

Acid Rain Links to Methane Emissions from Wetlands
Aspen Global Change Institute: Atmospheric Composition, Biogeochemical
Cycles and Climate Change

Vincent Gauci

As the most abundant hydrocarbon in the atmosphere and a powerful greenhouse gas, methane (CH₄) plays an important role in both the chemical composition and radiative balance of the earth's atmosphere. To understand its role in the atmosphere, its sources and sinks as well as processes governing the rates and fluxes of this gas is an important objective if we are to understand the function of the earth as a system and the role human activity may play in affecting the earth's natural balance.

Natural freshwater wetlands are the largest individual source of methane where the gas is formed in the terminal stage of anaerobic decomposition by a group of bacteria known as methanogens (or methane producing bacteria – MPB). This source is responsible for approximately 22% of the global methane source budget. Anthropogenic methane sources, however, provide the majority of methane to the atmosphere, which has led to a dramatic increase in the concentration of atmospheric methane since the onset of the industrial era. Although this has been the overall trend during the past century there has recently been a slow down in the rate at which atmospheric methane is accumulating (*Dlugokencky et al., 1998*). The reasons for this are as yet unknown.

Wetland micro-organisms can co-operate or compete depending on the sulfate status of the soil system.

In coastal wetlands and wetlands overlying sulfate rich deposits methane emissions are very much lower to otherwise comparable freshwater wetlands (*Rejmankova and Post, 1996*). It is thought that in sulfate rich environments this is due to microbial competition favouring sulfate reduction as an energetically more efficient means of carbon degradation than methanogenesis (fig 1).

Recent research has shown that in freshwaters, competition favouring SRB over MPB may also occur when concentrations of sulfate have been increased. In addition it has been found that in low sulfate anaerobic environments, SRB may supply substrates (Hydrogen) that allow MPB to produce methane and, in doing so, allow low concentrations of hydrogen to be maintained. This “syntrophic” association could subsequently become de-coupled upon the addition of sulfate with SRB gaining competitive superiority over the MPB (*Raskin et al 1996*). Natural fresh water wetlands and peatlands may receive sulfate from rainwater at very low concentrations and increases in the anthropogenic output of sulfur over the past century, through fossil fuel combustion, has meant that sulfate deposition has increased in North America and western Europe (although in both regions it is currently in decline) and, to a growing extent Asia, making the impact of sulfur deposition on wetlands increasingly likely.

An under-explored Sulfur / Carbon Cycle Link.

Although there is clear potential for the global methane budget to be perturbed by such an interaction it has not until recently been thoroughly examined in natural systems with work having been limited to large “fertilisation” dose experiments in rice paddy systems and work on peat cores in laboratories, somewhat removed from natural conditions and frequently with sulfate concentrations far in excess of that which can be expected in acid rain impacted wetlands.

A recent experiment has, however, been conducted with the following specific questions in mind:

- Do low rates of sulfate deposition, similar to those experienced in acid rain impacted regions suppress methane emissions from wetlands?
- If so, by how much?
- What are the controlling variables that determine the extent of any suppression e.g. is there a simple dose response?

The field scale, plot experiment was located in Morayshire in northern Scotland on an extensive area of peatland known as Moidach More. The site was selected for its

large expanse of pristine peat but, more importantly, for its low rate of ambient sulfate deposition of $5 \text{ kg S ha}^{-1} \text{ yr}^{-1}$. Plots within the experimental site were treated with a weekly spray of Na_2SO_4 solution which amounted to annual rates of SO_4^{2-} deposition of 25, 50, and 100 kg S ha^{-1} , a range of S deposition rates which is reflective of that which is experienced in areas affected by intermediate to high rates of acid rain and at far lower rates of S deposition than in previous experiments. An additional set of replicate plots, acting as controls, received only deionised water. A gas exchange chamber was inserted into each plot (fig 2) so that CH_4 flux measurements could be made. The site was then monitored for methane emissions for two years, from the spring of 1997 to 1999. The main results are summarised below:

- All three treatments emitted up to 30 % less CH_4 than the control plots over the course of the experiment (fig 3).
- When considering the second year alone the suppression was closer to 40%.
- There was no significant difference in fluxes between treatments.
- In 1999 (year 2) the degree of suppression seemed to vary with both temperature and water table i.e. a decline in treatment effect with an increase in temperature and an increase in treatment effect with a decrease in water table.

These results are broadly consistent with results from previous “high dose” field experiments as well as two similar low dose field experiments in Minnesota and Sweden. The temperature response in the treatment effect is also supported by recent laboratory findings which indicate that a change in the dominant substrate source with temperature alters the competitive interaction between MPB and SRB.

The interaction has been established - low levels of S deposition can affect CH_4 emissions from natural wetlands, but is the process important at the global scale?

To examine the global significance of changing patterns of S deposition on the wetland CH_4 source, output from two models was combined. The first, a regression model of a climate sensitive process model of methane emission from wetlands

(Walter, see summary in this volume), was used to generate global CH₄ emission fields from natural wetlands for 1960, 1990 and 2030. The second, a tropospheric sulfur simulation in the Goddard Institute for Space Studies GCM provided sulfur deposition fields for the same years. It is estimated that CH₄ emissions from northern wetlands (>30 degrees north) may have been suppressed by as much as 14 % in 1960, 17% in 1990 and then recovering to a suppression of 15% in 2030 as S deposition in these regions is reduced due to pollution control legislation.

The implications for natural wetlands in the tropics, where wetlands emitting the majority of CH₄ are located, are more difficult to estimate with confidence as their response to S pollution may be quantitatively different to that of mid to high northern latitudes. However, should they respond in the same way to increasing loads of sulfur deposition as northern wetlands, and experiments on rice paddy systems suggest that this may be the case, it is estimated that predicted increases in sulfur deposition, particularly in Asia, will result in CH₄ flux suppression of approximately 12% in 2030 from a suppression of 3% to 4% in 1960 and 1990 respectively. With our understanding of tropical wetland soil systems and their CH₄ fluxes limited by a scarcity of long-term monitoring, further investigations of this interaction in these systems should be prioritised.

References:

Dlugokencky E J, Masarie KA, Lang, PM, Trans PP (1998): Continuing decline in the growth rate of the atmospheric methane burden. *Nature* 393, 447-450

Raskin L, Rittmann BE, Stahl DA (1996) Competition and coexistence of sulfate-reducing and methanogenic populations in anaerobic biofilms *Appl Environ Microb* 62: (10) 3847-3857

Rejmankova E, Post RA, (1996) Methane in sulfate-rich and sulfate-poor wetland sediments. *Biogeochemistry* 34: 57-70