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# IMPACTS OF CLIMATIC CHANGE ON PEATLAND HYDROCHEMISTRY; A LABORATORY-BASED EXPERIMENT

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A laboratory simulation of a reduction in water table height that could be anticipated from current climate change models, resulted in a change in the efficiency with which a valley-bottom wetland acted as a sink/ source of nutrients. Effects were confined to the upper 10 cm of the profile, but since this depth has the greatest hydraulic conductivity, it was noted that the effects of hydrochemical changes therein would be readily transferred to receiving waterbodies. Marked changes in leachate chemistry were observed, including increases in nitrate and sulphate concentrations, while concentrations of phenolics, dissolved organic carbon, potassium, iron and ammonium decreased. These changes have implications for the quality and productivity of waters draining wetlands.

KEY WORDS Wetlands, peat, biogeochemistry, climatic change, water table, hydrochemistry, riparian zones, buffer zones

## INTRODUCTION

In terms of hydrochemistry, lands which are at least periodically waterlogged (wetlands), are of greater global significance than is suggested by the relatively small area (3%) of the Earth that they cover. Braekke (1981) for example, found that 62% of dissolved materials exported from a Norwegian watershed were chemically changed by passing through wetlands, even through the wetlands only accounted for 24% of the total catchment area. A variety of studies have indicated that, in terms of water-quality, the net effect of these changes can be highly beneficial, with the wetland acting as a nutrient sink, and thus reducing the mobility of many environmentally problematic elements that would otherwise be transferred to other ecosystems (Braekke, 1981; Gorham *et al.*, 1984; Weider *et al.* 1987).

Recent studies have also demonstrated the potential for a reversal of this situation, with the wetland becoming a nutrient source, as a consequence of man-imposed environmental changes such as acid precipitation (Urban and Bayley, 1986; Brown, 1985, 1986), drainage for agriculture (Heathwaite, 1990) or afforestation (Emmett and Reynolds, 1991; Lundin and Bergquist, 1990) and peat-cutting for fuel (Sallantaus and Patilla, 1985). Such a reversal can best be illustrated with reference to sulphur, which in the predominantly waterlogged anaerobic conditions of an undisturbed wetland, tends to be immobilised as insoluble sulphide (Ponnamperuma, 1972). On disturbance to more aerobic conditions, oxidation of sulphides to highly mobile sulphate is favoured which can then be washed out from the wetland during heavy rainfall events. Gosling and Baker (1980) have noted that the concomitant dramatic rise in acidity that is induced in poorly buffered receiving waters can even lead to fish kills.

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In the following study, we have investigated the potential implications of climatic change arising from an enhanced "greenhouse effect" on the efficiency with which wetlands act as a sink (or source) of dissolved materials. Of the many scenarios which could be induced by increased global warming, those suggesting an increased frequency of summer drought (Meteorological Office, 1989) and/or increased evapotranspiration (e.g. Rowntree *et al.*, 1989; Department of the Environment, 1991) are of particular relevance to peatlands. The reduction in water availability implicit in these scenarios threatens to compromise the very factor (abundant water) that gives wetlands their unique properties. It seems likely that global warming could reduce the ability of wetlands to act as nutrient sinks.

In order to test this hypothesis, drought-imposed water-table reductions were modelled using intact peat monoliths in a laboratory-based experiment.

## MATERIALS AND METHODS

## Peat core collection

Intact cores were collected from a valley-bottom wetland close to Cerrig-yr-Wyn, Plynlimon, mid-Wales (UK Nat. Grid Ref. SN 820 866), using a length of PVC pipe (central core chamber described below). This ensures minimal disturbance to the sample by avoiding the need to transfer material from a separate coring device into the perfusion system. Experience has shown that poor coring technique can result in compacted cores which are consequently unrepresentative of the field material. To avoid this, a three stage monolith-collection procedure was adopted, involving first cutting through the initial 15cm depth using a sharp knife (using the external face of the core chamber as a template). The chamber was then eased into the pre-cut peat to the full 15 cm depth. A 10 cm wide trench was excavated around the outside of the chamber, which then allowed access with the knife so that the next 15 cm of the core could be "cut, encased and excavated", as above. This was repeated until the desired core depth (0.5 m) was achieved. The final stage involved sliding an ABS-plastic cap under the core, followed by careful withdrawal of the intact monolith from the excavated pit, and immediate transportation back to the laboratory.

#### Perfusion system

The apparatus (Figure 1) was based around a central chamber containing a monolith of peat and consisted of a 60 cm length of 110 mm diameter  $Osma^{(TM)}$  PVC plastic piping. The top of each system was left open. This allowed a) the input of deionised water via a peristaltic pump (0.05 cm<sup>-3</sup> min<sup>-1</sup>) to prevent desiccation of the monolith, b) a free exchange of gases between the core and the atmosphere, and c) the transmission of light to the upper layer of living plant material (predominantly *Sphagnum*). The base of the chamber was plugged with an interference-fit ABS-plastic cap, drained by 12.5 mm diameter Durapipe<sup>(TM)</sup> tubing, which rises via two consecutive 90° Durapipe<sup>(TM)</sup> connectors to rise parallel to the core chamber in a 'J' shaped fitting. The key feature to note is that the height of the outlet from the 'J' tube can be raised or lowered to manipulate the height of the water table inside the column, thereby simulating the water table reductions predicted by certain climatic change scenarios.

At 10 cm intervals, 2.5 ml Plastipak<sup>(TM)</sup> syringes cut to 20 mm length and packed



Figure 1 The core perfusion system.

with glass wool, were inserted through drilled holes into the sides of the chamber, with the Luer tip outermost. These ports served two functions: First, they were used to sample fluids from within the core with minimal disturbance of the peat core, and secondly, when not in use for sampling, the outlet from the Luer tip was connected via (Auto-Analyser) transmission tubing to the 'J' drainage pipe. This simulated natural conditions where precipitation entering a wetland not only travels downwards, but can also travel laterally (particularly in wetlands lying on a gradient) to an extent dependent on the hydraulic conductivity of the medium.

## Climatic change simulation

Ten replicate perfusion systems were set up in a constant temperature laboratory (11°C) with a 12h light:dark cycle. Half of these were maintained with the water table near the surface (controls) while the water table in the remaining systems was gradually reduced over a 10 week period (by lowering the water outlet on the "J" side arm) to maximum 20 cm depth (within the range normally experienced during field observations of severe drought, R. Smit and H.A.P. Ingram, pers. comm.). This depth was maintained for a further 6 weeks, after which the water table was returned

to the surface for the final 2 weeks of the study to simulate the end of drought conditions. The core hydrochemistry was monitored every second week of the simulation.

### Hydrochemical analysis

Samples of water were taken from surface, 10, 20, 30, 40 and 50 cm depths using a syringe, with the first 5 ml discarded, and the following 10 ml collected and filtered through a Whatman GF/F filter (and DIONEX On-Guard P sample pretreatment cartridge for ion chromatography) prior to analysis. A DIONEX 2000i ion chromatograph was used to determine chloride, bromide, nitrate, phosphate and sulphate using an AS4A anion column with 1.7 mM NaHCO<sub>3</sub>/1.8 mM Na<sub>2</sub>CO<sub>3</sub> eluent at 2 ml min<sup>-1</sup> flow rate and 25 mN H<sub>2</sub>SO<sub>4</sub> regenerant. Sodium, ammonium, potassium, magnesium and calcium, were determined using the same system, but with a CS10 column and an eluent of 40 mM HCl/4 mM dl-2, 3-diaminopropionic acid (mono hydrochloride), at a flow rate of 1 ml min<sup>-1</sup> and 0.1 M tetra butyl ammonium hydroxide regenerant. Iron and aluminium were determined using atomic absorption spectroscopy: Iron using a Perkin Elmer 280 AAS flame system at 248.3 nm with an air/acetylene mixture, while aluminium was determined using a Thermo Jarrell Ash video 11E AAS with graphite furnace atomiser 188, at 309.3 nm. Phenolics were determined using the spectrophotometric technique of Box (1983). Dissolved organic carbon (DOC) was estimated using a Skalar auto-analyser with UV digestion/colorimetric detection system. Dissolved oxygen and pH were monitored using conventional electrometric techniques.

## RESULTS

From Figure 2 (a-p), it can be seen that the impact of drought on wetland hydrochemistry was generally confined to the upper 10 cm. At this depth, three types of response were observed among the different measured parameters and these were investigated statistically using Statgraphics Version 2.1 (STSC inc, Rockville Maryland, 20852, USA). First were those solutes that showed a significant (ANOVA) increase: a, sulphate (p < 0.001), b, nitrate (p < 0.05) and c, oxygen (p<0.01); secondly those that were not significantly affected (p>0.05): d, chloride, e, sodium, f, phosphate, g, magnesium, h, bromide, i, calcium j, aluminium and k, pH. Finally, there were those that significantly decreased in concentration: j, potassium, (p>0.05), m, ammonium (p<0.05), n, iron (p<0.001), o, phenolics (p < 0.05) and p, dissolved organic carbon (p < 0.05). Potassium is included among the significant decreases because a comparatively weak but nevertheless significant Spearman rank correlation was found between water-table depth and potassium concentration (correlation = 0.58, p<0.05). The correlations between water table depth and the other parameters that were affected by the simulated drought were of greater significance and degree of correlation; the chemicals that increased (oxygen, nitrate, sulphate) exhibited strong negative correlations (range -0.73 to -0.93, p < 0.01), while those that decreased (DOC, iron, ammonium, phenolics) showed strong positive correlations (range 0.67 to 0.75, p<0.01).

T-tests showed that the two replicate treatments were not significantly different at the beginning of the simulation. As the simulation progressed, however, differences between the treatments became significant with maximum responses as follows:



**Figure 2** Mean concentration profile (time-averaged over 16 week simulated climate-change) of a, sulphate, b, nitrate, c, oxygen, d, chloride, e, sodium, f, phosphate, g, magnesium, h, bromide, i, calcium j, aluminium and k, pH, j, potassium, m, ammonium, n, iron, o, phenolics and p, dissolved organic carbon. Shaded bars indicate controls and open bars indicate manipulated cores, error bars indicate  $\pm$  standard error.





phenolics -80% (p<0.01), ammonium -94% (p<0.001), potassium -61% (p<0.01), DOC -77% (p<0.05) iron -93% (p<0.05). Nitrate reached a maximum 340-fold increase (p<0.05) and sulphate a 29-fold increase (p<0.05). With all ions except ammonium and potassium, simulation of the end of the drought on week 16 resulted in a rapid return towards the concentration within the control cores (Figure 3).

It will be noted that no concentration values were reported for the surface waters of the cores subjected to simulated drought. This was because the treatment caused the surface of the peat to fall by approximately 2 cm, to a point below the sampling port. This phenomenon is often observed in the field as "Mooratmung" (mire breathing) (Ingram, 1983). Many of the phosphate concentrations were below detectable levels, and thus even though more phosphate was observed during drought-simulation, the findings could not be considered significantly different.

## DISCUSSION

The laboratory system used in this study gave a great deal of control over the rate and extent of water-table draw-down, and increased the ease with which biogeochemical responses along the peat profile could be monitored. At first sight, however, the effects of this simulated climatic change on peatland hydrochemistry appear minimal. Only the upper 10 cm appears to be affected with little evidence for the vertical migration of the induced chemical changes into the lower depths of the profile. However, the impacts may be of somewhat greater significance than the restricted depth would suggest, the reason being that the upper layers have the greatest hydraulic conductivity of the profile (Mathur and Lavesque, 1985). Water movement is always likely to be greatest within this layer (Gafni and Brooks, 1990), and thus the effects of any hydrochemical changes there are likely to be transmitted to waterbodies receiving drainage from the wetlands, with the potential for pronounced effects on their water chemistry/quality.

Of the induced hydrochemical changes, the increases in nitrate and sulphate concentrations are particularly striking. The increase in sulphate concentration can be explained in terms of established theories of the effects of increased aeration of water-logged soils, and is likely to have been due to the oxidation of sulphides (Ponnamperuma, 1972). The abundant sulphate can be readily mobilised during subsequent rainfall events, with serious implications for the biota in poorly buffered waters draining the wetlands, due to dramatic increases in acidity (Gosling and Baker, 1980). The increase in nitrate concentration is likely to have been induced by increased mineralisation of nitrogen-containing organic compounds in the more aerobic conditions within the cores undergoing simulated drought (cf. Williams and Wheatley, 1988). Both nitrates and sulphates are implicated in environmental acidification, and nitrate is significant from a eutrophication and environmental health perspective. The results of the drought simulation suggest that climatic change could cause wetlands to become less effective as nitrate sinks (cf. Cooper, 1990) than they are at present, thus limiting their increasingly appreciated role as nitrate buffer zones (Lowrence *et al.*, 1985).

For the reduced form of nitrogen, the substantial fall in ammonium-N concentration contrasts with the observations of Williams and Wheatley (1988) who found that reduced water table heights increased ammonium concentrations (and the number of ammonifying bacteria) in a forested peatland. Our observation of reduced ammonium but increased nitrate concentrations suggests that reducing the water-table may have promoted a substantial population of ammonium oxidising bacteria (Zimenco and Misnik, 1970).



**Figure 3** Temporal variation in the hydrochemical responses of the upper 10 cm during the climatechange simulation: a) Increases in sulphate  $-\bullet$ -, nitrate  $-\blacktriangle$ - and oxygen  $-\blacksquare$ -; b) decreases in iron  $-\bigstar$ -, DOC  $-\blacksquare$ - and phenolics  $-\bullet$ -; c) decreases in ammonium  $-\bullet$ - and potassium  $-\blacksquare$ -.

The reduced ammonium concentration, together with the reduction in the concentrations of potassium, iron, phenolics and DOC, indicate the potential for enhanced element immobilisation (including inorganic-N, when the overall balance of nitrogen and ammonium are considered (Figure 2b/2m)). The reduction in potassium concentration was not anticipated, and may represent an increase in wetland plant uptake, while the reduction of iron, phenolic and DOC concentrations may have a more physical cause. Iron, for example, is likely to precipitate as Fe (III) compounds as redox potential increases, while DOC, and in particular phenolic-rich humic compounds, tends to adsorb on to the precipitated particles, thus coming out of the aqueous phase in the process (Tipping and Woof, 1990). Microbial processes are also likely to contribute to the depletion of DOC. In the more anaerobic waterlogged conditions which normally prevail in wetlands, a proportion of the products of metabolism are organic solutes such as organic acids, alcohols, aldehydes and ketones (Ponnamperuma, 1972). However, under aerobic conditions, carbon metabolism is more efficient, and tends to favour the rapid production of carbon dioxide and thus inorganic (rather than dissolved organic) carbon end-products. For the majority of the affected ion-concentrations, the longevity of the above responses were closely coupled to the drought duration (Figure 3a, b) as the concentrations rapidly returned towards control concentrations on simulation of the end of the drought. However, for ammonium and potassium, it is interesting to note that the effects seem likely to persist longer than the drought itself (Figure 3c).

The net effect of these changes is likely to be expressed at the level of the microorganisms which form a trophic link (Hynes, 1970) between dissolved materials leached from the wetland, and the higher trophic levels of the aquatic ecosystem. Reductions in ammonium and potassium could constrain the growth of autotrophic (algal) parts of the community, while the reduction in DOC could limit the heterotrophic (bacterial) populations for which DOC is the primary energy source. However, it is significant that phenolic materials have been suggested to be inhibitory to both bacterial (Freeman et al. 1990) and algal components (Provasoli et al., 1957). Thus the reduction in the concentration of this putative inhibitor, in combination with an increased nitrate availability, may well counteract any nutrientlimitation effects. It is nevertheless clear that if this response should prove to be a general phenomenon, then the changes in peatland hydrochemistry (induced by climate change) could affect the structure of microbial communities at the base of the aquatic food chain of the receiving waters, with significant implications for their higher trophic levels. Perhaps the most disturbing prospect, however, is that the effects described could be observed, not just in an isolated area (for example, where a particular wetland has been drained and afforested), but simultaneously across many wetlands over a very substantial part of the Earth.

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