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Gas Exchange in Wetlands: Controls and Remote Sensing

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Introduction

This project was directed toward the quantification of fluxes of gaseous biogenic sulfur compounds from freshwater wetlands. These compounds (primarily hydrogen sulfide (H_2S), dimethyl sulfide (DMS), and carbonyl sulfide (OCS)) have been implicated in the regulation of planetary albedo by the formation of microscopic atmospheric aerosols when they oxidize, and the further role of these aerosols as cloud condensation nuclei (CCN). The role of continental sources and sinks for these compounds is poorly understood. The present study was undertaken to quantify the source and sink strength of high latitude wetlands, and to delineate factors that regulate this flux.

Sampling Sites and Methods

The majority of research during the one-year project was conducted in Sallie's Fen in New Hampshire, which is a poor fen dominated by *Sphagnum* mosses (de Mello and Hines, in press). Preliminary work in this fen revealed it as an unusually strong source of DMS when compared to marine sites that are rich in sulfur (Hines, in press). Preliminary work also suggested that these types of wetlands emit more DMS from ombrotrophic areas than from mineral-rich ones which is in contrast to other gases like methane. Therefore, the goals of the project were to test the hypotheses that DMS emissions are high in these systems, and that they are highest from nutrient poor areas. The data were put into a seasonal framework. In addition, we tested that hypothesis that increased inputs of inorganic S would stimulate the emissions of gaseous S.

Emissions of biogenic S gases were determined using dynamic (use of a sweep gas) flux chambers as described in Morrison and Hines (1990). Experiments comparing static chambers and dynamic ones demonstrated that both chambers were suitable for DMS measurements, but that only the static chamber technique could be used for OCS which is consumed by the wetland (de Mello and Hines, in press). Gases were collected from chambers using a mass flow controller system with volume totalizing, and samples were trapped in Teflon loops immersed in liquid argon. Gases were analyzed in the laboratory by gas chromatography with flame photometric detection.

An experiment was conducted to examine the effect of S additions on the production and emission of S gases. Plots were fertilized with an inorganic S compound and the depth distribution of S gases, and the rate at which they were emitted from the surface, were monitored. In one plot, the surficial vegetation (primarily *Sphagnum*) was removed prior to the amendment with S.

Another set of flux measurements was made in three wetlands in the Experimental Lakes Area (ELA) in western Ontario, Canada in July, 1992. This work was conducted as part of a larger experiment to determine the effects of flooding on the production and release of biogenic gases, and on the methylation and demethylation of mercury. The work conducted in 1992 was during a pre-flood year. Post-flood measurements will be made in 1994 with funding from another source. During the pre-flood year we determined S gas emission rates along wetland gradients from the central pond to the surrounding upland. We also measured the concentrations of S gases in the ponds to determine the relative importance of wetlands and open water as sources of biogenic S gases to the atmosphere.

Results and Discussion

Much of this work is presented in documents that have been either accepted for publication, are in review for publication, or are being prepared for publication from graduate theses that have been completed. The following is a summary.

The study comparing the static with the dynamic chamber technique for measuring S gas exchange yielded information which was extremely useful. Virtually all of the data available on fluxes of S gases from continental habitats was made using dynamic chamber approaches. Earlier studies reported that dynamic chambers that utilize S-free sweep gas will underestimate flux rates for OCS and carbon disulfide (CS_2) from forest soils. Our work showed that this is true for wetlands as well (de Mello and Hines, in press). However, our work demonstrated that the dynamic chambers are adequate for use with gases that emitted from a habitat, and that previous DMS flux data are probably correct in most cases. Our data also showed that wetlands are net sinks for OCS, which is in contrast to all other published studies which employed S-free

sweep air and dynamic chamber techniques. Our data also revealed that the anaerobic peats in these wetlands are sources of OCS, but that the surficial peat and living vegetation consume sufficient OCS to make the ecosystem a net sink (de Mello and Hines, in press).

Emissions of DMS greatly dominated S gas fluxes in all of the *Sphagnum*-dominated wetlands examined. This differed from marine wetlands where methane thiol (MSH) and other S gases were a significant portion of the total (Morrison and Hines, 1990; Hines, in press). Fluxes of DMS varied by nearly two orders of magnitude throughout the wetlands (Hines, in press). Fluxes at individual sites were controlled strongly by temperature. We were unable to measure emissions of DMS when temperatures were below ~5° C. During 24 hr studies, DMS emissions varied by several fold as temperatures changed. However, temperature changes did not explain two order of magnitude changes in DMS flux from one site to the next on the same day. Fluxes in the minerotrophic sections of Sallie's Fen were less than those in the nutrient-poor (also low pH) areas as proposed. The high fluxes in the ombrotrophic areas were faster than those measured in many salt marshes despite the fact that the latter contain >100 fold more S (de Mello *et al.*, submitted).

Additions of inorganic S to experimental plots in Sallie's Fen caused a rapid increase in S gases in peat pore waters, particularly DMS and MSH. In a site in which all green vegetation had been removed, these gases increased to nearly millimolar levels in pore waters within three days. In undisturbed sites, the dissolved gases increased for one day and then decreased again to low levels (de Mello *et al.*, submitted). However, the maximum concentrations at the undisturbed sites were 10-fold lower than those at the "bare" site. Although the concentrations of dissolved gases increased in response to S additions, the fluxes did not increase, at least for 3-4 days following the S amendment. These results indicated that the system is capable of producing large quantities of S gases when additional S is available. However, the presence of plants prevents the accumulation of S gases. Interestingly, sites with plants always emitted more S gases than unvegetated sites, and the addition of *Sphagnum* to bare sites enhanced S gas emissions greatly. Sites with no *Sphagnum* emitted very small quantities of S gases. Although

MSH concentrations increased greatly in response to S additions, this gas was rarely measured within flux chambers even when DMS fluxes were high. It appears that MSH is selectively oxidized prior to transport, probably during its capillary movement in *Sphagnum* (de Mello *et al.*, submitted).

All of the experimental data indicated that DMS (and MSH) was produced from the methylation of inorganic S (H_2S) (i.e., H_2S methylated to MSH, followed by the methylation of MSH to DMS). This differs greatly from DMS in marine environments where the bulk of the DMS produced is derived from the hydrolytic cleavage of an organic S compound which serves as an osmoregulant in vascular plants and algae.

Emissions of DMS from the ELA wetlands were quite high in some cases even though the atmospheric input of S to this part of Canada is very low relative to the New Hampshire sites. The wetlands emitted much more S gases than did the central ponds. This is important since estimates of wetland emissions of S gases have been based on data from samples of standing water or from small ponds, indicating that previous estimates of flux have been grossly underestimated. In fact, S gas emissions become very slow when an active site becomes flooded after a prolonged rain event.

We noted a pronounced spatial trend in the magnitude and speciation of the S gas flux in the wetlands at the ELA as one moves from the pond toward the upland. The floating *Sphagnum* mat emitted primarily H_2S with very little DMS. The central part of the wetland emitted all DMS at the highest rates measured. Near the upland, DMS continued to dominate flux, but rates were quite slow. This trend agrees with our hypothesis that the ombrotrophic areas of wetlands are the primary sources of DMS.

Biogenic S gas emissions are unusually high in the northern wetland environments. Because of the relatively small global cover of these wetlands and the short growing season, they are not large contributors to the global atmospheric S burden. However, since S gases are short lived in the atmosphere, these wetlands can be important contributors on a regional basis in remote areas.

Theses and Publications:

de Mello, W. Z. 1992. Factors controlling fluxes of volatile sulfur compounds in *Sphagnum* peatlands. Ph.D. thesis. University of New Hampshire.

Murray, G. 1994. Rates of sulfate reduction and methanogenesis in an artificially acidified northern wetland. M.S. thesis. University of New Hampshire.

Hines, M.E. in press. Emissions of sulfur gases from wetlands. In: D.D. Adams, S.P. Seitzinger and P.M. Crill (eds.), Cycling of Reduced Gases in the Hydrosphere.

de Mello, W.Z. and M.E. Hines. in press. Application of static and dynamic enclosures in determining DMS and OCS fluxes in *Sphagnm*-dominated peatlands. Implications for the direction and magnitude of flux. J. Geoophys. Res.

de Mello, W.Z., M.E. Hines and S.E. Bayley. submitted. Northern freshwater wetlands as sources of dimethyl sulfide to the atmopshere. Global Biogeochemical Cycles,

Presentations at Scientific Meetings :

de Mello, W.Z., M.E. Hines and S.E. Bayley. 1992. Factors controlling sulfur gas exchange in *Sphagnum*-dominated wetlands. American Society of Limnology and Oceanography Annual Meeting. Santa Fe, New Mexico.

Hines, M.E., W.Z. de Mello and C. A. Porter. 1993. Sulfur gas exchange in *Sphagnum*-dominated wetlands. Biogeochemistry of Wetlands Symposium, Baton Rouge, Louisiana.

In Press: Journal of Geophysical Research

Application of static and dynamic enclosures for determining dimethyl sulfide and carbonyl sulfide exchange in *Sphagnum* peatlands: Implications for the magnitude and direction of flux

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Abstract. A static enclosure method was applied to determine the exchange of dimethyl sulfide (DMS) and carbonyl sulfide (OCS) between the surface of *Sphagnum* peatlands and the atmosphere. Measurements were performed concurrently with dynamic (flow through) enclosure meas-urements with sulfur-free air used as sweep gas. This latter technique has been used to acquire the majority of available data on the exchange of S gases between the atmosphere and the continental surfaces and has been criticized because it is thought to overestimate the true flux of gases by disrupting natural S gas gradients. DMS emission rates determined by both methods were not statis-tically different between 4 and >400 nmol m^{-2} h^{-1}, indicating that previous data on emissions of at least DMS are probably valid. However, the increase in DMS in static enclosures was not linear, indicating the potential for a negative feedback of enclosure DMS concentrations on efflux. The dynamic enclosure method measured positive OCS flux rates (emission) at all sites, while data using static enclosures indicated that OCS was consumed from the atmosphere at these same sites at rates of 3.7 to 55 nmol m^{-2} h^{-1}. Measurements using both enclosure techniques at a site devoid of vegetation showed that peat was a source of both DMS and OCS. However, the rate of OCS efflux from decomposing peat was more than counterbalanced by OCS consumption by veg-etation, including *Sphagnum* mosses, and net OCS uptake occurred at all sites. We propose that all wetlands are net sinks for OCS.