WORKING GROUP 2

Global Environmental Change (GEC)

Donovan P Kelly (Rapporteur)

Institute of Education
University of Warwick
Coventry CV4 7AL
England

Working Group Participants: O van Cleemput, R Conrad, A Costello, S Jensen, L Kargiolaki, G King, N Kubilay, M Lidstrom, P Megonigal, R Oremland, P Steudler.

Trace gases and global environmental change

Atmospheric trace gases exert one or more of a series of possible effects on climate homeostasis, potentially leading to climate change or altered radiative input to the biosphere. Most important of these are:

1. *"Greenhouse" effects*, caused by gases reacting with input solar radiation to retain heat in the atmosphere, and thus raising mean global temperature. Most important are water vapour and carbon dioxide, primarily because of their abundance in the atmosphere (and currently accounting for at least 85% of the warming effect of the sun in maintaining the Earth at a mean temperature some 30°C higher than the -18°C it would enjoy in the absence of an atmosphere). There has, however, been an increase in mean temperature due to radiative forcing by other trace gases. Over the past 15 years this forcing has totalled around 550 mW/m^2/decade, and is attributed to carbon dioxide (~56%), methane (~15%, including that due to water vapour from

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atmospheric oxidation of CH_4 by OH), nitrous oxide (~6%) and anthropogenic chlorofluorocarbons (CFCs; ~24%).

2. *Ozone-depleting gases*. Most significant among these are the CFCs and biogenic chlorine and bromine compounds, which persist in the atmosphere long enough to penetrate to the stratosphere and react in the ozone layer. The CFCs thus exert a dual role, but it has to be noted that stratospheric ozone is also a "greenhouse gas", and there is some evidence suggesting that ozone destruction in the Antarctic partly offsets global warming due to CFCs in the Northern hemisphere.

3. *Cloud cover and water condensation*. Some trace gases (or their atmospheric oxidation products, such as methanesulfonate from DMS) act as cloud condensation nuclei, potentially resulting in droplet formation, increased cloud cover, and enhanced precipitation. They could thus counter the increased atmospheric warming resulting from a greater atmospheric burden of water vapour, and potentially reduce radiative forcing by increasing global albedo.

Modelling change and trace gas dynamics

Major factors modelled in short- to medium-term considerations of GEC are (i) atmospheric CO_2, and its effect on atmospheric temperature and on plant growth, (ii) temperature change and its consequences, (iii) depositional change, and (iv) global water relations. To these, the work of the past decades in atmospheric chemistry and physics and in microbiology has added (v) methane, nitrogen oxides, organosulfur gases, the chloro- and chlorofluoro-carbons, and diverse other trace compounds containing nitrogen or halogens.

The trace gases discussed in the ARW affect and influence, or are influenced by, all these factors. Two aspects of microbiology are relevant: (i) the effect of variation in trace gas production through microbiological processes on possible GEC; and (ii) the prediction of effects of GEC on trace gas dynamics as driven by microbiological processes. These

interrelated aspects depend on having knowledge of the bacteria and communities involved, and the numbers, functions, activities and potentials of these organisms.

Two blocks of inter-related studies need to inform a consideration of trace gases in GEC. First, the range, nature, sources and sinks, and atmospheric effects of the trace gases themselves; and secondly, the physical, chemical and anthropogenic influences on those gases and their dynamics.

The gases of interest are methane, sulfur gases (dimethyl sulfide, carbonyl sulfide), nitrogen gases (NO, N_2O, NO_x), and halogenated gases primarily of biogenic (Cl, Br) or anthropogenic (Cl, F) origins.

Among the principal factors affecting dynamics, both of sources and sinks and of atmospheric turnover, are (i) pCO_2, (ii) temperature, (iii) hydrology, (iv) N-deposition, (v) land use change (anthropocentric), (vi) non-biological source strengths, (vii) physiological diversity and interactions between microbial communities with internal element cycling having variable freedom of exchange of intermediates (which includes the trace gas output) with the adjacent environment and the atmosphere, and (viii) variability, unknown and unquantified sinks.

We are currently very patchy in our understanding of the interrelations and controls over trace gas outputs and the "feedback" effects (both positive and negative) that affect the fluxes of trace gases between their sources and sinks. The discussions in this Working Group concentrated on defining the major factors affecting processes and ensuring that these received priority recognition by experimentalists in field microbiology.

Modelling feedback loops and homeostasis

In principle it is possible to correlate all the factors influencing trace gas turnover (output from soils or aquatic sources, sinks in the atmosphere and the biosphere, interactions with physical and anthropocentric processes) to a set of differential equations, as the various factors can each be

defined with a greater or lesser degree of precision. Thus, change in methane input to the atmosphere with respect to change in temperature could be expressed in relation to the changes due to altered nitrogen deposition, soil disturbance, altered wetting, water activity (a_w), and so on, e.g.:

$$dCH_4/dt = [\partial CH_4/\partial N_{dep} + \partial CH_4/\partial T + \partial CH_4/\partial a_w + \partial CH_4/\partial_{toxins} + \partial \ldots]$$

Clearly each component expression would be subject to variable uncertainty: for example, the change of CH_4 with temperature would be a function of the effect of temperature on bacterial methanogenesis and methanotrophy (by both methanotrophs and ammonia-oxidizers). These contributory processes could also be directly or indirectly affected by altered water activity or aeration (due to land disturbance or altered hydrology), making the $\partial CH_4/\partial T$ function a combined physical (solubility and diffusion) and biochemical variable. Nonetheless it should be an aim of the biological and physical studies of trace gases and their turnover to identify the principal numerical components needed in order to express gross atmospheric input and output in such terms. Only in this way can the interrelations of the major physical and biological variables on the cumulative effect of diverse gases be quantified, however crudely.

Effects of physicochemical change on trace gas turnover by the biosphere

Increases in pCO_2 and temperature both potentially increase trace gas turnover and flux of gases like methane and nitrous oxide to the atmosphere. Raised CO_2 would be expected to enhance primary production (especially of C_3 plants), thereby making more carbon available for methanogenesis and nitrate reduction. By enhancing biological activity, temperature rise could stimulate all gas-producing (and consuming) processes. Temperature could, however, also affect water availability (and the water table in methane-producing wetlands for example) and also thereby exert a negative effect both by reducing the volume

of the habitat and through influencing the water potential of a system.

Globally it is likely that the Northern wetlands will decrease in area both by human activity and by hydrological changes resulting in drying. This would reduce methanogenesis, but a counteractive activity is likely to be the expansion of methane-producing rice paddies in Asia over the next half century, and possible increases in CH_4 arising from increased populations of ruminants in the tropics. Increased drying due to temperature rise might decrease the methane-productive area of the Arctic wetlands but it seems likely that these regions also become less effective as CH_4 sinks if temperature is raised. This seems to be due to decreased methanotrophy, while methanogenesis is enhanced. Modelling the effect of temperature and drying on wetland methanogenesis is thus complex and requires more data.

The effect of human land use changes is also variably predictable. Draining and enhancing land aeration would be expected to reduce methanogenesis and nitrous oxide output, but drainage of wetland has been seen to result initially in enhanced output of N_2O, possibly attributable to exposure of more carbon to organisms capable of denitrification.

Interactions between GEC and trace gas dynamics: a model for methane

The effects of the factors, ∂pCO_2, ∂T, $\partial N_{deposition}$, $\partial N_{fertilization}$, $\partial_{land\ use}$, $\partial_{hydrology}$ on the sources and sinks for methane were considered by the Working Group in drawing up a scheme of relative importance of the factors to the source and sink terms.

1. Source terms

Wetlands: Elevated pCO_2 would increase primary production by C3 plants in wetlands, thereby increasing all microbial processes involved in the mineralization of organic matter. This effect

could be enhanced by nitrogen deposition or eutrophication, and amplified by increase in mean temperature.

Elevated temperature will generally enhance microbial metabolism (Q_{10} values may exceed 2), but also decrease gas solubilities. Lowered oxygen solubility could possibly reduce the rate of CH_4 oxidation, but methanogenesis could increase, with decreased solubility also meaning that ebullition of dissolved CH_4 could be raised.

Change in water status (+ or -) would be likely to have an equivalent effect on methanogenesis, as the volume of the methanogenic habitat varied. This would be time-dependent, as wetland plant (and hence carbon input) changes would require successional seres, and carbon and mineral availability might be rate-limiting to methanogenesis.

Increased nitrogen input by atmospheric deposition could increase primary production, stimulating methanogenesis. Similarly ingress of N from agricultural sources would have an effect that was interdependent with changes in pCO_2, temperature and water.

Land use changes resulting in decreased wetland would enhance CH_4 oxidation and decrease observed CH_4 output.

Rice paddies: Elevated pCO_2 might increase the rice primary production, and root-associated methanogenesis could be stimulated if recent photosynthate is a major input for methanogenic carbon. If below-ground biomass from previous rice culture (and any added organic matter) are major sources, the effect of pCO_2 would be delayed until accumulated biomass increased seasonally.

Effects of other parameters would be similar for other wetlands, although atmospheric N deposition would have at best a marginal effect.

Ruminants: Changes in pCO_2, temperature etc. would not have direct effects on ruminant methanogenesis, but this could be affected by land use and fodder possibly consequent on those other changes.

Termites: GEC might affect habitat distribution (geographical areas suitable for colonization), and consequently the regions producing methane from termites. Any changes affecting the availability of plant fibre (wood) available for termite nutrition (e.g. ∂T, $\partial N_{deposition}$, hydrology) would influence CH_4 output, and increased temperature could raise CH_4 production simply by enhancing activity and metabolism.

Landfills. In that these are man-managed, only directed changes in drainage, area of land used, and hydrologic regime would affect them, and changes in pCO_2 would not have any effect. Any temperature enhancement would probably have only marginal effects on a large, self-heating, landfill but any gross increase might enhance methanogenesis and hence CH_4 venting, but an increase in surface temperature, possibly accompanied by consequent drying, might decrease methanotrophy, thereby allowing greater CH_4 input to the atmosphere.

Oceans: Coastal eutrophication might increase near-shore methanogenesis and sea-level rise could alter the areas of coastal marshes from which CH_4 is emitted. No significant effect on oceanic CH_4 generation would be expected, although surface temperature rise could increase the rate of loss from the ocean to the atmosphere.

2. Sink terms

Soils: pCO_2 would have no direct effect on CH_4 consumption in soils, except indirectly if ammonia-oxidizing autotrophs were to become more abundant and effect enhanced CH_4 destruction. Temperature would have little direct effect as atmospheric methane consumption by soils is diffusion-limited. Enhanced oxidation might accompany enhancement of methane transport resulting from decreased soil moisture at elevated temperature.

Nitrogen deposition from the atmosphere can result in long-term decreases in CH_4 oxidation, and changes in the relative importance of the activities of methanotrophic and ammonia-oxidizing bacteria. The magnitude of the nitrogen input effects

is likely to be a function of soil type (texture) and the *in situ* nitrogen mineralization and nitrification potentials. Losses of forests, prairies or other land types (e.g. conversion to agricultural use) and intensive forest management all result in long-term decreases in CH_4 oxidation, and potential loss of sinks for this gas.

Other methane sinks: Methane oxidation in wetlands appears primarily to be a function of oxygen availability. Decreases in the water table levels increases availability, while higher temperature and greater organic content reduce dissolved oxygen supply. One would expect latitudinal variation in wetland methanotrophy consequent on GEC.

The factors considered would have minimal effects on the oxidation of CH_4 in rice paddies, landfills or the oceans, although the value of the two former as sinks could be enhanced by appropriate human management. Little methane oxidation appears to be associated with ruminants or termites, although oxidation in the soil around the latter would obviously be influenced by ∂T, ∂_{water}, and ∂N.

The analysis given above is of necessity superficial and serves to show the kind of effects that would apply to biogenic gases other than methane. Thus, plant-produced gases (carbon disulfide, volatile acids and esters, DMS) could be affected by pCO_2, temperature and nutrient status (e.g. iron or phosphate for marine sources), but many of the principles are generally applicable. For most biogenic trace gas sources we have little secure knowledge of the stability of the source ecosystems and the main drivers of any homeostasis they exhibit. Systems such as the DMS-producing oceans are of very uncertain "stability". It is known that much DMS never leaves the ocean surface, as it is reoxidized and recycled within the ocean ecosystem: this may account for as much as 90% of all biogenic DMS. Consequently temperature and nutrient effects on the oceanic DMS source (and consequent sulfur input to the atmosphere) are impossible to model at this time. Indeed, we have to admit to an overall lack of predictive understanding of the correlations between CO_2 production, pCO_2, temperature and sink regulation in the modelling of atmospheric inputs of the major trace gases.

Other factors affecting gas cycling

Some processes are subject to marked chemical limitations. Thus, the oxidation of NO to NO_2 ($2\ NO + O_2 = 2\ NO_2$) is dependent on two NO molecules reacting with O_2 and is consequently slow when NO concentrations are low. This means that below 10 ppm, NO exhibits an atmospheric lifetime exceeding 100 h, and oxidation of concentrations in the ppb to 1 ppm range in soils will be a balance of chemical and biological processes, dependent on the [NO]. Also, the proportions of DMS oxidized methylotrophically, phototrophically and venting to the atmosphere from the ocean varies with latitude: biological oxidation in the tropical ocean appears maximal near the equator, with all three options being equivalent at 12°S.

The effects of toxic materials and the interdependence of processes involving different trace gases can influence output rates and steady state levels. Thus a gas such as methyl fluoride (and some CFCs) can be inhibitory to methanotrophy, but inhibition by the former can be overcome as the "toxic" material is also a substrate and will eventually be oxidized. The processes of denitrification, nitrification and methanotrophy show overlaps in physiology and the first can be linked to the anaerobic destruction of methylamines and sulfides.

Other element cycling

Although the ARW (and this Working Group) focused primarily on the atmospheric aspects of global change as catalyzed by microorganisms, a further dimension was recognized that affects environmental quality. This concerned the involvement of microorganisms in the global cycling of toxic elements. as exemplified by mercury, and to a lesser extent elements such as selenium and arsenic, all of which undergo volatilization *via* microbial methylation. Broadly-based anthropogenic activities, including fossil fuel combustion, hydrological alterations, and other industrial operations have mobilized these elements and increased their flux to the atmosphere from various point sources. Their fall-out from the atmosphere has resulted in

large-scale contamination problems in a number of ecosystems. The involvement of microbes in their immobilization, volatilization, and detoxification is relatively poorly understood and merits further quantitative and biochemical assessment because of its significance to plant and animal health, and as a factor in trace gas cycling that might affect the activities of bacteria whose normal metabolism, for example, uses non-toxic methylated compounds.

Future work

Predicting the effects of climate change on the trace gas dynamics driven by microorganisms (and the consequent further change driven by any modification of those microbial dynamics) depends on having knowledge of the bacterial types involved, community interactions, and *in situ* numbers, functions and activities. This requirement cannot yet be fully met: the development of methodologies still lags behind need. In particular the development of techniques is needed that will establish the identity, physiological capabilities, and reaction velocities (for target processes relating to trace gas turnover) for the 95% of all natural microbial populations which have as yet resisted attempts to culture them in the laboratory.

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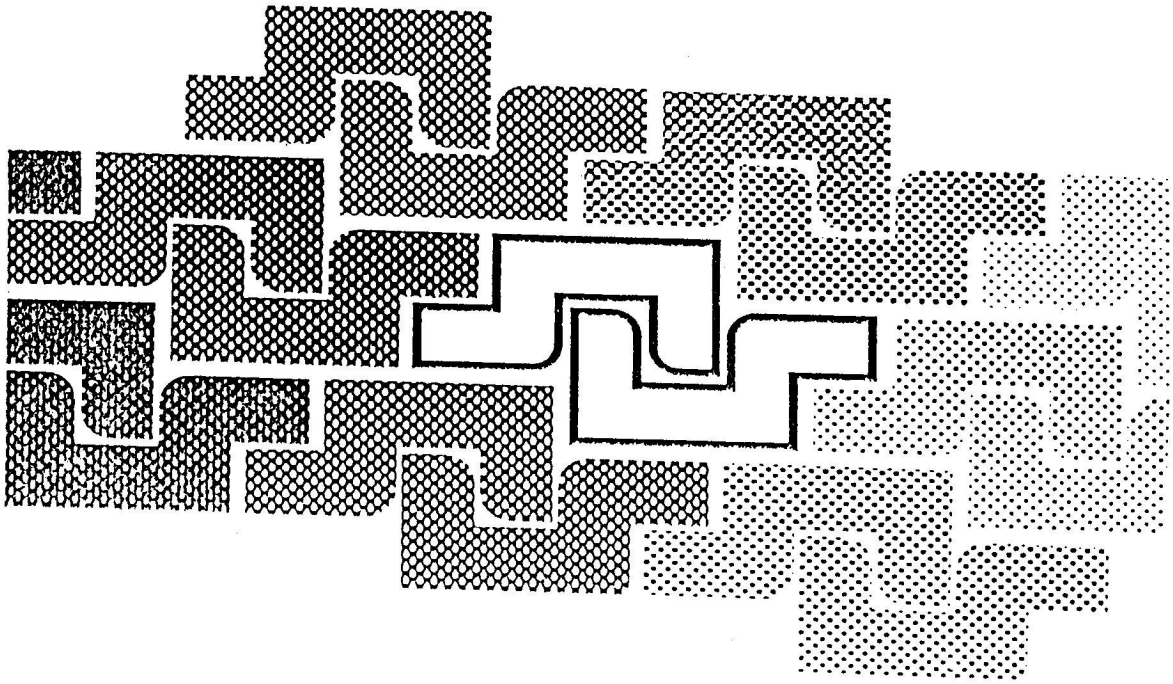

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