical temperature decrease for the continents (Farrera et al. 1999, 32°N, 33°S) and for the surface ocean (Rosell-Melé et al. 1998, alkenone data) with AGCM results either using prescribed CLIMAP (1981) sea surface temperatures (green dots) or by computing those (blue squares) coupling a surface mixed layer to the atmospheric general circulation model (Pinot et al. 1999) (Figure from Kohfeld and Hamson 2000).

boundary conditions is facilitated by comparison of modeling results with reconstructions of past features such as global surface temperatures.

The major tasks identified for this first EPILOG workshop were:

1. To establish an international consensus on the definition of the "Ice Age" or "LGM (Last Glacial Maximum)" time slice for orientation of any further syntheses considering this period.
2. To discuss and critically evaluate the potential of both commonly used and new techniques for estimation of past surface temperatures in the ocean and on the continents.
3. To initiate a new synthesis of Ice Age surface temperatures and to promote the generation of new global and regional compilations. In this context it was agreed that standard criteria are required for the application of the different paleotemperature methods as well as for procedures for data archiving in a manner which best facilitates access to the new data by the entire scientific community.

The above topics were comprehensively discussed in plenary and group discussions amongst 51 scientist from Australia, Canada, France, Germany, Great Britain, Spain, The Netherlands, and USA. Short individual oral and poster presentations introduced the entire audience to the need for finding a marine-terrestrial consensus for the Last Ice Age time slice, new and improved methods for



paleotemperature estimation, and new regional and basin-wide data syntheses available for the ocean and the continents. Furthermore, the outcome of recent AGCM experiments for the LGM (e.g. PMIP) were presented. In this context, the discussion focused on differences in results amongst model runs with prescribed CLIMAP (1981) surface ocean temperatures and those employing new global data sets, e.g. the TEMPUS (Temperature Mapping using Unsaturated Ketons, Rosell-Méle et al. 1998) compilation, or, as shown in Figure 1, those with computed surface ocean temperatures (PMIP, <http://www-pcmdi.llnl.gov/pmip/index.html>, see also Pinot et al. 1999). New terrestrial temperature syntheses (e.g. Farrera et al. 1999) were also taken into account. International paleoclimate data archives such as BIOME 6000,

WDC-A and PANGAEA, including the IMAGES data curation, were also discussed. These archives have the potential to serve as electronic platforms for EPILOG time slice temperature data archiving, synchronisation and dissemination in the future.

The workshop participants agreed on a new definition of the Ice Age time slice which is defined by the period of maximum globally integrated ice volume in accordance with glacial eustatic sea-level low stand. As shown in Figure 2, the EPILOG Last Ice Age time slice ranges from 19,000 to 23,000 calendar years, centered at 21,000 calendar years BP, the time interval that spans the period where coral reefs and drilled coastal sediments indicate greatest eustatic sea-level low stand (Fleming et al. 1998).

Since the rationale of this first EPILOG workshop evolved from

ongoing international discussion on the uncertainties in the CLIMAP (1981) reconstructions of Last Ice Age surface ocean temperatures and sea-ice extent, a major part of the workshop time was spent on extensive discussions of the advantages and shortcomings of the different transfer-function or modern analog techniques applied to sediment assemblages

of planktonic foraminifera, diatoms and radiolaria, as well as to dinoflagellates. In this context it was heavily debated whether attributing the entire magnitude of variations in microfossil assemblages solely to a change in surface ocean temperature is appropriate or if changes in nutrient conditions and

surface layer structure must be considered as major control mechanisms. As an alternative or complementary approach participants also examined the relatively new geochemical methods of alkenone paleothermometry and Mg/Ca elemental ratios in foraminifera. The consensus was that these innovative methods already provide valuable paleotemperature information, however, their calibration should be improved by considering season and depth habitat of the living organisms which produce the organic markers or calcareous shells. For the alkenone method the European TEMPUS project and an international workshop held in Woods Hole in October 1999 dedicated to the application of alkenones in paleoceanography (Eglinton et al. submitted) have already promoted broad acceptance of the method. The use of elemental

ratios in foraminiferal shells is, however, still at the beginning of a more general application in time slice temperature reconstructions at global or even regional scales. With respect to the latter it was therefore agreed to start a new initiative for an international laboratory calibration project on foraminiferal Mg/Ca ratio as a quantitative

**“...for the marine environment major efforts are still needed to step forward from various individual and research group initiatives producing regional or basin wide compilations to a new multiproxy global temperature synthesis for the Last Ice Age.”**

paleotemperature indicator.

During the course of the workshop it became evident that for the marine environment major efforts are still needed to step forward from various individual and research group initiatives producing regional or basin wide compilations to a new multiproxy global temperature synthesis for the Last Ice Age. As a first step in this direction it was envisaged that existing surface sediment data sets for the calibration of the various transfer equations should be made accessible to the different research groups applying these methods in different ocean basins for comparison. This should allow significant progress in statistical evaluation of the performance of different transfer-function and modern-analog techniques on the same calibration data set as well as comparison with results from the

geochemical methods. These calibration-related and technical issues will be paralleled by initiatives already active in compiling new temperatures for the Last Ice Age, such as the GLAMAP (Glacial Atlantic Ocean Mapping, <http://www.pangaea.de/Projects/GLAMAP2000>) and TEMPUS projects.

For the continents a new synthesis for the Last Ice Age has recently been presented by Farrera et al. (1999). This “21 ka tropical paleoclimate synthesis” ([http://www.bgc-jena.mpg.de/bgc\\_prentice/start1.html](http://www.bgc-jena.mpg.de/bgc_prentice/start1.html)) focuses on the terrestrial evidence for tropical climates at 21,000 calendar yr B.P. The synthesis includes, amongst other parameters, estimates of Mean Annual Ground Temperature (MAT)

based on noble gas paleothermometry and speleothems and estimates of Mean Temperature of the Coldest Month (MTCO) based on pollen response. The latter is reconstructed applying “surface or modern” analog methods, shifts in treeline or montane-vegetation belts using local lapse-rate calculations, and changes in pollen-based biome reconstruction using physiological temperature limits on individual biomes. In context of this synthesis EPILOG workshop discussions concentrated mainly on the problems in dating land records, on methods for land data regionalisation in order to produce temperature maps, and on better reconstruction of past lapse rates. It was further recommended to consider more marine sediment cores adjacent to desert and tropical rainforest regions as pollen archives which have the

advantage of recording climate information from both environments in the same material, thus

**“The workshop ... served as a basis for new collaborative research between paleoclimatologists working on land and in the ocean, and modelers.”**

allowing direct evaluation of land-ocean linkages. This could also help to better constrain the timing of climate change on land due to often better age control in marine records. As is true for the marine community, a lot of compilation work and methodological harmonisations are still needed before global maps of Last Ice Age continent temperatures can be presented in the near future.

In conclusion, the workshop served to set up an international agreement for the temporal range of the Last Ice Age time slice and provided a forum for extensive discussion of recently gained paleotemperature data and conflicting views on these new

data. The workshop also served as a basis for new collaborative research between

paleoclimatologists working on land and in the ocean, and modelers. Following this encouraging start in 1999, the second EPILOG workshop is planned to be held in October 2000 in order to reconcile “Global Ice Sheets and Sea Level during the Last Glacial Maximum” (<http://www.images.cnrs-gif.fr/workshops.html>).

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## Scenarios of Global Biodiversity

by Osvaldo E. Sala and Terry Chapin

**Human activities are having a major impact on the biological diversity of the Earth. The magnitude of the biodiversity change is so large and the effect on the functioning of ecosystems and on their ability to provide goods and services to humans so important that biodiversity change is now considered an important global change in its own right.**

Humans and their various activities are responsible for a large fraction of recent extinctions. For example, 20 % of the species of mammals and 10 % of the species of birds are currently threatened by extinction with current levels of extinction

100 to 1000 times greater than background levels (1).

Scientists, policy-makers, and people in general are familiar with the idea of scenarios of the state of the environment. Scenarios of future conditions have been developed for various components of our environment, ranging from the concentration of carbon dioxide in the atmosphere to changes in precipitation and temperature. Our societies increasingly use those scenarios when analyzing their behavior and the consequences for the future. The first attempts of policy-makers at addressing global issues are rooted in the different scenarios provided by the scientific community. Although it has been clear for some time that human activities drastically change biodiversity and that those changes have major effects on the well-being of humans, scenarios for biodiversity change, comparable with scenarios for climate change and greenhouse gases, were not available. GCTE Focus 4 in collaboration with the InterAmerican Institute for Global Change Research (IAI) and the National Center for Ecological Analysis and Synthesis, University of California, Santa Barbara (NCEAS), launched an activity to develop scenarios of biodiversity change for the year 2100 (2).

The exercise focused on developing scenarios of biodiversity change for 10 terrestrial biomes and freshwater ecosystems for the year 2100. The first step in building the biodiversity scenarios was to identify the major drivers of biodiversity change at the global scale: changes in land use; climate; nitrogen deposition; atmospheric concentration of carbon dioxide; and biotic exchange (the deliberate or accidental introduction of species into an ecosystem). The second step was to assess the expected change of each one of these drivers in the various

biomes, based on available global scenarios for each driver. The next step consisted of estimating the sensitivity of each biome to a unit change of each driver. The expected change in biodiversity for each biome resulted from the product of the expected change of each driver times the sensitivity of each biome to changes in that driver. Finally, the exercise presented three scenarios for the expected change in biodiversity for each biome. The three scenarios differed in the assumptions used to estimate the interactions among drivers. The simplest scenario assumed no interactions among drivers and consequently the change in biodiversity for each biome resulted from the sum of the effects of each driver. The second scenario assumed an antagonistic interaction among drivers and therefore the driver with the largest impact overshadowed the effects of the other drivers. In this case, the total biodiversity change for each biome was equal to the effect of the driver with the largest effect. Finally, the third scenario assumed synergistic interactions among drivers and was represented as the product of the effects of each driver.

A synthesis of the results from the exercise of building the biodiversity scenarios have been published early this year in a journal article (2) and a book with a more thorough biome-by-biome analysis will be published soon (3). Land-use change appeared as the driver with the largest effect on

biodiversity when all biomes were averaged (Figure 1). The kinds of land-use change that are expected to occur in the next 100-years range from the transformation of

“...those areas reverting to their potential natural vegetation will not compensate for the simultaneous losses that will occur in other parts of the world that support a different flora and fauna.”

forests or grasslands into agricultural land to the more subtle changes resulting from selective logging or grazing intensification. Land-use change affects biodiversity mainly by reducing habitat availability for species. Scenarios of land-use change also

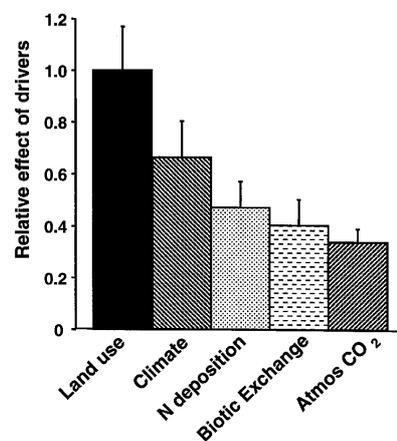


Figure 1. Relative effects of the five most important drivers of biodiversity change for the year 2100 as resulting from the biodiversity scenarios (2). Biodiversity change was calculated as the product of the expected change of each driver times the biome sensitivity to a unit change of the driver. Values in this figure are averages across biomes that were made relative to the maximum value which was land-use change. Thin bars are standard errors and represent variability among biomes.

highlighted areas of the world where reforestation or abandonment of agricultural land will occur.

However, those areas reverting to their potential natural vegetation will not compensate for the simultaneous losses that will occur in other parts of the world that support a different flora and fauna. The second driver after land-use change, at the global scale, is climate change (Figure 1). The major effect of climate change on biodiversity is expected to occur as a result of warming at high latitudes. Nitrogen deposition, biotic exchange, and atmospheric CO<sub>2</sub> follow land use and climate in their effects on biodiversity. Nitrogen deposition will negatively affect plant species diversity and the associated animal diversity. Numerous studies have shown that increases in nitrogen availability results in a reduction of species diversity as species with higher relative growth rate take advantage of the high nitrogen availability and outcompete the slower growing species (4). Changes in the competitive balance are translated first into local extinctions that, if the phenomenon is extended in space or time, may result in global extinction. The mechanism that accounts for the effect of increased atmospheric CO<sub>2</sub> on biodiversity is similar to that of nitrogen deposition. CO<sub>2</sub> enrichment has differential effects on plant species and those that are benefited most will outcompete first and later may drive to extinction the other species that show a smaller response to CO<sub>2</sub>.

Biodiversity scenarios

show large differences among biomes in the causes of future changes in biodiversity (Figure 2). Tropical and southern temperate forests will be affected mostly by a single driver (land-use change) whereas the effects of the other drivers will remain low, either as a result of small expected change of the driver or as a result of low

sensitivity. Similarly, arctic ecosystems will be affected by a single driver in this case, climate change (warming is expected to be most pronounced at higher latitudes). In contrast, biomes such as savannas, grasslands, and Mediterranean ecosystems will be affected significantly by a combination of drivers. Freshwater

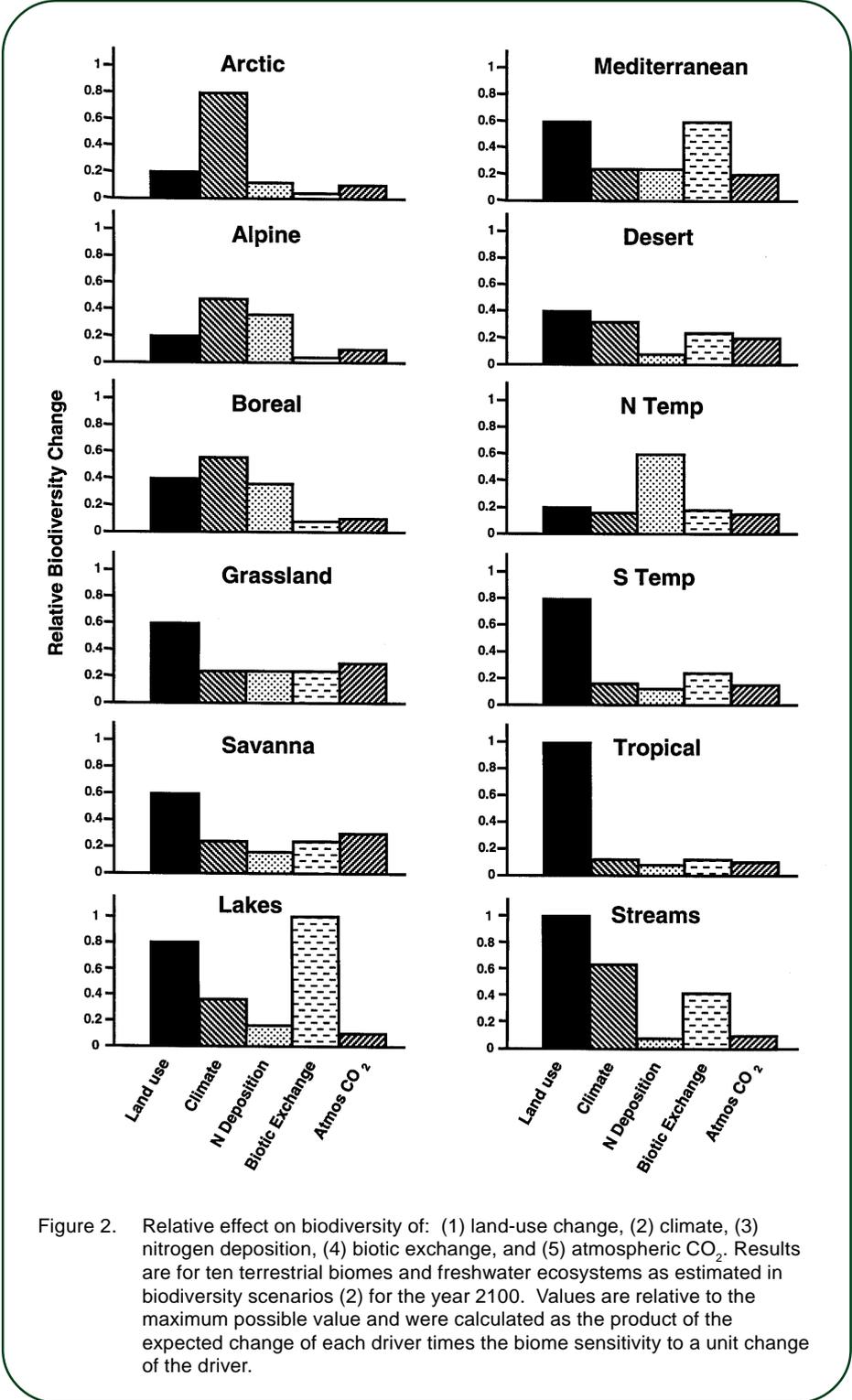


Figure 2. Relative effect on biodiversity of: (1) land-use change, (2) climate, (3) nitrogen deposition, (4) biotic exchange, and (5) atmospheric CO<sub>2</sub>. Results are for ten terrestrial biomes and freshwater ecosystems as estimated in biodiversity scenarios (2) for the year 2100. Values are relative to the maximum possible value and were calculated as the product of the expected change of each driver times the biome sensitivity to a unit change of the driver.

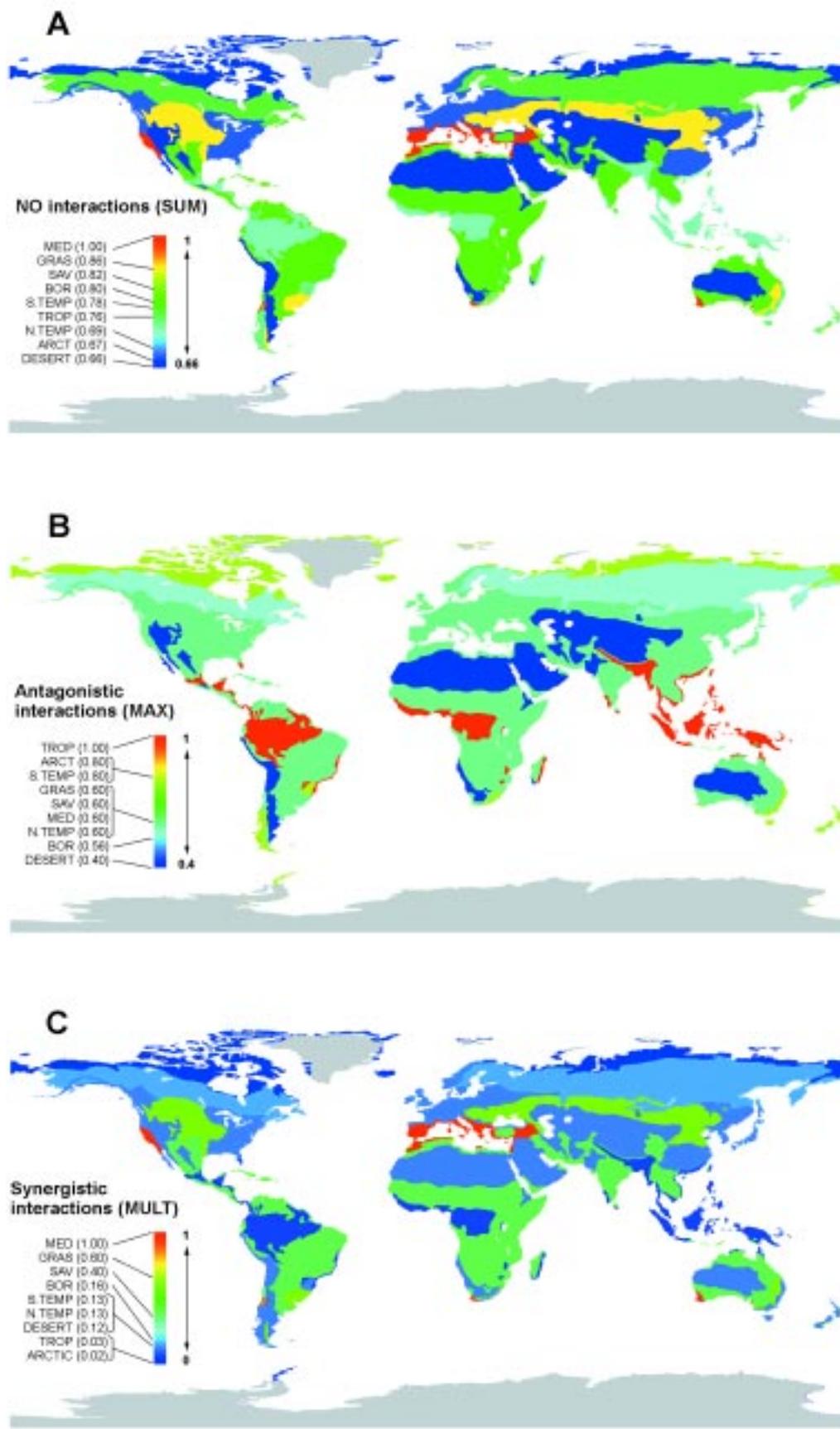


Figure 3.

Maps of the expected change in biodiversity for the year 2100 as estimated in the biodiversity scenarios (2). (A) No interactions among the drivers of biodiversity change. The total change per biome was calculated as the sum of the effects of each driver for each biome. In turn, the effect of each driver was calculated as the product of the expected change in driver times the biome sensitivity. (B) Antagonistic interactions among drivers. Total biodiversity change for each biome equals the driver effect with the maximum value. (C) Synergistic interactions. Total biodiversity change for each biome is calculated as the product of the effects of each driver. The numbers in parenthesis represent the total change in biodiversity relative to the maximum value projected for each scenario. The biomes are MED Mediterranean ecosystems, GRAS Grasslands, SAV Savannas, BOR Boreal forest, S. TEMP Southern temperate forest, TROP Tropical forest, N. TEMP Northern temperate forest, ARCT Arctic ecosystems, DESERT Desert.

ecosystems will be affected largely by land use, biotic exchange, and climate change. Humans settle preferentially around waterways that consequently receive large quantities of nutrients, sediments, and pollutants. The effect of biotic exchange is larger in freshwater ecosystems than in terrestrial ecosystems because lakes and streams have been the target of extensive intentional and unintentional introductions of species.

The predicted total biodiversity change for each biome will depend on the expected change of each driver, the biome sensitivity, and the assumption about the interactions among drivers. The exercise provided three scenarios based on assumptions of no interactions, antagonistic interactions, and synergistic interactions (Figure 3). Which of the three assumptions is the most plausible? Examples of synergistic interactions among drivers are abundant. For example, fragmentation and biotic exchange occurring simultaneously in a tropical forest have a larger effect on biodiversity than the sum of the individual effects of the two drivers. Similarly, the interaction between the effects on biodiversity of CO<sub>2</sub> and N deposition is very likely to be synergistic based on the experimental results showing a larger CO<sub>2</sub> response when N availability was experimentally high (5). However, under extreme conditions, the assumption of antagonistic interactions among drivers may be the most appropriate. The drastic effects of land-use change may not be further enhanced by N deposition or CO<sub>2</sub>. For example, increased CO<sub>2</sub> or N availability may not damage biodiversity more in a patch of tropical forest that already has been logged, burned, plowed, and planted with a crop and in the

process has destroyed the habitat of all native plant species and of most of the associated animals and microorganisms. The understanding of the interactions among the drivers of biodiversity is so poor that each of the three scenarios seems plausible. The three scenarios presented in this exercise represent the boundary conditions and consequently the

**“In all three scenarios, grasslands and Mediterranean ecosystems are located among the biomes that will experience the largest biodiversity change.”**

response of most biomes will lie between the synergistic and the antagonistic scenarios.

The no-interactions scenario indicates that Mediterranean and grassland ecosystems will be the biomes with the largest biodiversity change for the year 2100 primarily due to the moderate-to-large effect of all drivers (Figure 3A). In contrast, arctic and desert ecosystems will experience a relatively small change. The synergistic-interaction scenario amplifies the differences among biomes but still yields a ranking of biomes similar to the no-interactions scenario (Figure 3B). Tropical forests appear with a relatively small effect on biodiversity because only one factor, land use, will have a large effect while the other drivers will have moderate-to-low effects. The antagonistic-interaction scenario yields a different ranking of biomes with tropical forest as the biome that will experience the largest biodiversity change (Figure 3C). The top location of tropical forests in this scenario results from the large expected change in land use for this biome and the high sensitivity that all biomes have to

land-use change. In all three scenarios, grasslands and Mediterranean ecosystems are located among the biomes that will experience the largest biodiversity change. The three scenarios yield similar results regarding the location of savannas that always show a moderate change, and deserts, arctic, and north temperate forests that, in all cases, will experience a relatively low biodiversity change. In contrast, tropical and south temperate forests show different locations in the ranking of biomes depending on the scenario chosen. Tropical and temperate forests seem quite sensitive to the assumption about interactions whereas the other biomes are much less sensitive.

Improvements in the scenarios of climate change, land use, and carbon dioxide concentration in the atmosphere will directly improve the results of biodiversity scenarios. Moreover, a better understanding of the interactions among drivers and

Continued on page 19.

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## The cleansing capacity of the atmosphere

Many people consider the atmosphere's role in global change to be primarily associated with climate. However, human activities are also profoundly affecting the chemistry of the atmosphere in its own right, irrespective of the greenhouse properties of trace gases. One of the most important features of the atmosphere is its 'cleansing ability', its capability to transform a wide range of gases emitted from the Earth's surface. The primary chemical species responsible for this cleansing ability is the hydroxyl radical, OH.

In this series of articles from the IGAC (International Global Atmospheric Chemistry) project, we examine how human activities are changing the concentration of OH in the atmosphere, and the implications for the atmosphere's cleansing capacity.

## Is the "cleansing capacity" of the atmosphere changing?

by Guy Brasseur and Ron Prinn

**The capacity of our atmosphere to remove a chemical injected into it is conveniently expressed as the inverse of the lifetime of the chemical. This lifetime, over which a molecule, atom, free radical, or aerosol particle remains in the atmosphere, is determined in turn by a number of atmospheric chemical and physical processes. For example, certain pollutants are rapidly removed from the atmosphere either because their chemical reactivity is high or because they are highly soluble in water. Others that are chemically stable and relatively insoluble in water (such as the chlorofluorocarbons) may remain in the atmosphere for years or even decades. In this case, they are transported to remote Polar Regions and to the middle atmosphere where they can play important roles in chemistry (such as that of ozone depletion).**

The atmosphere is an oxidising medium. Almost all hydrogen-containing gases of natural and anthropogenic origin are oxidised by the hydroxyl (OH) free radical, a species often referred to as the "detergent" of the atmosphere. Other oxidation processes include reactions with ozone (O<sub>3</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), the nitrogen trioxide free radical (NO<sub>3</sub>), and halogen species. Hydrogen peroxide, for example, converts sulphur dioxide to sulphuric acid in cloud and rain droplets at low pH, and hence contributes to the formation of acid precipitation. The NO<sub>3</sub> free

radical plays a significant role at night, primarily in polluted areas. Halogen compounds (including chlorine and bromine) contribute to oxidation primarily in the marine boundary layer and above ice sheets in the Polar Regions.

The rate at which oxidation occurs varies widely from species to species. For example, the oxidation of methane typically takes nine years, while that of isoprene takes less than a day. Thus, even though the magnitude of the surface emissions of these two hydrocarbons is similar, their atmospheric burdens differ by

several orders of magnitude.

The rate at which chemical compounds are eliminated from the atmosphere is very often not determined by the precipitation rate, but by the rate at which they are oxidised into a water-soluble compound. This oxidation rate therefore plays a central role in many global environmental problems. An important issue is to quantify any potential change in the oxidising power of the atmosphere that may have resulted from human activities (Thompson, 1992).

Over the past decade and century, the oxidising power of the atmosphere may have changed. For example, the increasing penetration of solar UV light in response to stratospheric ozone depletion and the increased emissions of NO<sub>x</sub> and nonmethane hydrocarbons from combustion tend to increase ozone and OH concentrations in the troposphere. Conversely, the increase in carbon monoxide emissions, which have also resulted from increased biomass and fossil fuel burning since the pre-industrial era, tend to reduce the O<sub>3</sub> and OH abundances. Similarly, increases in the methane abun-

dance due to increases in cattle, rice, and natural gas usage should have contributed to a decrease in the global OH concentration and therefore in the oxidising power of the atmosphere.

Since there is presently no instrumentation for regional to global scale observations of tropospheric OH, the change in the oxidation power of the atmosphere cannot be directly monitored. Estimates must therefore rely primarily either on model calculations or deductions using measurements of compounds destroyed by OH. Model calculations suggest that global tropospheric levels of OH have probably decreased significantly since the pre-industrial era. The quantitative value of this decrease varies from model to model, however, with figures ranging from 3% in the model of Lelieveld and Van Dorland (1995) to 22% in the model of Roelofs et al. (1997). Intermediate values of 9% are provided by Wang and Jacob (2000) and 10-15% by Crutzen and Zimmermann (1991). Earlier estimates based on one-dimensional models suggested a decrease ranging from 10 to 30% (Thompson, 1992). The general consensus from modelling studies is that, despite the large increase in the emissions of carbon monoxide, hydrocarbons and nitrogen oxides, and the stratospheric ozone depletion during the 20<sup>th</sup> century, the partially offsetting effects of these factors implies that the globally averaged concentration of OH has remained relatively constant. Decreases probably do not exceed 20% (Wang and Jacob, 2000).

The analysis of the methylchloroform (CH<sub>3</sub>CCl<sub>3</sub>) observations performed since 1978 at several surface monitoring stations of the Atmospheric Lifetime Experiment/Global Atmospheric Gases Experiment/Advanced Global Atmospheric

Gases Experiment (ALE/GAGE/AGAGE) (Prinn et al., 2000 and references therein) provides an indirect method to derive trends in the global concentration of tropospheric OH.

Methylchloroform's sources, which are purely anthropogenic, are believed to be known very accurately. By combining the estimates of these sources with the CH<sub>3</sub>CCl<sub>3</sub> measurements, little change in the OH density was deduced by Prinn et al. (1995) for the period 1978-1994 (specifically 0.0±0.2% per year, 1s error range). A similar study by Krol et al. (1998) suggested a small increase in the OH density (0.46±0.6% per year, full error range) from 1978-1993.

In summary, recent analyses suggest that the oxidising power of the atmosphere has remained relatively constant since the pre-industrial era, with a decrease in the OH concentration, and hence in the lifetime of major primary pollutants (or greenhouse gases like methane) that has not exceeded 20%. On shorter time scales, the abundance of OH may have changed rather substantially, however; for example, in response to rapid ozone depletion in the stratosphere, fluctuations in tropospheric water vapor, or in the emissions of nitrogen oxides or carbon monoxide (see, e.g., Madronich and Granier, 1992; Granier et al., 1996). Future changes in the oxidising power of the atmosphere will depend on future anthropogenic emissions and hence on future economic development and population growth.

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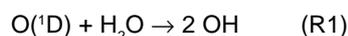
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# Tropospheric OH: In the beginning

by Hiram Levy II

**Prior to 1971, most of the troposphere, with the exception of a few uniquely polluted regions, was thought to have a relatively benign photochemistry with the only exceptions being some possible ozone reactions. The oxidizing of trace gases, such as CO and CH<sub>4</sub>, was thought to occur only in the stratosphere. For reviews from this period, see Bates and Witherspoon [1952], Junge [1963], and Cadle and Allen [1970]. Our theoretical understanding of the role of hydroxyl radicals (OH) in tropospheric chemistry evolved from earlier (1950s and 1960s) work in both the stratosphere and the polluted boundary layer.**

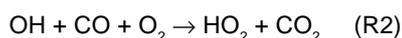
Although an H<sub>2</sub>O–O<sub>3</sub> chemical mechanism was developed in the 1950s for the mesosphere [e.g., Bates and Nicolet, 1950], it was not until the 1960s that Engleman [1965] identified the reaction that became essential to OH production in the troposphere:



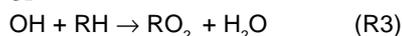
This reaction and the earlier H<sub>2</sub>O–O<sub>3</sub> reactions from the mesosphere were used to construct a H<sub>2</sub>O-based catalytic destruction mechanism for stratospheric O<sub>3</sub> [Hampson, 1964; Hunt, 1966], but revised O(^1D) quenching rates greatly reduced its stratospheric significance. The work of this period, which just precedes Crutzen's development of the NO<sub>x</sub> catalytic destruction scheme [1970], is nicely summarized by Nicolet [1970].

At the same time that stratospheric research was identifying the key source of OH in the troposphere, studies of smog chemistry were beginning to focus on O<sub>3</sub> formation from hydrocarbon oxidation in polluted environments (for a detailed discussion of the early research, see P.A.

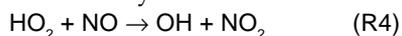
Leighton, Photochemistry of Air Pollution, 1961). In the 1960s, smog chemistry research began to consider OH. Westberg and Cohen [1969] and Heicklen, Westberg and Cohen [1971] then proposed a catalytic mechanism to explain the O<sub>3</sub> formation observed in smog chambers, which would also provide an important component of the photochemical mechanism for the troposphere as a whole.



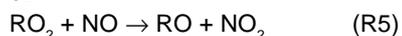
or



followed by



or



However, the rate coefficients for R4 and R5, which were the key, had not yet been measured. While estimates ranged from 1 × 10<sup>-11</sup> (cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup>) to 2 × 10<sup>-15</sup>, they needed to be at least 5 × 10<sup>-13</sup> to match the smog chamber data. At about the same time Weinstock [1969] argued, based on carbon isotope studies, that tropospheric CO had a short lifetime (~0.2 year) and that most of its destruction must occur in

the troposphere. One of the suggested destruction paths was OH oxidation (R2), but no general tropospheric source of OH was known.

Motivated by Weinstock's 1969 paper, Levy [1971] constructed a O<sub>3</sub>-H<sub>2</sub>O-CO-CH<sub>4</sub>-NO<sub>x</sub> photochemical mechanism for the background or clean troposphere which combined: 1. The O(^1D) production of OH (R1) from the stratosphere with tropospheric H<sub>2</sub>O levels; 2. The Heicklen, Westberg and Cohen catalytic OH–HO<sub>2</sub> cycle, the known NO<sub>x</sub> oxidation chemistry, and the CH<sub>4</sub> oxidation cycle; and 3. Existing "measurements" of background surface NO<sub>x</sub> levels of a few ppbv. This mechanism predicted for the summertime mid-latitude boundary layer, noon OH concentrations of ~3 × 10<sup>6</sup> molecules cm<sup>-3</sup>, a CO tropospheric lifetime of ~0.2 year, and daytime H<sub>2</sub>CO mixing ratios of 2 ppbv. McConnell *et al.* [1971] then extended the mechanism to include the oxidation of H<sub>2</sub>CO and predicted a large natural source for CO from the completed CH<sub>4</sub> oxidation path. Chameides and Walker [1973] and Crutzen [1974] next employed the peroxy radical oxidation of NO to NO<sub>2</sub>, first devised to explain O<sub>3</sub> formation in smog chambers, to produce a global tropospheric source of O<sub>3</sub> that was fueled by CH<sub>4</sub> and CO oxidation and driven by a NO–NO<sub>2</sub> catalytic cycle. By 1974 the basic tropospheric photochemistry, which predicted OH concentrations of ~10<sup>6</sup> molecules cm<sup>-3</sup>, large chemical production of tropospheric O<sub>3</sub>, and OH control of CH<sub>4</sub> and CO destruction as well

as  $\text{NO}_x$  conversion to  $\text{HNO}_3$  was qualitatively well developed (see a review by Levy [1974] for a summary up to that point). While those early calculations remain remarkably reasonable, the estimates of background  $\text{NO}_x$  were much too high and the estimated rate coefficients for R4 and R5 were much too low. Fortunately these errors compensated.

For the rest of the 1970s there was a rapid development and quantification of the chemical mechanism and OH's reactive role in the troposphere. Kineticists began to measure many of the key rate coefficients that had previously only been estimated. Most important of these was the measurement by Howard and Evenson [1977], which increased the rate coefficient for R4 from an estimated  $5 \times 10^{-13}$  to a measured  $8 \times 10^{-12}$ . At the same time, sophisticated measurement devices were being developed for the trace gases in the troposphere, the first of which was a chemiluminescence NO instrument that lowered the detection limit to the pptv

range and measured background  $\text{NO}_x$  levels of 0.1 ppbv or less (see McFarland *et al.* [1979] as an example of this development). Attempts to make direct measurements of tropospheric OH also began. Theoretical calculations improved quantitatively with the inclusion of more accurate rate coefficients and increased in complexity with the addition of non-methane hydrocarbon oxidation. A more realistic global picture of OH and its impact on other trace gases was also developing through the use of approximate 2-D global models. It is not possible to accurately capture the explosion of theoretical, laboratory and field studies of tropospheric chemistry during the 1970s and early 1980s in this short introduction. Rather, I have selected a few examples that provide an idea of the evolution of our theoretical and observational understanding during this period: Fishman *et al.* [1979]; Oltmans [1981]; Logan *et al.* [1981]; Gregory *et al.* [1985]; Beck *et al.* [1987]; Liu *et al.* [1987]; Fehsenfeld *et al.* [1988]; Crutzen [1988].

The following articles examine the current state of our understanding of tropospheric OH and its role in tropospheric chemistry. William Brune discusses our current understanding of OH chemistry and its interactions with  $\text{NO}_x$  and  $\text{O}_3$ . Hans-Peter Dorn and Andreas Hofzuma-haus review the current state of local OH measurements and their intercomparison with photochemical models. Ivar Isaksen focuses on the important relationship between OH and  $\text{CH}_4$  and the impact of this relationship on our current understanding of  $\text{CH}_4$  sources and lifetime. Leonid Yurganov examines the role of OH in the current inter-annual variations and trends in CO. And Yuhang Wang reports on recent measurement and modeling studies that attempt to constrain global tropospheric OH concentration and its past and future trends.

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## OH and $\text{HO}_2$ : Sources, interactions with nitrogen oxides, and ozone production

by William Brune

**Hydrogen oxides and nitrogen oxides are two basic components of atmospheric chemistry. Hydrogen oxides ( $\text{HO}_x$ ) consist of the hydroxyl radical (OH) and the hydroperoxyl radical ( $\text{HO}_2$ ). Nitrogen oxides ( $\text{NO}_x$ ) consist of nitric oxide (NO) and nitrogen dioxide ( $\text{NO}_2$ ). Together they determine the atmosphere's oxidizing, or cleansing, power and the troposphere's ozone production.**

OH and  $\text{HO}_2$  concentrations typically increase during the day and are larger in polluted environments than in clean ones. Two factors are responsible for most

observed  $\text{HO}_x$  variance: the  $\text{HO}_x$  production rate, denoted as  $P(\text{HO}_x)$ , and the  $\text{NO}_x$  concentration [Logan *et al.*, 1981; Ehhalt *et al.*, 1991; Jaeglé *et al.*, 1999, 2000a].

Reactions that destroy  $\text{HO}_x$  are also important, but as we shall show, the dominant  $\text{HO}_x$ -destroying reactions are basically determined by the  $\text{HO}_x$  production rate and the  $\text{NO}_x$  concentration. In this article, we discuss the production of OH and  $\text{HO}_2$ , the interactions between  $\text{HO}_x$  and  $\text{NO}_x$  that establish the OH and  $\text{HO}_2$  concentrations and the ozone production rate,  $P(\text{O}_3)$ , and the lessons garnered from a growing body of atmospheric measurements of OH and  $\text{HO}_2$ .

## The production of OH and HO<sub>2</sub>

Globally the most important HO<sub>x</sub> source is the photodestruction of ozone to produce the excited state oxygen atom, O(<sup>1</sup>D), which reacts with water vapor to produce two OH molecules [Levy, 1971]. It is by far the largest HO<sub>x</sub> source in the lower troposphere. However, in the upper troposphere and in some continental environments, other sources can be important and indeed dominant. Some of these other sources are made elsewhere by oxidation processes initiated by the reaction of OH with a hydrocarbon. They are then transported to a new location where they become important or dominant HO<sub>x</sub> sources (Figure 1). The convection associated with clouds appears to be effective at lifting HO<sub>x</sub> sources from planetary boundary layer (~0.5-2 km) to the middle and upper troposphere [Prather and Jacob, 1997]. These HO<sub>x</sub> sources become more important than O(<sup>1</sup>D)+H<sub>2</sub>O above ~6 km altitude. Precursor gases to these HO<sub>x</sub> sources may also be lifted by convection. Thus, pollution from megacities and biomass burning, lofted into the upper troposphere, can become the dominant HO<sub>x</sub> source and result in efficient ozone production. It can also be transported great distances before descent, possibly influencing the chemistry of remote regions.

Several of these convectively lifted gases that have origins near Earth's surface have been identified. They include acetone (CH<sub>3</sub>C(O)CH<sub>3</sub>) [Singh *et al.*, 1995; Arnold *et al.*, 1997], methylhydroperoxide (CH<sub>3</sub>OOH) [Prather and Jacob, 1997; Cohan *et al.*, 1999], and formaldehyde (CH<sub>2</sub>O) and other aldehydes [Müller and Brasseur, 1999]. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is another source [Chatfield and Crutzen, 1984], but it is so water

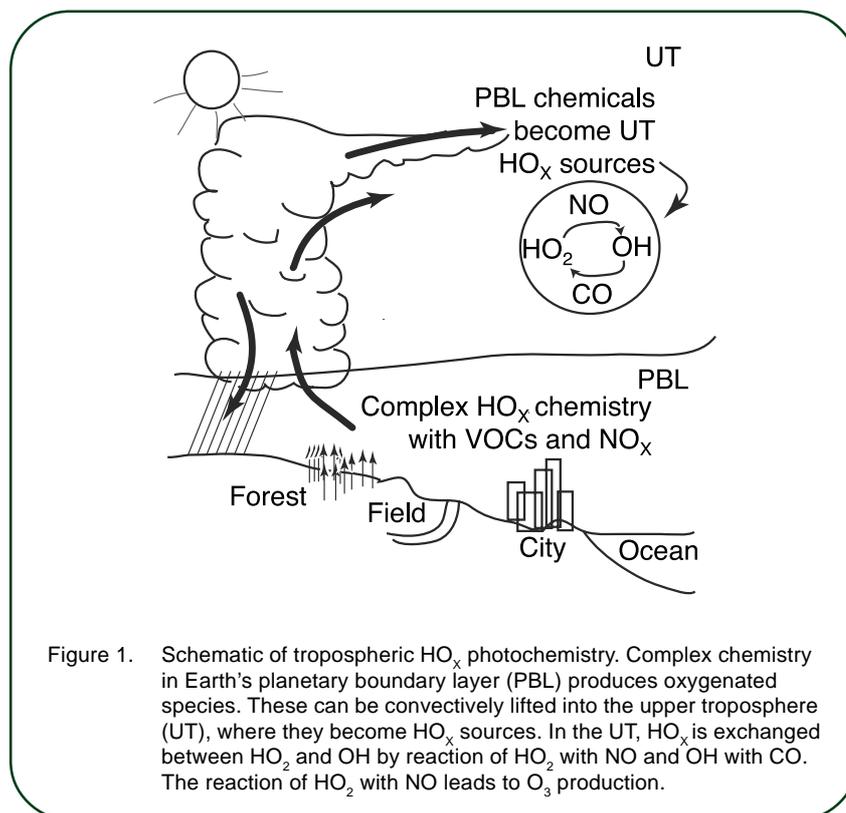


Figure 1. Schematic of tropospheric HO<sub>x</sub> photochemistry. Complex chemistry in Earth's planetary boundary layer (PBL) produces oxygenated species. These can be convectively lifted into the upper troposphere (UT), where they become HO<sub>x</sub> sources. In the UT, HO<sub>x</sub> is exchanged between HO<sub>2</sub> and OH by reaction of HO<sub>2</sub> with NO and OH with CO. The reaction of HO<sub>2</sub> with NO leads to O<sub>3</sub> production.

soluble that it is probably scavenged by precipitation as it is drawn up through clouds. All of these chemical species produce OH or HO<sub>2</sub> after they have been destroyed by sunlight. For acetone and methylhydroperoxide, the photodestruction leads to production of formaldehyde (CH<sub>2</sub>O), which is rapidly destroyed by sunlight to produce HO<sub>2</sub>. Other as-yet-unidentified source gases are also likely lifted from the surface into the upper troposphere [Crawford *et al.*, 1999], especially in convection over continents.

Another HO<sub>x</sub> source is the reaction of OH with methane [Logan *et al.*, 1981; Wennberg *et al.*, 1998]. This reaction initiates an oxidation process that eventually produces water vapor and carbon dioxide. Even though OH is destroyed in the initial reaction with methane, generally more HO<sub>x</sub> is produced than destroyed. This behavior is called autocatalytic. The amount of HO<sub>x</sub> produced depends on the amount of NO present, but for much of the

atmosphere, this autocatalytic process produces a net ~0.6 HO<sub>x</sub> molecules for every methane and OH molecule initially consumed.

For larger non-methane hydrocarbons, such as those found in urban areas and forests, the oxidation pathways can be much more complex than for those of methane [Trainer *et al.*, 1987]. After the initial reaction between OH and these volatile organic compounds (VOCs), RO<sub>2</sub> soon forms, where R is a hydrocarbon radical. Formation of RO<sub>2</sub> often leads to formation of HO<sub>2</sub>. Whether the oxidation of a particular hydrocarbon is a net HO<sub>x</sub> source or sink depends on a number of factors, particularly the amount of NO present. While VOCs are certainly important for the chemistry in Earth's planetary boundary layer, where people live, they may have a more global role if they are carried to the upper troposphere.

Because HO<sub>x</sub> production, P(HO<sub>x</sub>), is generally driven by sunlight, we would expect that OH and HO<sub>2</sub> exist only during

daylight. However, HO<sub>2</sub> has been observed to persist through the night at levels of a few parts per trillion by volume (1 pptv = 10<sup>-12</sup> molecules per total molecules in the air). Such observations point to possible nighttime HO<sub>x</sub> sources, such as OH production in the reaction between ozone (O<sub>3</sub>) and certain terpenes [Paulson and Orlando, 1996]. While measurements hint at such sources [Kanaya *et al.*, 1999; Hard *et al.*, 1992], observations have not firmly established their presence. Even if these sources exist, their impact on even regional chemistry is uncertain.

### The roles of NO<sub>x</sub> and P(HO<sub>x</sub>) in HO<sub>x</sub> photochemistry

Some HO<sub>x</sub> sources create OH; some create HO<sub>2</sub> (Figure 2). Once created, HO<sub>x</sub> is partitioned within seconds into OH and HO<sub>2</sub> by a few fast reactions. The reaction of OH with CO, volatile organic compounds (VOCs), ozone, and other chemicals produce HO<sub>2</sub>. Similarly, reactions of HO<sub>2</sub> with NO and O<sub>3</sub> produce OH. Throughout much of the atmosphere, the production of OH and HO<sub>2</sub> through these reactions is much faster than the OH and HO<sub>2</sub> production from other sources. When this is true, the interchange between OH and HO<sub>2</sub> comes into steady-state relative to the production and destruction of HO<sub>x</sub> (i.e., the OH and HO<sub>2</sub> concentrations maintain a balance with each other, but the total HO<sub>x</sub> concentration adjusts to the changing environmental conditions, such as sunlight).

The dominant reactant with OH is usually CO, although other species can be important. In forested regions, the dominant reactant with OH is often isoprene, a 5-carbon molecule that is emitted mostly by deciduous trees. In urban environments, the dominant reactant can be oxygenen-

ated species, particularly formaldehyde and other aldehydes.

The relative rates of reaction of OH with CO, VOCs, and O<sub>3</sub> and HO<sub>2</sub> with NO and O<sub>3</sub> determine how much HO<sub>x</sub> is OH and how much is HO<sub>2</sub>. The greater the amount of CO or VOCs, the more HO<sub>2</sub> there is relative to OH. With rare exceptions, the concentration of HO<sub>2</sub> is more than five times greater than the concentration of OH and is usually 10's to 100's of times larger.

During the cycling between OH and HO<sub>2</sub>, O<sub>3</sub> is produced. Ozone production occurs when HO<sub>2</sub> and RO<sub>2</sub> react with NO to form OH (or RO) and NO<sub>2</sub>. The NO<sub>2</sub> is rapidly destroyed by sunlight into NO+O, and the O atom rapidly reacts with O<sub>2</sub> to make O<sub>3</sub>. On the other hand, the production of HO<sub>x</sub> can destroy O<sub>3</sub>, as can the reactions of OH and HO<sub>2</sub> with O<sub>3</sub>. Thus the net ozone production is dictated by the expression:

$$d[O_3]/dt = (k_{HO_2+NO}[HO_2] + k_{RO_2+NO}[RO_2])[NO] - \{J_{O_3}f[H_2O] + k_{OH+O_3}[OH] + k_{HO_2+O_3}[HO_2]\}[O_3]$$

where [OH] is the OH concentration, k<sub>x+y</sub> is the reaction rate

coefficient for X+Y → products, and J<sub>O<sub>3</sub></sub>f[H<sub>2</sub>O] is the production rate of O(<sup>1</sup>D) times the fraction that react with H<sub>2</sub>O. The level at which NO becomes more important than O<sub>3</sub> depends on the [NO] and [O<sub>3</sub>] [Crutzen, 1979]. For typical [O<sub>3</sub>] values, it occurs when the NO mixing ratio exceeds a few tens of pptv.

HO<sub>x</sub> is permanently lost when its hydrogen atom is recombined into water vapor. HO<sub>x</sub> can be destroyed by several reactions, although the relative importance of the different reactions depends on the amount of NO<sub>x</sub> present (Figure 2). At low NO<sub>x</sub>, HO<sub>2</sub> is hundreds of times more abundant than OH. Most HO<sub>x</sub> loss occurs by HO<sub>2</sub> reactions with either HO<sub>2</sub> or RO<sub>2</sub> (R = CH<sub>3</sub> or other hydrocarbon radicals denoted as R) to form peroxides (HOOH, CH<sub>3</sub>OOH, ROOH). Peroxides do not represent a permanent HO<sub>x</sub> loss because they can be destroyed by sunlight to produce HO<sub>x</sub> again. For conditions in which the peroxide sources and sinks come into steady-state, HO<sub>x</sub> is lost when OH reacts with the

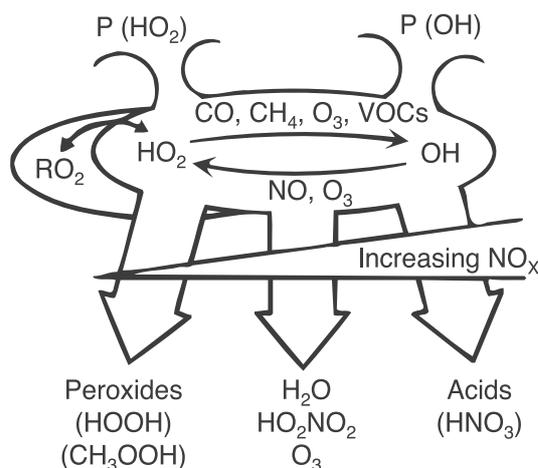


Figure 2. Schematic of the influence of NO<sub>x</sub> and P(HO<sub>x</sub>) on HO<sub>x</sub> photochemistry. HO<sub>x</sub> is produced as either OH or HO<sub>2</sub>, is rapidly exchanged between HO<sub>2</sub> and OH, creating O<sub>3</sub> in the process, and is removed by reactions that eventually form H<sub>2</sub>O. The dominant removal reactions are determined by the NO<sub>x</sub> abundance and the HO<sub>x</sub> production rate.

peroxides to produce H<sub>2</sub>O.

At low levels of NO<sub>x</sub>, below a hundred pptv in remote areas and below a thousand ppbv in polluted urban areas, NO shifts HO<sub>x</sub> from HO<sub>2</sub> to OH, so that the fast reaction OH+HO<sub>2</sub> → H<sub>2</sub>O+O<sub>2</sub> becomes an important loss as OH increases. At the same time, sufficient NO<sub>2</sub> usually exists in photostationary state with NO that pernitric acid, HO<sub>2</sub>NO<sub>2</sub>, is formed by the reaction HO<sub>2</sub>+NO<sub>2</sub>+M → HO<sub>2</sub>NO<sub>2</sub>+M, where M is an air molecule. Pernitric acid is unstable to both sunlight and thermal decomposition; its production and loss often balance, so that it is neither a HO<sub>x</sub> source nor sink. Its main loss is by reaction with OH to produce H<sub>2</sub>O.

Finally, at high NO<sub>x</sub>, HO<sub>x</sub> is increasingly shifted from HO<sub>2</sub> to OH. The increased OH reacts with NO<sub>2</sub> to form nitric acid (HNO<sub>3</sub>). Nitric acid is only slowly destroyed by sunlight and may be removed by rapid scavenging by aerosols, cloud drops, and rain

drops. For much of the atmosphere, it is permanently removed by reaction with OH to produce H<sub>2</sub>O.

The concentrations of OH and HO<sub>2</sub>, and ozone production, P(O<sub>3</sub>), display this strong dependence on NO<sub>x</sub>, as in Figure 3. Two midday cases are presented: a low P(HO<sub>x</sub>) case typical of the upper troposphere and a high P(HO<sub>x</sub>) case typical of the urban planetary boundary layer. In both cases, as NO<sub>x</sub> increases, HO<sub>2</sub> initially is constant, then decreases at first linearly and then as the square of NO<sub>x</sub> as more HO<sub>x</sub> is shifted by reaction with NO to OH, which then forms and reacts with HNO<sub>3</sub>. As NO increases, OH initially has little NO dependence, but develops a near-linear dependence, eventually peaking at mid-range NO<sub>x</sub> values, and finally decreases linearly with NO<sub>x</sub> as nitric acid (HNO<sub>3</sub>) is formed at high NO<sub>x</sub> values.

The HO<sub>x</sub> production rate, P(HO<sub>x</sub>), also influences OH and

HO<sub>2</sub> values. At low NO<sub>x</sub>, the dominant HO<sub>x</sub> loss reactions are HO<sub>2</sub>+HO<sub>2</sub> → H<sub>2</sub>O<sub>2</sub>+O<sub>2</sub> and HO<sub>2</sub>+OH → H<sub>2</sub>O+O<sub>2</sub>, both of which are quadratic in HO<sub>x</sub>. So, if P(HO<sub>x</sub>) balances the HO<sub>x</sub> loss rate, then the HO<sub>x</sub> concentration depends on the square root of P(HO<sub>x</sub>) and HO<sub>x</sub> only doubles when P(HO<sub>x</sub>) quadruples. At high NO<sub>x</sub>, HO<sub>2</sub> and OH depend linearly on P(HO<sub>x</sub>).

The production of ozone, P(O<sub>3</sub>), is intimately tied to HO<sub>x</sub>, and for high enough values of NO<sub>x</sub>, P(O<sub>3</sub>) ~ k<sub>HO<sub>2</sub>+NO</sub> [NO][HO<sub>2</sub>]. For very low [NO], which are typical in the clean tropical Pacific lower troposphere, O<sub>3</sub> is destroyed [Schultz et al., 1999]. As NO<sub>x</sub> increases, P(O<sub>3</sub>) increases almost linearly with NO<sub>x</sub>, reaches a peak when HO<sub>2</sub> becomes proportional to [NO<sub>x</sub>]<sup>-1</sup>, and then decreases linearly with NO<sub>x</sub> as HO<sub>2</sub> decreases as the square of NO<sub>x</sub>. The peak in the ozone production shifts to higher NO<sub>x</sub> as P(HO<sub>x</sub>) increases.

If P(O<sub>3</sub>) increases as NO is increased, then ozone production is said to be NO<sub>x</sub>-limited. If P(O<sub>3</sub>) is constant or decreases as NO<sub>x</sub> is increased, then ozone production is said to be NO<sub>x</sub>-saturated. Whether a region of the atmosphere is NO<sub>x</sub>-limited or NO<sub>x</sub>-saturated is an important question for determining the impact of future human pollution, particularly NO<sub>x</sub> on that region.

### Observational tests of HO<sub>x</sub> photochemistry

How well do the observations fit this basic picture of HO<sub>x</sub> and its relationship with NO<sub>x</sub>? One test is the comparison of observed HO<sub>x</sub> to models that are constrained by simultaneous measurements of other chemical species and environmental parameters. Field studies have sampled environments with wide ranges of NO<sub>x</sub> and P(HO<sub>x</sub>). In general, the daytime observations agree to within a factor of two or better

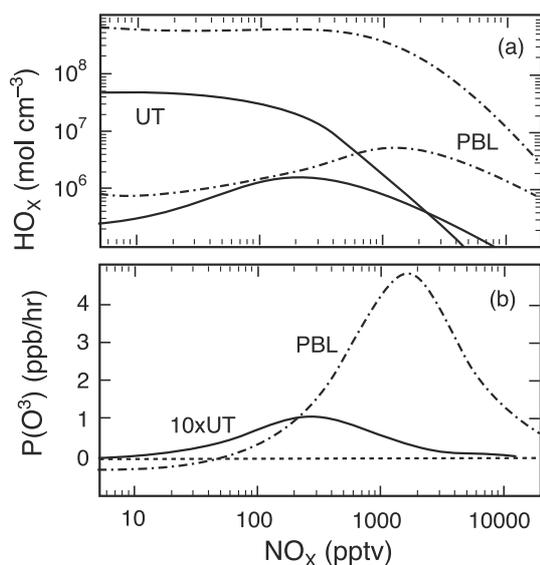


Figure 3. (a) HO<sub>x</sub> concentrations and (b) O<sub>3</sub> production rates as a function of NO<sub>x</sub> for conditions in the upper troposphere, UT (solid line), and planetary boundary layer, PBL (dashed line). In (a), the higher lines are HO<sub>2</sub> and the lower lines are OH at low NO<sub>x</sub>. In (b), P(O<sub>3</sub>) in the UT is multiplied by 10. For the UT, P(HO<sub>x</sub>) = 2.5 × 10<sup>4</sup> molecules cm<sup>-3</sup> s<sup>-1</sup>; for the PBL, P(HO<sub>x</sub>) = 2.5 × 10<sup>6</sup> molecules cm<sup>-3</sup> s<sup>-1</sup>.

with models that are tightly constrained by a large number of simultaneous measurements of other chemical species and environmental parameters. Considering the range of conditions sampled, this level of agreement is remarkable. Despite this general good agreement, some disagreements persist. The ways that observations and models disagree are different for different regions.

In the upper troposphere, observations are sometimes greater than model values, implying that additional HO<sub>x</sub> sources are not being measured [Wennberg *et al.*, 1998; Jaeglé *et al.*, 1997; Brune *et al.*, 1998]. It is presumed that these source species were acetone and methylhydroper-oxide, which were not measured during these studies. Neither the global extent of their importance nor the possibility of other sources is known.

Near Earth's surface, observed OH and HO<sub>2</sub> have generally been equal to or less than modeled OH and HO<sub>2</sub> by as much as a factor of 0.7 [Plass-Dülmer *et al.*, 1998; Eisele *et al.*, 1996; Mount and Williams, 1997; Frost *et al.*, 1999]. Even though the deviation of the observations from the models is within the combined uncertainties, it has occurred in enough environments to be troubling.

Proposed causes for the deviations include OH reactions with unmeasured hydrocarbons and HO<sub>2</sub> loss on aerosols.

In the upper troposphere over the North Atlantic, recent measurements suggest an NO dependence of the deviation between measured and modeled HO<sub>x</sub> [Brune *et al.*, 1999; Faloon *et al.*, 2000]. HO<sub>x</sub> observations are about 60% of the model values for NO less than a hundred pptv and increase to roughly twice the model values at NO values exceeding a few hundred pptv. This effect is seen for both OH and HO<sub>2</sub>. At the same time, observations and models give the same HO<sub>2</sub>/OH ratio. It is not understood what is causing this NO-dependent discrepancy. It may be that additional HO<sub>x</sub> sources accompany the increased NO<sub>x</sub> or that the photochemical interactions between HO<sub>x</sub> and NO<sub>x</sub> are not well understood for the cold, upper troposphere. These problems could involve pernitric acid (HO<sub>2</sub>NO<sub>2</sub>) or nitric acid (HNO<sub>3</sub>) formation or destruction.

No matter what the cause for the NO-dependency, these observations suggest that more of the atmosphere is NO<sub>x</sub>-limited than models calculate and that it remains NO<sub>x</sub>-limited to higher values of NO<sub>x</sub>. Currently, models

calculate that the upper troposphere would quickly become NO<sub>x</sub>-saturated if much more NO<sub>x</sub> were added. In other field studies in the upper troposphere, NO<sub>x</sub>-limited conditions are also observed more frequently than calculated by models [Jaeglé, 2000b]. If this is true, then increases in pollution from biomass burning, urban smog, or aircraft could produce more O<sub>3</sub> than expected.

Challenges lie ahead. Measuring the dependence of OH, HO<sub>2</sub>, and P(O<sub>3</sub>) on varying NO<sub>x</sub> and P(HO<sub>x</sub>) a few times in a few places is not enough. The fundamental properties of atmospheric chemistry must be examined in several environments, such as cities, forests, the marine boundary layer, and the free troposphere. They must be studied with different HO<sub>x</sub> instrumentation to ensure that the observations are real. Only then will we be able to develop confidence in the understanding of atmospheric oxidation and ozone production and to reduce the potential for surprises in chemical mechanisms.

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...continued from page 11.

their effect on biodiversity will reduce the uncertainties of the exercise. The shape of the interactions will change depending on the biome and the drivers under consideration, as well as, the magnitude of the drivers.

Results of this exercise of developing biodiversity scenarios suggest that actions to mitigate the human effects on biodiversity on the different biomes of the Earth should occur at two scales. All efforts at reducing the rate of

change of the drivers will result in reductions in biodiversity change. For example, actions aimed at reducing the rate of increase of CO<sub>2</sub> in the atmosphere or the rate of nitrogen deposition will directly reduce the expected change in biodiversity. Actions at the global scale should be complemented with management practices carefully tailored to take into account the ecological, social, and economic characteristics of each region.

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**Oswaldo Sala**

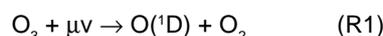
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# Global tropospheric OH: Observational constraints and model simulations

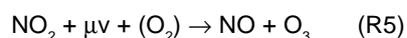
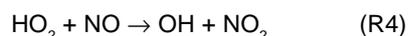
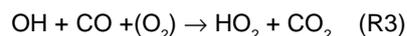
by Yuhang Wang

**The abundance of tropospheric hydroxyl radicals (OH) largely defines the oxidizing capacity of the atmosphere. A healthy level of tropospheric OH keeps in check atmospheric concentrations of many potent greenhouse gases such as CH<sub>4</sub> and HCFCs and prevents large amounts of O<sub>3</sub>-depleting halogenated hydrocarbons from reaching the stratosphere. Monitoring global tropospheric OH concentrations and understanding the controlling factors, both anthropogenic and natural, are necessary to protect our living environment. I will briefly review recent scientific works related to these two global issues.**

A tutorial of simplified OH chemistry is in order. In the troposphere, OH production is largely initiated by photolysis of O<sub>3</sub> to O(<sup>1</sup>D), O atoms in an energetically excited state, which reacts with H<sub>2</sub>O,

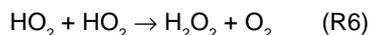


The reaction sequence leads to primary production of OH since an OH radical (with an unpaired electron) is produced from a much more stable molecule. A large fraction of OH is recycled during oxidation of reduced compounds in the presence of nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>),



In this sequence, a CO molecule is oxidized to CO<sub>2</sub> and an O<sub>3</sub> molecule is produced. Radicals of HO<sub>x</sub> (OH+HO<sub>2</sub>) and NO<sub>x</sub> are

conserved. Removal of OH is generally through the self reaction of its HO<sub>x</sub>-family sibling, HO<sub>2</sub>,



H<sub>2</sub>O<sub>2</sub> is lost from the atmosphere by deposition to surface and rainout.

Although highly simplified (see Brune, this issue, for more detail), the above scheme suggests that in order to understand tropospheric OH, it is necessary that we understand the distributions of O<sub>3</sub>, NO<sub>x</sub>, CO (and hydrocarbons), water vapor, solar radiance (for photolysis), and atmospheric deposition processes. Global simulations of OH, its precursors, and its proxies are generally carried out using 3-D models. In the following section, I will describe atmospheric observations that can be used to constrain tropospheric OH concentrations. In the discussion on global OH modeling, I will examine three categories, constrained respectively by emission sources and atmospheric transport, observed distributions of OH

precursors, and observed distributions of OH proxies. The division among the categories is somewhat artificial but streamlines the discussion.

## Constraints from observations

Dorn and Hofzumahaus [this issue] review instruments employed for *in situ* measurement of OH near the surface or onboard aircraft, and the comparison studies among these observations and model simulations. Surface observations are occasionally lower than model results at continental sites; heterogeneous loss of HO<sub>2</sub> to surfaces or unknown biogenic hydrocarbons, not measured at the sites, may account for the difference [e.g., McKeen *et al.*, 1997]. Jaeglé [2000] reviewed upper tropospheric OH measurements in comparison to model simulations for recent aircraft campaigns; measurements generally support the current understanding of HO<sub>x</sub> chemistry. The issues of additional HO<sub>x</sub> sources not from reactions R1-2 are also discussed by Brune [this issue]. Although significant for OH concentrations in the upper troposphere, these issues bear far less significance on model predictions of the global mean OH concentration, which are largely dictated by concentrations in the lower and middle tropical troposphere [Spivakovsky *et al.*, 2000]. The most comprehensive *in situ* measurements of regional OH concentrations to date were conducted onboard DC-8 and P-3 aircraft over the tropical

Pacific during the Pacific Exploratory Mission (PEM)-Tropics B. Good agreement was found between observed and simulated OH concentrations [Tan *et al.*, 2000; Mauldin *et al.*, 2000], lending some confidence to model simulations of tropospheric OH.

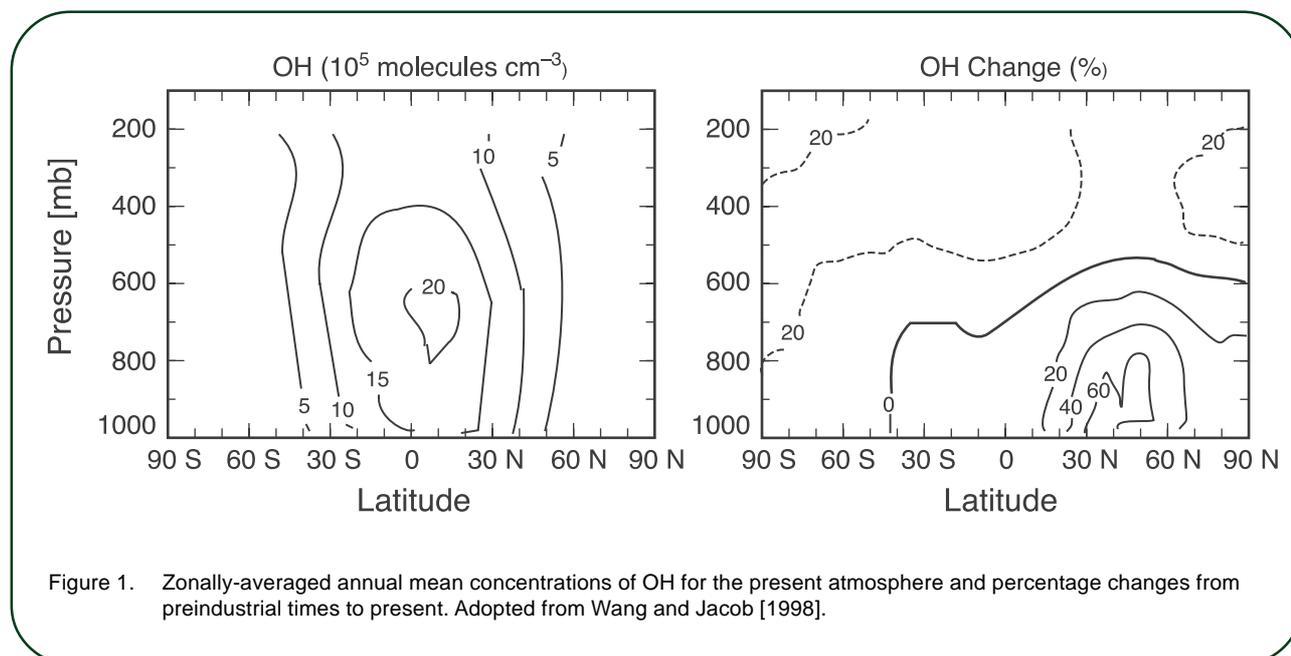
Direct monitoring of tropospheric OH on a global scale is unattainable at present. The global mean OH concentration, however, can be estimated indirectly from the concentrations of proxy gases, such as  $\text{CH}_3\text{CCl}_3$  [Singh, 1977; Lovelock, 1977], through budget calculations. Good proxy gases have known source distributions, relatively long atmospheric lifetimes, significant OH oxidation compared to other loss pathways, and long-term measurements. Spivakovsky *et al.* [2000] reviewed five commonly used proxies,  $\text{CH}_3\text{CCl}_3$ , HCFC-22,  $\text{CH}_2\text{Cl}_2$ ,  $\text{C}_2\text{Cl}_4$ , and  $^{14}\text{CO}$ . Observations of  $^{14}\text{CO}$  turned out to be most difficult to interpret. The lifetime of  $^{14}\text{CO}$  against OH oxidation is 1-2 months in the tropics and midlatitude summer. The short lifetime implies high sensitivities of observed concentrations to transport of cosmically generated  $^{14}\text{CO}$  in the stratosphere and high latitudes to the lower-latitude

troposphere. The lifetimes of  $\text{CH}_2\text{Cl}_2$  and  $\text{C}_2\text{Cl}_4$  are also short in the tropics, 2 and 4 months, respectively. However, the industrial proxies have better known source strength and distribution. Particularly since their anthropogenic sources are mostly located at northern midlatitudes, the north-south gradients of their concentrations pose some constraints on the global and hemispheric means of OH concentrations. Observations of  $\text{CH}_2\text{Cl}_2$  are more useful because of Cl-oxidation of  $\text{C}_2\text{Cl}_4$ . In comparison,  $\text{CH}_3\text{CCl}_3$  has a lifetime of about 5 years accompanied by decade-long observations around the globe, making it an ideal proxy for global tropospheric OH [e.g., Prinn *et al.*, 1995]. The atmospheric lifetime of HCFC-22 is about 11 years [Miller *et al.*, 1998]. As the concentrations continue to grow in the atmosphere, the constraints afforded by HCFC-22 observations will be increasingly important. The proxy constraints, although powerful, depend on the accuracy of source magnitudes and distribution, absolute measurement calibration, loss pathways other than OH oxidation, and kinetic data for the reaction with OH. The cumulative uncer-

tainty in derived global mean OH concentration is up to 20-30% [Spivakovsky *et al.*, 2000].

### Chemistry and transport modeling

This class of modeling, unlike the other two discussed in following sections, is not specifically designed to simulate tropospheric OH. It simulates the primary components of the natural system, emissions, atmospheric transport, chemistry, and deposition. As reactions R1-6 implied, tropospheric  $\text{O}_3$ - $\text{HO}_x$ - $\text{NO}_x$ -CO-hydrocarbon chemistry is tightly coupled. Emissions for  $\text{NO}_x$ , CO and nonmethane hydrocarbons (NMHCs) in the models include anthropogenic sources from fossil fuel combustion, industry, and biomass burning, and natural sources from vegetation (isoprene, terpenes, acetone), lightning ( $\text{NO}_x$ ), and soils ( $\text{NO}_x$ ). Concentrations of  $\text{CH}_4$ , well mixed in the troposphere, are generally specified in the models. The uncertainties in emission estimates, except for fossil fuel combustion and industry, are a factor of 2 or more. Transport is generally simulated in the models using meteorological fields from a general circulation model or weather forecast



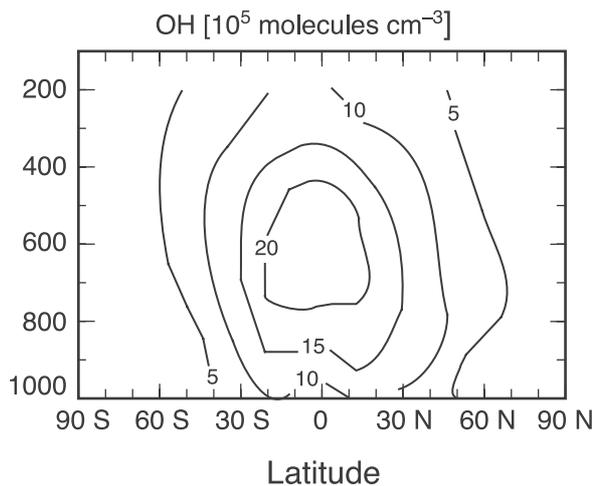


Figure 2. Zonally-averaged annual mean concentrations of OH for the present atmosphere computed by Spivakovsky *et al.* [2000]. (Courtesy of C.M. Spivakovsky.)

model. Extensive model evaluations for all related species using observations from surface sites, balloons, aircraft, and satellites, are carried out to ensure the quality of model results [e.g., Müller and Brasseur, 1995; Roelofs and Lelieveld, 1995; Berntsen and Isaksen, 1997; Wang *et al.*, 1998a; Hauglustaine, 1998; Lawrence *et al.*, 1999]. The complexity of the models offers the flexibility to investigate various factors affecting the system, including sources of  $\text{NO}_x$  [Lamarque *et al.*, 1996; Penner *et al.*, 1998; Horowitz and Jacob, 1999; Levy *et al.*, 1999], CO [Holloway *et al.*, 2000], and NMHCs [Houweling *et al.*, 1998; Wang *et al.*, 1998b; Poisson *et al.*, 2000], emissions from aircraft [e.g. Brasseur *et al.*, 1996] and ships [Lawrence and Crutzen, 1999; Kasibhatla *et al.*, 2000],  $\text{O}_3$  transport from the stratosphere [Roelofs and Lelieveld, 1997; Wang *et al.* 1998b; Lelieveld and Dentener, 2000], and heterogeneous chemistry [e.g., Dentener and Crutzen, 1993; Lary *et al.*, 1997].

One particularly relevant issue is the change of tropospheric composition since preindustrial times. Wang and Jacob [1998] reviewed available observations

for preindustrial times and found the best constraints existed for near-surface  $\text{O}_3$ . Even these (reconstructed) records have seasonal and altitude variations that can hardly be reconciled with our current understanding of tropospheric  $\text{O}_3$ . They estimated that the sources of  $\text{NO}_x$  ( $S_N$ ) and of CO and hydrocarbons ( $S_C$ ) in-

$$\Delta[\text{OH}] \propto \Delta(S_N / S_C^{3/2})$$

creased by factors of 4.7 and 2.5, respectively, from preindustrial times to present. Whereas both sources contribute, respectively by 60% and 40%, to the estimated 60% increase in the global  $\text{O}_3$  burden, they have offsetting effects on the global mean OH concentration [Thompson, 1992]. Wang and Jacob [1998] showed a model sensitivity of resulting in a 9% decrease of the global (mass-weighted) mean OH concentration from preindustrial times in their model. Their results of much smaller OH change compared to  $\text{O}_3$  are consistent with other global 3-D model studies [e.g., Crutzen and Zimmermann, 1991; Martinerie *et al.*, 1995; Levy *et al.*, 1997; Roelofs *et*

*al.*, 1997; Berntsen *et al.*, 1997; Mickley *et al.*, 2000]. Figure 1 shows the zonally-averaged annual mean OH concentrations for the present atmosphere and model simulated changes from preindustrial times. Large increases of 20-60% occur in the lower troposphere of the Northern Hemisphere while decreases of about 20% take place in the northern upper troposphere and most of the Southern Hemisphere. The asymmetry reflects the longer range transport of CO and hydrocarbons than that of  $\text{NO}_x$ . The distribution shift toward warmer lower troposphere from preindustrial times boosts OH oxidation of  $\text{CH}_3\text{CCl}_3$ , the rate of which increases with temperature; the model estimated the same 5.1 years for the lifetimes of tropospheric  $\text{CH}_3\text{CCl}_3$  against OH oxidation for preindustrial times and present.

### Precursor-constrained modeling

Uncertainties in emissions and atmospheric transport can be minimized to some extent by constraining the model using atmospheric observations. Spivakovsky [2000] carefully compiled climatologies for meteorological variables and OH precursors including  $\text{O}_3$ , CO,  $\text{NO}_x$ , and hydrocarbons from available atmospheric observations and applied them to global OH simulations. This work heralds the 3-D chemical data assimilations that will take the center stage in the years to come. Figure 2 shows the simulated annual mean OH distribution. The resulting lifetime of tropospheric  $\text{CH}_3\text{CCl}_3$  against OH oxidation is 4.8 years. The striking difference compared to Figure 1 is the symmetry in OH distribution across the Equator. The two results have about the same mean

OH concentrations in the Northern Hemisphere but Figure 2 is higher by 30% in the Southern Hemisphere. The inter-hemispheric asymmetry with higher OH concentrations in the Northern Hemisphere, as illustrated in Figure 1, is common among chemistry and transport models. The more up-to-date simulation by Mickley *et al.* [2000] shows mean OH concentrations 16% higher in the Northern than Southern Hemisphere. The smaller interhemispheric ratio is due solely to less OH in the Northern Hemisphere compared to Wang *et al.* [1998a].

The interhemispheric OH asymmetry in chemistry and transport models arises from the asymmetry in anthropogenic emissions, which boost OH in the vicinity but depress OH in remote areas (Figure 1). The latter effect was observed over the tropical Pacific during PEM-Tropics B [Wang *et al.*, 2000]. Presently most models have symmetric (across equator) biomass burning emissions, the only large anthropogenic source in the Southern Hemisphere. A symmetric OH distribution would imply much larger emissions from biomass burning in the southern than northern tropics.

The observational evidence for a hemisphere-symmetrical OH distribution is not yet affirmative. Observations of  $\text{CH}_3\text{CCl}_3$  tend to support this distribution [Spivakovsky *et al.*, 2000; Montzka *et al.*, 2000]. The constraint on the inter-hemispheric ratio will improve to  $\pm 50\%$  as  $\text{CH}_3\text{CCl}_3$  emissions are phased out [Spivakovsky *et al.*, 2000]. Montzka *et al.* [2000] suggested that the air mass boundary is more appropriately defined by the Inter-Tropical Convergence Zone (ITCZ), the annual-mean position of which is north of the equator. They found that  $\text{CH}_3\text{CCl}_3$  observa-

tions implied a higher mean OH concentration in the southern than northern air mass. The observations of  $^{14}\text{CO}$  also support the symmetric distribution or even a higher mean OH concentration in the Southern Hemisphere [e.g., Brenninkmeijer *et al.*, 1992]; however, the interpretation is marred by large uncertainties in  $^{14}\text{CO}$  transport [Spivakovsky *et al.*, 2000; Quay *et al.*, 2000]. Observations of  $\text{CH}_2\text{Cl}_2$  suggest, on the other hand, higher OH concentrations by 45-95% in the northern than Southern Hemisphere [Spivakovsky *et al.*, 2000].

### Proxy-gas constrained modeling

This class of modeling takes full advantage of long-term observations of OH proxy gases using sophisticated statistical analysis. The best data series to date was gathered by the Atmospheric Lifetime Experiment / Global Atmospheric Gas Experiment (ALE/GAGE). Prinn *et al.* [1995] and Krol *et al.* [1998] applied different statistical methods to analyze the data series from 1978 to 1993. Global HCFC-22 measurements have been collected since 1992 by the NOAA Climate Monitoring & Diagnostics Laboratory (CMDL); the program also measures  $\text{CH}_3\text{CCl}_3$  (beginning in 1988). Miller *et al.* [1998] demonstrated the utility of HCFC-22 observations using the method similar to Prinn *et al.* [1995] and found results consistent with the earlier work.

The gist of the modeling technique is trying to deduce global OH concentrations from proxy observations; I will discuss the case for  $\text{CH}_3\text{CCl}_3$ . The deduction is an inverse problem since the observed atmospheric accumulation of  $\text{CH}_3\text{CCl}_3$  results from industrial emissions, OH oxidation, and minor losses to the

oceans and in the stratosphere. Starting with *a priori* global OH distribution, the inverse modeling aims to find the global mean OH concentration and its linear trend (with respect to time) that best fit observed  $\text{CH}_3\text{CCl}_3$ . A long-term data series is essential for the inversion. The *a priori* global OH distribution is taken from a global chemistry and transport model like the ones previously discussed. Prinn *et al.* [1995] used a 2-D model and Krol *et al.* [1998] relied on the 3-D model by Crutzen and Zimmermann [1991]. Prinn *et al.* [1995] applied a recursive weighted least squares (Kalman) filter to the inversion. With a more complicated 3-D OH distribution, Krol *et al.* [1998] employed a Monte-Carlo ensemble method for the fitting optimization.

Prinn *et al.* [1995] derived an atmospheric lifetime of  $\text{CH}_3\text{CCl}_3$  of 4.6 years with no apparent trend from 1978-1994. Krol *et al.* [1998] found a similar  $\text{CH}_3\text{CCl}_3$  lifetime of 4.5-4.7 years but an increasing trend of 7% in 15 years. The estimated global mean (mass-weighted) OH concentration from the two studies is  $9.7\text{-}10.7 \times 10^5$  molecules  $\text{cm}^{-3}$  in the troposphere. Prinn and Huang [2000] and Krol *et al.* [2000] examined the causes for the trend discrepancy. The different treatment of  $\text{CH}_3\text{CCl}_3$  concentrations at the beginning of the observation series appears to be a significant factor. Prinn *et al.* [1995] computed  $\text{CH}_3\text{CCl}_3$  concentrations from 1951 and had only two free parameters (mean OH and trend) in their inverse model. Krol *et al.* [1998], on the other hand, computed  $\text{CH}_3\text{CCl}_3$  concentrations from 1978 and needed a third optimizing parameter to adjust model initial  $\text{CH}_3\text{CCl}_3$  concentrations.

The 7% OH increase from 1978 to 1993 estimated by Krol *et al.* [1997] is significant in light of

±10% change from preindustrial times to present found in most global 3-D simulations [Wang and Jacob, 1998]. One factor not considered in the other global 3-D studies is the decrease of stratospheric O<sub>3</sub> concentrations since the late 1970s, which, Krol *et al.* [1998] estimated, contributes to a 2% increase of the global mean OH concentration. They suggested that increasing water vapor

concentrations in the tropics and a decoupling of NO<sub>x</sub> and CO emissions (with increasing NO<sub>x</sub> but decreasing CO emissions) by about 10% each could explain the rest of the OH increase. A shift in the global mean OH concentration by this magnitude would therefore signify substantial changes taking place in anthropogenic emissions or global climate. Resolving the difference between

the two studies and obtaining additional independent estimates are critical.

### Acknowledgements

I thank Clarissa Spivakovsky and Loretta Mickley for informative discussion and data.

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## Perspectives on the Earth System

Recent issues of the NewsLetter have carried various articles on the nature of the Earth System, the effects of human activities on the System (e.g., 'The Anthropocene', see NL 41), and the scientific challenges to studying the Earth System. We invite continued contributions on this theme. Please be as speculative, provocative or controversial as you like! Reactions to these articles are invited in the new Correspondence section of the NewsLetter.

This issue's contribution comes from Victor Gorshkov and Anastasia Makarieva, who explore the fundamental role of life in the stability of the Earth System.

## Environmental safety, climate stability and the non-perturbed biota

by V.G. Gorshkov and A.M. Makarieva

**Humanity is currently faced with the prospect of further development of civilisation. On the one hand, the inherent human claim for improving living standards urges further acceleration of economic growth and exploitation of biospheric resources. On the other hand, it becomes evident that uncontrolled spontaneous development of modern civilisation in the direction determined by catering for immediate human demands goes hand-in-hand with global environmental devastation. This, in turn, inevitably impairs quality of life and undermines the security of human existence.**

In searching for a compromise between the two trends, hopes for sustainable development are most often associated with creation of technologies capable

of imposing a stabilising impact upon the global environment (e.g. struggling with anthropogenic pollution). This necessitates further enhancement of civilisa-

tion power, growth of human population and inevitable cultivation of the remaining natural biota and other biospheric resources. However, the very possibility of a technological solution to the global environmental stability problem remains entirely unproved.

A different path of development compatible with long-term environmental safety lies in conservation and restoration of a substantial part of the Earth's biosphere in its natural non-perturbed state, bearing in mind the stabilising potential of the natural biota of Earth with

respect to the global environment. Restoration of the stabilising biotic potential would mean relaxation of anthropogenic pressure on perturbed territories and complete abandonment of further cultivation of the remaining natural biota. This strategy sets a ceiling to exploitation of biospheric resources, economic growth and global human population number.

The global stabilising environmental impact of the natural

biota of Earth becomes especially clear from the analysis of the problem of climate stability. There are two physically stable states of the Earth's climate, that of complete ice coverage with global mean surface temperature close to  $T \sim -100\text{C}$ , Fig. 1 (1), and that of total evaporation of the Earth's hydrosphere with temperature close to  $T \sim +400\text{C}$ , Figure. 1 (3) (Gorshkov *et al.*, 2000). In both stable states life is impossible. The modern climate

of Earth, Figure. 1 (2), where the predominant part of the hydrosphere exists in the liquid state, proves to be physically unstable. The observed stability of the suitable-for-life global mean surface temperature over geological timescales can be only explained if one allows for appearance of biotically controlled singularities in temperature-dependent behaviour of the greenhouse effect and albedo within the life-compatible temperature interval from  $5\text{C}$  to  $25\text{C}$ .

Biotic processes aimed at maintenance of climate stability should be necessarily characterised by strictly defined succession, direction and duration, i.e., fluxes and stores of information. Such information is contained in the genetic programme of biological species combined into ecological communities of the global biota. Anthropogenic disturbance of natural ecological communities results in violation of the natural population density distribution of species and of genetic programs of natural species due to creating artificial sorts of plants and breeds of animals. This leads to degradation of the stabilising environmental potential of the biota, which may ultimately cause rapid spontaneous transition of the Earth's climate to either of the two life-incompatible physically stable states.

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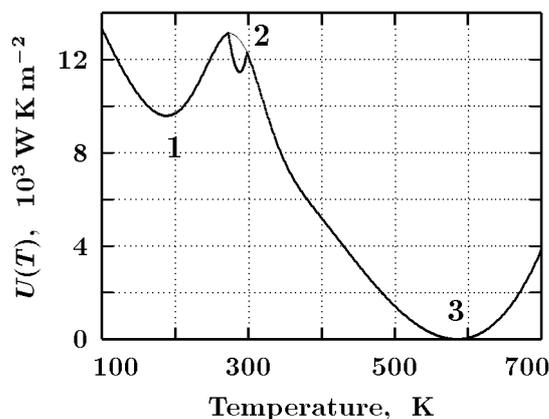


Figure 1. The potential (Liapunov) function  $U(T)$  for the mean global surface temperature.

$U(T)$  is determined to the accuracy of integration constant from the equation  $C dT/dt = -dU/dT$ , where  $C$  is the average heat capacity per unit area of the Earth's surface,  $C dT/dt$  is the rate of change of energy content per unit surface area. It is equal to the difference between the absorbed solar radiation ( $l/4$ )  $a(T)$  and thermal radiation of the Earth's surface emitted into space, which is equal to  $(sT^4)$   $b(T)$ . Here  $l/4$  is the flux of solar radiation averaged over the whole planet's surface,  $l$  is the solar constant,  $a(T)$  is the share of absorbed solar radiation ( $1-a(T)$  is equal to planetary albedo),  $s$  is the Stephan-Boltzmann constant,  $b(T)$  is the share of equilibrium thermal surface radiation leaving the planet ( $1-b(T)$  is the normalized greenhouse effect).

Physically stable states 1 and 3 correspond to minima of the potential function  $U(T)$ . In these states functions  $a$  and  $b$  remain practically temperature independent over a relatively broad range of temperatures. On a lifeless Earth the physical behaviour of these functions are generally governed by the Clausius-Clapeyron equation for atmospheric water and corresponds to the central unstable maximum of  $U(T)$  (2, thin line). To account for the observed stability of the modern climate (2, thick line) it is necessary to introduce non-physical singularities of functions  $a(T)$  and  $b(T)$  within the life-compatible temperature interval. Such singularities may only appear as the result of regulatory impact of the global natural biota.

## Reference

Gorshkov, V.G., Gorshkov V.V., Makarieva, A.M., 2000. Biotic Regulation of the Environment: Key Issue of Global Change. Springer-Verlag, London.

## Global Change and Sustainable Development in Southeast Asia (START Open Science Conference)

17 – 19 February 2001, Chiang Mai, Thailand

<http://www.icsea.or.id/sarcs2001/>

A conference for researchers, business leaders, policy analysts and decision-makers, natural resource managers and others concerned about sustainable development pathways in Southeast Asia.

The conference objectives are to explore recent global environmental change and sustainable development research in Southeast Asia, its implications for policy, and application to the transition to ecologically, sociologically, and economically sustainable societies in the region.

Conference themes include:

- Agricultural Development
- Forest and Water Resources
- Coastal and Marine Resources
- Atmosphere and Climate Change
- Land-use and Land-cover Changes
- Globalisation of Trade and Investment
- Industrialisation and Urbanisation
- Institutions for Sustainable Development
- Integrated Regional Assessment

## Atmospheric Chemistry in the Tropics: From Local to Global, From Air Pollution to Climate Change (IGAC Symposium)

22-23 January 2001, Bangkok, Thailand

<http://www.start.or.th/IGAC7/>

The objective of this Symposium is to bring scientists together to discuss current knowledge regarding atmospheric chemistry in the tropics. The highlights of the Bangkok IGAC Symposium are partnership strategies and tools for understanding the changing atmosphere and developing sustainability towards the future environment.

The Symposium agenda will be divided into 4 sessions:

- Urban Air Pollution
- Land Use Change/Management and Atmospheric Change
- Impacts of Biomass Burning in the Tropics
- From Air Pollution to Climate Change

A complete meetings list for the IGBP network will be published in the next edition of the Global Change Newsletter

## People and events



Clemencia

### A new face at the Secretariat

Clemencia Widlund, Administrative Officer

Hardly two weeks at the IGBP Secretariat and I can already say that it is going to be a challenging job, especially considering the multidisciplinary nature of the programme.

I am taking over primarily the administrative functions of the Secretariat (and a little of Finance). Having finished Economics and a Masters in Management, and with my experience from previous quite similar positions, I sincerely hope these skills will help make my stay at the Secretariat a fruitful one.

My years in Sweden began with a one-year scholarship grant in 1989 at the International Graduate School, University of Stockholm. I stayed on in Sweden and took a job with an Embassy for six years. Just before joining IGBP, I was Project Manager at a Swedish-based international rural development consultancy group. I admit I like working in an international environment, which is probably one reason why things were easier for me here at the Secretariat, even on my first day.

I look forward to working with the rest of the group and during the next few weeks (months is acceptable, I have heard!) I am sure it will be an ideal learning process for me - tough but fun!

# Global Change Open Science Conference

The Earth's environment and habitability are now, as never before, affected by human activities. This conference presents the latest scientific understanding of natural and human-driven changes on our planet. It will examine the effects on our societies and lives, and explore what the future may hold. Co-sponsored by IGBP, IHDP and WCRP, the Conference will emphasize the results of IGBP synthesis culminating from a decade of global change research, and will point the way forward towards the next decade of Earth System science.

10-13 July 2001  
Amsterdam,  
The Netherlands

Poster Abstract  
submissions  
now open



CHALLENGES OF A CHANGING EARTH

Registration now open via the [Conference Home Page](#)

[www.sciconf.igbp.kva.se](http://www.sciconf.igbp.kva.se)

Correspondence

## Crop residue: a sink for soil N<sub>2</sub>O

In calculating global N<sub>2</sub>O budgets, A. Mosier and C. Kroeze have mentioned crop residue as a sole source of N<sub>2</sub>O emitted directly from agricultural soils, representing ca. 20% of the emissions (IGBP Newsletter, No. 34, p. 10, June 1998). They have used the emission factor for fertilizers as default to account for the N<sub>2</sub>O emitted from the residue, in the budget. I recently discovered a novel mitigating effect of soil N<sub>2</sub>O by crop residue acting as a sink, where soil surface mulch application almost completely eliminated the N<sub>2</sub>O emission at a temperature encountered in tropics (i.e. 30°C, Seneviratne, *Ambio*, 28, 378, 1999; Seneviratne and Van Holm, *Soil Biology and Biochemistry*, 30, 1619-1622, 1998). Current studies show that the dissolution of the N<sub>2</sub>O in moisture contained in the residue and possibly chemical reduction (ca. 25%) and also microbial reduction (ca. 75%) are attributable to this mitigation effect (G. Seneviratne, unpublished). A similar effect should occur in residue incorporated into the soil, although it has other N interactions. It is important to consider this effect in future budgeting, particularly in tropics, which are considered as large emitters of N<sub>2</sub>O and, in which crop residue management is rather common at the same time. However, further studies are needed to fully evaluate the effect and potentials of this.

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Letters can be in response to an article in an earlier edition of the Newsletter or about IGBP science/issues in general. Please keep letters as brief as possible (maximum of 200 words) and send to Susannah Elliott at the IGBP Secretariat (Email: [Susannah@igbp.kva.se](mailto:Susannah@igbp.kva.se), Fax: 46 8 16 64 05).

In coming editions of the IGBP Newsletter ...

- Special on the Global Change Open Science Conference  
[www.sciconf.kva.se](http://www.sciconf.kva.se)
- Special edition on LBA (Amazonian global change research)



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