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Effects of summer drought on peat soil solution chemistry in an acid gully mire

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Abstract

In a field experiment to investigate potential impacts of climatic change, a small area of flush wetland in Wales was subjected to three successive years of simulated summer drought/rewetting (autumn–spring) cycles (1992–94). Drought was simulated achieved by diverting stream water around the experimental wetland during the summer, so that the wetland received only precipitation inputs during that time. The effects on peat–water chemistry in the rhizosphere were monitored at regular intervals until spring 1996, and comparisons made with a control. Simulated summer drought decreased, significantly, the natural summer peaks in dissolved organic carbon (DOC) and iron, whilst subsequently increasing the natural autumn–winter peaks in sulphate concentrations and acidity in the peat water. The effects of simulated drought on SO_4 concentrations in the peat water compared favourably with subsequent events monitored following a natural summer drought in 1995. Autumn–winter peaks in SO_4 concentrations in the control wetland following the natural drought were of similar magnitude to those induced by the drought simulated in the experimental wetland in the previous three years.

Introduction

Wetlands form an important component of many upland catchments in Wales and elsewhere in western Britain. The relatively wet and cool temperate climate in the uplands provides ideal conditions for the formation and establishment of wetlands of various types—including blanket bogs, flushes, raised bogs and valley bottom mires. Wetlands can act as ‘buffer zones’ improving the quality of surface waters flowing through them; *e.g.* wetlands may play an important role in mitigating the effects of anthropogenic acid deposition by actively retaining some of the SO_4 inputs within the wetland. Hemond (1980) reported that SO_4 uptake in Thoreau’s Bog in Massachusetts neutralized about two thirds of atmospheric acid deposition, despite this being an area of high atmospheric S deposition. In Swedish catchments containing from 8–33% bogs, Calles (1983) found a range of 25–65% retention of SO_4 whilst Bayley and co-workers (1987) reported that much of the sulphuric acid experimentally applied to a bog in western Ontario was neutralized by SO_4 uptake.

However, there have been concerns that disturbances to wetlands, such as may occur during periods of drought, may reverse some of the previously beneficial effects of SO_4 uptake (Gorham *et al.*, 1984). Indeed, various studies have reported that during years with hot, dry summers,

SO_4 may be produced from reoxidation of reduced S compounds in the peat and subsequently released to surface waters as an autumnal pulse (Wieder & Lang, 1982; Bayley *et al.*, 1986; LaZerte, 1993). In base-poor wetland areas recipient of high acid deposition loadings, proton export accompanies SO_4 release (LaZerte, 1993), whilst in more base-rich wetlands, or in areas which receive less acid deposition, Ca and Mg are released along with SO_4 (Bayley *et al.*, 1986).

Growing concerns over the prospect of global climate change, including climate models predicting an increased frequency of summer drought over western Europe and North America (Mitchell & Warrilow, 1987), have increased the need to investigate the potential impacts of summer drought on biogeochemical processes within wetlands and the possible implications for surface water quality. This paper reports some results of a study investigating the effects, on wetland biogeochemistry, of an experimental manipulation of the hydrological conditions in a flush wetland in Mid-Wales. Specifically, the effects of three successive years of simulated summer drought/rewetting (autumn–spring) cycles (1992/93–94/95) on peat hydrochemistry are described. These are compared to a control wetland and to subsequent events monitored following a natural summer drought in 1995.

Study Area and Experimental Design

The catchment chosen for study, Cerrig-yr-Wyn in the Upper Wye catchment on Plynlimon (UK National Grid Ref. SN 820 866), is a small gully, typical of many in the uplands of Wales in which flush wetlands have developed as discontinuous serial cascade systems. The gully mire (peat pH range 4.0–4.8) is characterised by *Sphagnum* and *Juncus* communities. Water movement consists mainly of flow in a meandering channel, alternately subterranean or exposed, located at the interface between the peat and the underlying bedrock (consisting of base-poor Ordovician mudstones or shales). The individual patches of wetland are well defined, making it relatively simple to control the supply of stream water to individual areas of wetland to manipulate the hydrological conditions in the gully mire. Thus, a study of simulated drought and rewet effects on peat water chemistry in the wetland.

This enabled water table within each patch of flush wetland is controlled naturally by a combination of recharge and discharge of the peat in the vicinity of the soil pipes and the surface balance between rainfall inputs, vertical and lateral drainage and evapotranspiration. A flow manipulation system was set up (Fig. 1) with a control wetland at the head of the system fed by rainfall and streamflow. Below the control wetland, a dam was constructed to allow diversion of streamflow through 150mm diameter pipes around an 'experimental' wetland in which summer droughts were simulated. However, the artificial barrier was not fully watertight and some seepage reached the

experimental wetland during base flow conditions; this permitted realistic rates of compensation flow and prevented complete drying. Over a three-year period (1992–94), the wetland was subjected to simulated drought for lengths of time varying between 16 and 20 weeks between late-spring and early-autumn. After simulation of each drought, the rewetting of the experimental wetland was achieved by distributing surface recharge through 150mm pipes across the head of the wetland. The areas of the control and experimental patches of wetland were 348 m² and 336 m², respectively.

Methods

WETLAND FIELD SAMPLING

Peat-water samples were extracted, usually at fortnightly intervals, at 10 cm depth in the peat profile using five soil solution samplers placed in each wetland at 2.5 m intervals along a transect down the two wetlands. The approximate sampling time for each sample extracted was 2–3 minutes. The soil solution samplers were designed to minimize the extraction volume and any unnecessary dead volumes. This ensured that excessive disturbance of the wetland was avoided and that the integrity of the sample extracted (in particular the redox potential) was unaffected. The samples were constructed by removing the ends of ten 2.5 cm³ Plastipak^R syringes 1–1.5 cm from the luer tip. The luer end was retained and packed with glass wool and connected by Tygon^R autoanalyser transmission tubing to the surface, where suction could be applied using a 30 cm³

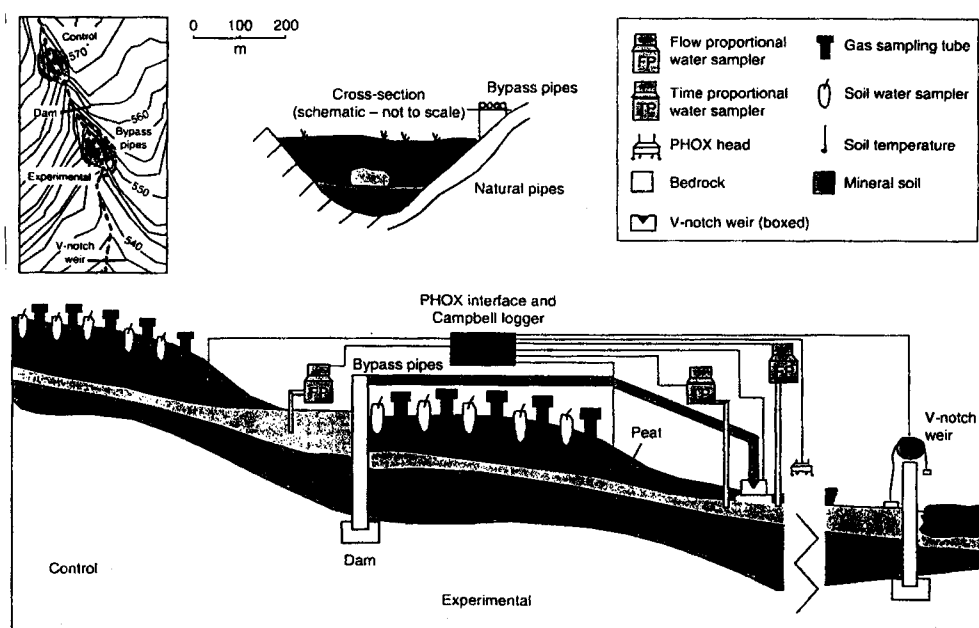


Fig. 1. The layout of the drought manipulation experiment at Cerrig-yr-Wyn.

Plastipak^R syringe, in which the samples were collected (Freeman *et al.*, 1993a).

Peat temperature was measured in the field using a portable electrometric meter and probe. Likewise, pH was determined potentiometrically on sub-samples of peat water immediately after sampling using a portable pH meter. Some problems in measuring pH with the portable pH meter during the first winter (1992/93), were traced later to a faulty electrode which was replaced during the spring of 1993; pH measurements during the winter of 1992–93, therefore, should be treated with caution. Water table levels were measured using a variant of the dip-well technique (comprising a wide, shallow 60cm depth, 15cm diameter, PVC pipe) sited in the centre of the transect through each wetland.

CHEMICAL ANALYSIS OF PEAT-WATER

Samples of peat water were collected, fortnightly, as described above. On return to the laboratory, samples were filtered through 0.2 µm diameter membrane syringe filters and analysed for Na, K, Ca, Mg, Fe, NH₄-N, NO₃-N, PO₄-P, SO₄, Cl and DOC. Sodium and K were measured by flame atomic emission spectrophotometry, and Ca, Mg

and Fe by flame atomic absorption spectrophotometry, respectively. Chloride, NO₃-N, PO₄-P and SO₄ were measured by ion chromatography (Dionex 2000), using an AS4A analytical column and conductivity detection with auto self-regenerating suppression. Ammonium was measured by segmented-flow colorimetry (Na salicylate/Na dichloroisocyanurate method) using a Skalar autoanalyser (until 03/94), and thereafter by the (improved) method of ion chromatography (CS12 analytical column). Dissolved organic carbon was determined by autoanalyser following a UV-digestion technique, and colorimetric detection. The validity of the analytical data generated by the laboratory was monitored by participation in a regular inter-laboratory proficiency scheme (WRC AQUACHECK).

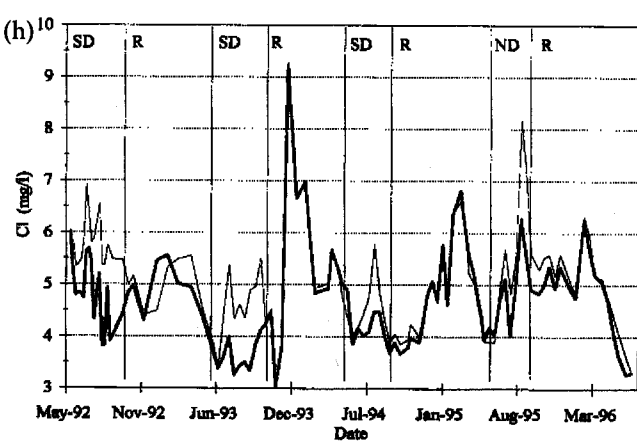
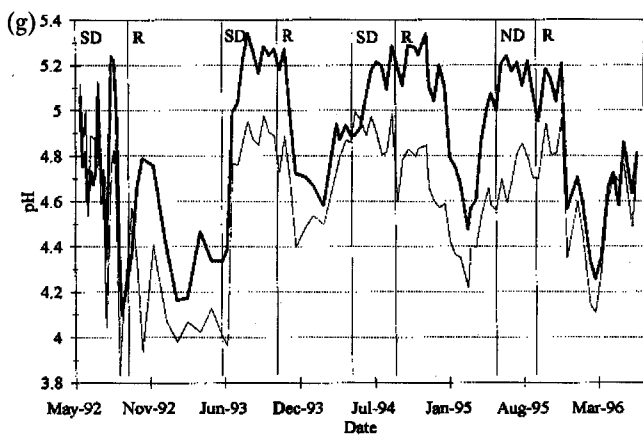
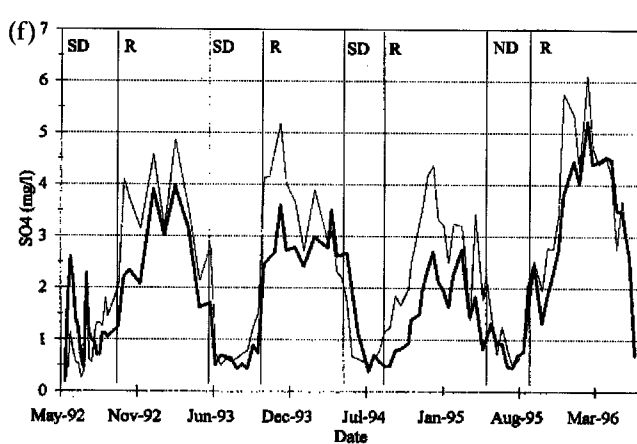
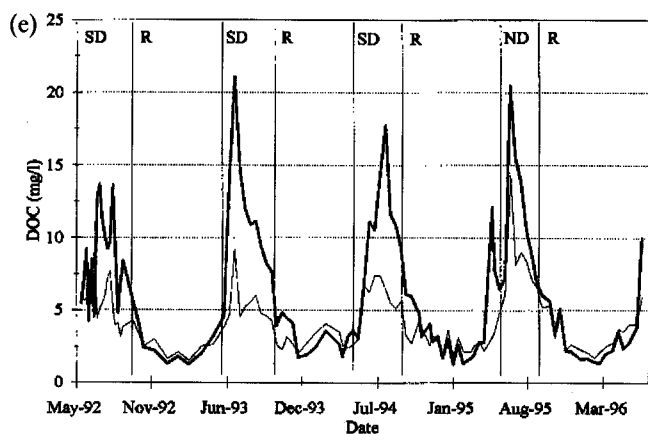
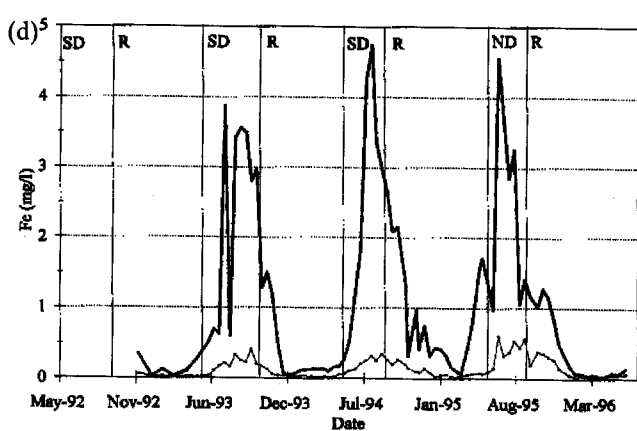
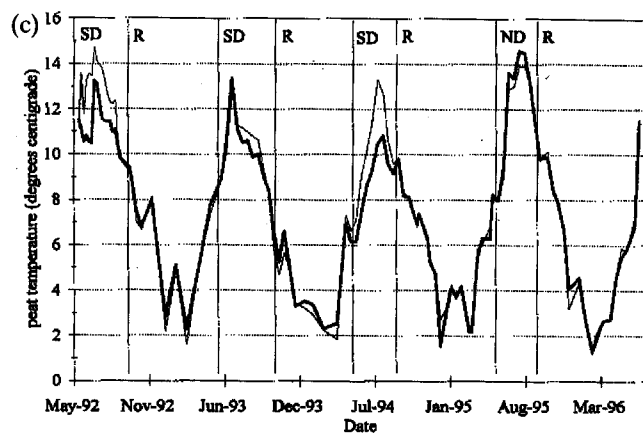
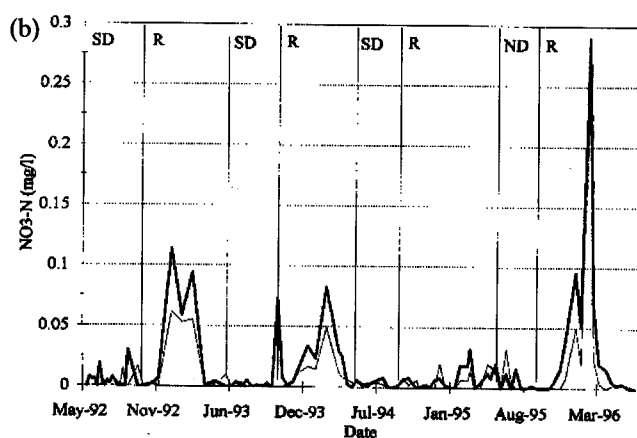
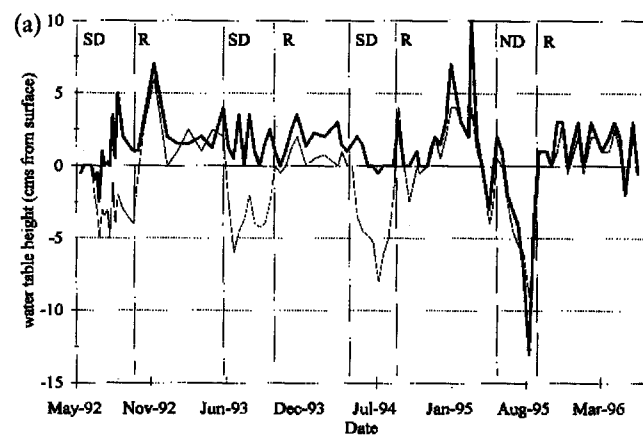
STATISTICAL ANALYSIS

Means for each of the five sampling points in the control and experimental sites were calculated for four distinct time periods i) over three simulated drought periods (maximum of 36 records) ii) over three approximately 30-week periods after the simulated drought had ended (max 35 records) iii) over the natural drought period (max 7 records) and iv) after the natural drought period had ended

Table 1. Means of annual mean concentrations of selected determinands from the 5 sampling points (± s.e.) from both of the control and experimental sites. All units (except pH) are in mg l⁻¹.

Determinand	Control site				Experimental site			
	Year				Year			
	1992/93	1993/94	1994/95	1995/96	1992/93	1993/94	1994/95	1995/96
pH	4.65 (0.03)	4.97 (0.04)	5.02 (0.02)	4.90 (0.06)	4.48 (0.02)	4.69 (0.03)	4.68 (0.02)	4.63 (0.03)
Na	2.85 (0.06)	2.76 (0.04)	3.03 (0.06)	2.93 (0.09)	2.95 (0.05)	2.88 (0.05)	2.98 (0.06)	3.17 (0.06)
K	0.12 (0.01)	0.12 (0.02)	0.07 (0.00)	0.05 (0.01)	0.06 (0.01)	0.05 (0.01)	0.02 (0.00)	0.06 (0.03)
Ca	0.41 (0.03)	0.55 (0.02)	0.65 (0.03)	0.74 (0.02)	0.65 (0.05)	0.59 (0.03)	0.44 (0.04)	0.55 (0.04)
Mg	0.49 (0.01)	0.56 (0.03)	0.54 (0.02)	0.66 (0.00)	0.76 (0.02)	0.68 (0.01)	0.60 (0.01)	0.65 (0.01)
Fe	N/A	1.27 (0.17)	1.33 (0.14)	1.15 (0.16)	N/A	0.12 (0.01)	0.14 (0.01)	0.22 (0.01)
NH ₄ -N	0.02 (0.00)	0.02 (0.00)	0.02 (0.00)	0.02 (0.00)	0.02 (0.00)	0.02 (0.00)	0.02 (0.00)	0.02 (0.00)
NO ₃ -N	0.01 (0.00)	0.01 (0.00)	0.01 (0.00)	0.03 (0.01)	0.01 (0.00)	0.01 (0.00)	0.00 (0.00)	0.02 (0.00)
Cl	4.91 (0.05)	4.47 (0.08)	4.63 (0.05)	4.90 (0.07)	5.42 (0.06)	5.01 (0.06)	4.75 (0.04)	5.26 (0.09)
SO ₄	1.92 (0.15)	1.87 (0.09)	1.49 (0.17)	2.57 (0.17)	2.22 (0.12)	2.42 (0.09)	2.16 (0.11)	2.88 (0.10)
DOC	5.95 (0.61)	6.91 (0.31)	6.01 (0.28)	5.75 (0.18)	3.98 (0.25)	3.94 (0.26)	3.89 (0.16)	4.83 (0.18)

N/A = Not available



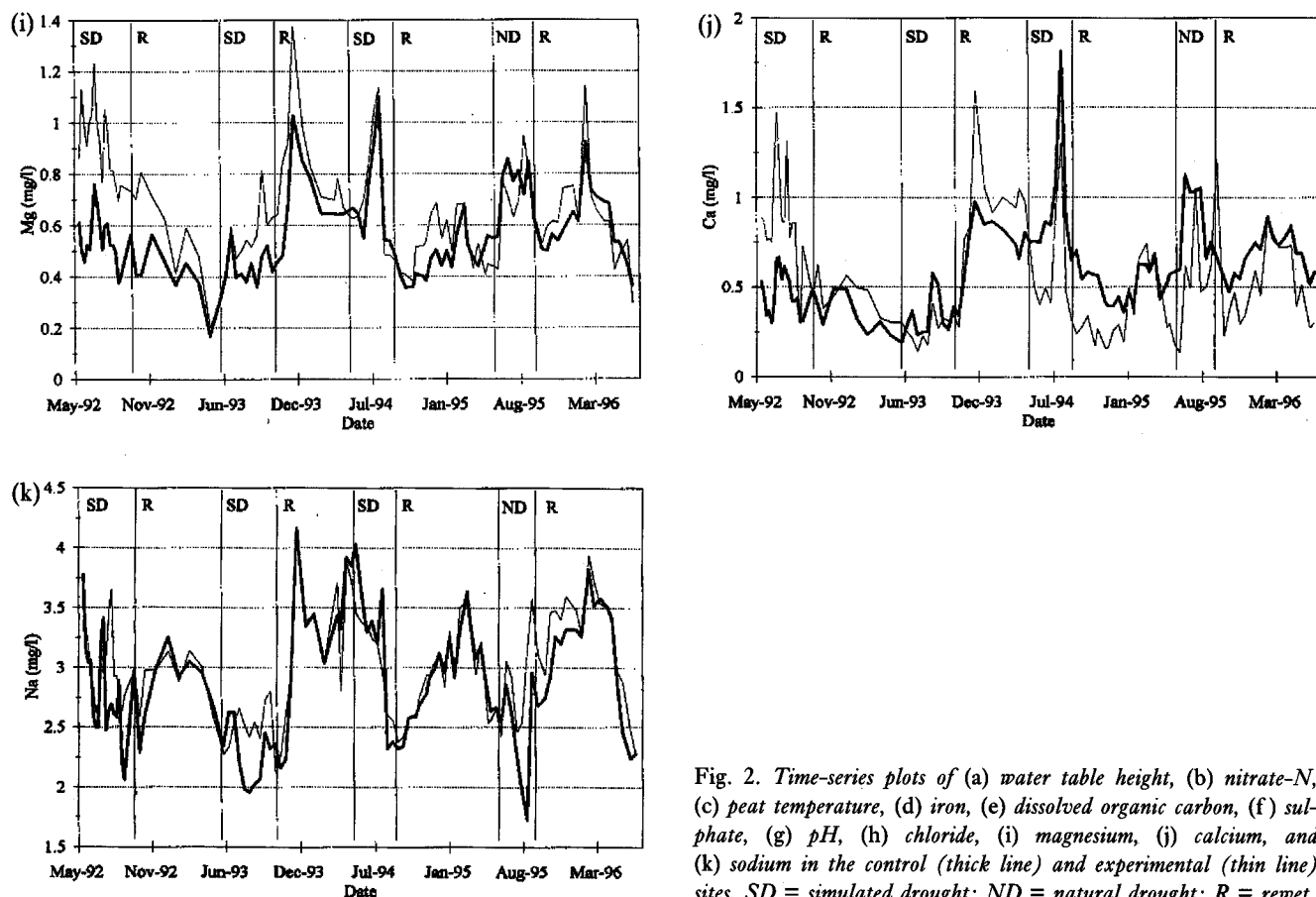


Fig. 2. Time-series plots of (a) water table height, (b) nitrate-N, (c) peat temperature, (d) iron, (e) dissolved organic carbon, (f) sulphate, (g) pH, (h) chloride, (i) magnesium, (j) calcium, and (k) sodium in the control (thick line) and experimental (thin line) sites. SD = simulated drought; ND = natural drought; R = rewet.

(max 13 records). The experimental and control sites were compared using a two sample paired t-test. No assumption of equal variances was made for these tests. In the absence of a period of lead-in, pre-treatment, data it has had to be assumed that the control and experimental areas of wetland had similar properties before experimental manipulations.

Results and Discussion

Figure 2a demonstrates that simulated summer drought lowered the water table in the experimental wetland by between 5–10 cm relative to the control in each of the three years; the control generally remained waterlogged throughout these periods (Fig. 2a). A more intense natural drought, which affected the wetlands in the summer of 1995 (see Fig. 3), resulted in a more severe drop in water table levels in the two wetlands.

In the control wetland, the peat water (10 cm depth) was characteristically acid with low concentrations of base cations and inorganic nutrients (Na, K, Ca, Mg, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$) (Table 1). Indeed, concentrations of $\text{PO}_4\text{-P}$ were below detection limits (<0.05 mg/l). The low concentration of inorganic nutrients (N, P, K) in the peat water is as expected for such a nutrient-poor and base-poor wetland site, which is typical of many in the uplands in Wales.

Sodium and Cl^- were the dominant inorganic ions, reflecting the marine influence on deposition inputs at the site.

Concentrations of $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$ and K tended to be smaller in the experimental wetland during and after the three simulated drought periods (although the results of the t-tests for $\text{NO}_3\text{-N}$ were not significant) (Table 2). This scenario is contrary to earlier laboratory studies of experimental peat-cores from Cerrig-yr-Wyn which, in contrast to cores from the control, revealed a significant increase in

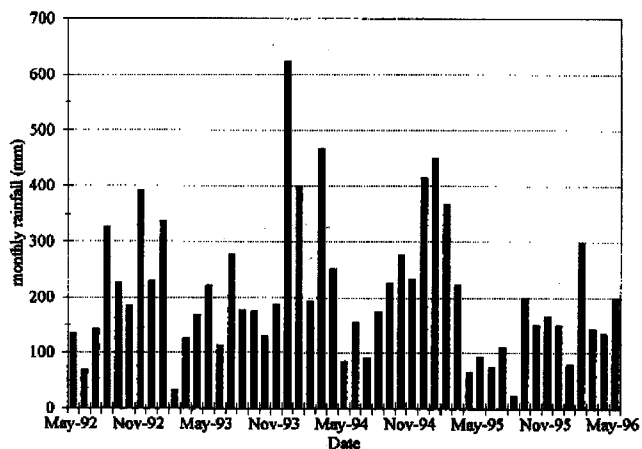


Fig. 3. Monthly precipitation volumes for the Cerrig-yr-Wyn site.

NO₃-N concentrations in the peat water (10cm depth), relative to those of control cores, when the water table was lowered; the increase in NO₃-N concentrations (10cm depth) in the experimental peat-cores was attributed to an increase in the population of ammonium oxidising bacteria (Freeman *et al.*, 1993b). Under field conditions, the droughts simulated were less severe than those imposed under laboratory conditions, which may have increased the N-mineralisation rate. However, examination of seasonal trends in NO₃-N at this site reveals that natural peaks in the peat water occur in winter, coinciding with temperature minima (Figs 2b & 2c). This suggests a source of NO₃-N to the peat water (possibly by lysing of soil microorganisms) during times of frost—a possible example of a freeze-thaw effect (Mitchell *et al.*, 1996).

Simulated summer drought significantly decreased pH and the concentrations of Fe and DOC in the peat water in the experimental wetland relative to the control (Table 2). By contrast, simulated drought had no significant effects on the concentrations of SO₄²⁻ during the three drought periods (Table 2). However, evidence points to the existence of a delayed or 'lag' effect of drought on this anion because the concentrations of SO₄²⁻ were very significantly increased after rewetting, and this phenomenon was accompanied by a significant decrease in pH (Table 2).

As indicated above, these effects differed greatly in their seasonality. Figures 2d & 2e show clearly that concentrations of Fe and DOC peaked during the summer in both wetlands; both solutes were strongly positively correlated with peat temperature. For the control wetland: Fe $r = 0.74$, $P = <0.001$; DOC $r = 0.84$, $P = <0.001$. For the experimental wetland Fe $r = 0.77$, $P = <0.001$; DOC $r = 0.82$, $P = <0.001$, but the concentrations were markedly lower in the experimental wetland. Concentrations of DOC began to recover in the experimental wetland during the summer of 1995 (*i.e.* when it was no longer subjected

to simulated drought), but the natural drought which affected the wetlands between July–August curtailed the recovery. In contrast, Fig. 2f shows that SO₄ concentrations peaked naturally during the autumn–winter periods in both wetlands, but also shows that these peaks were enhanced in the experimental wetland, relative to the control, following simulated drought. The temporal trends in pH mirrored those of SO₄, with the lower pH values occurring during winter (Fig. 2g).

During simulated drought, peat temperature was significantly higher in the experimental wetland but was similar to the control during other periods (Table 2; Fig. 2c). Likewise, Cl⁻ and Mg²⁺ concentrations were significantly higher in the experimental wetland relative to the control during simulated drought (Table 2; Figs. 2h & 2i). This suggests a 'concentration effect' on these ions in the experimental wetland during simulated drought, caused by high evapotranspiration rates in the mire during the summer coupled with the absence of streamflow recharge in the experimental site. However, Na (and Ca) did not show this concentration effect (Table 2). In the case of Na⁺, ion exchange reactions between Na⁺ and H⁺ in the peat may have masked the 'concentration effect' on the former. Indeed, the proposed mechanism, which involves displacement of H⁺ from the cation exchange sites in the peat by Na⁺, may be partly responsible for a lowering of pH of the peat water in the experimental wetland during simulated drought (Table 2). Further evidence for the ion exchange mechanism obtains from a comparison of the results for Na⁺ and Cl⁻ for the control and experimental wetlands; the mean Na:Cl molar ratio in the experimental wetland (Na:Cl = 0.86) decreases relative to the control (Na:Cl = 0.98) during simulated drought. In contrast, the Na:Cl molar ratios were similar for both wetlands in each of the other time periods—*i.e.* i) the post-simulated drought periods Na:Cl = 0.92 experimental, Na:Cl = 0.92

Table 2. Mean bi-weekly peat temperature and solute concentrations for the four time-periods and significance of the t-test.

	Simulated droughts			Post-simulated droughts			Natural drought			Post-natural drought		
	C	E	sig	C	E	sig	C	E	sig	C	E	sig
Temperature	10.3	11.5	***	5.1	5.0	ns	12.9	12.6	ns	4.9	4.8	ns
pH	5.0 ^a	4.8 ^a	**	5.0 ^a	4.6 ^a	***	5.1	4.7	*	4.7	4.6	ns
Na	2.8	2.9	ns	3.0	3.0	ns	2.5	3.0	ns	3.3	3.5	ns
K	0.13	0.07	**	0.09	0.03	**	0.09	0.12	ns	0.04	0.03	ns
Mg	0.56	0.78	***	0.51	0.64	**	0.78	0.74	ns	0.64	0.68	ns
Ca	0.54	0.64	ns	0.54	0.53	ns	0.92	0.71	ns	0.69	0.55	*
Cl	4.4	5.2	***	5.0	5.0	ns	5.1	6.0	ns	5.2	5.4	**
SO ₄	1.1	1.0	ns	2.3	3.3	***	1.1	1.1	ns	3.6	4.2	*
NH ₄ -N	0.03	0.02	*	0.02	0.02	ns	0.02	0.02	ns	0.01	0.01	ns
NO ₃ -N	0.00	0.00	ns	0.02	0.01	ns	0.00	0.01	ns	0.05	0.03	ns
Fe	2.2	0.2	***	0.7	0.1	***	2.6	0.4	**	0.4	0.1	ns
DOC	9.6	5.4	**	3.3	2.9	ns	11.9	8.4	*	2.6	2.8	ns

KEY: C = control; E = experimental; sig = significance from t-test; *0.01 < p < 0.05; **0.001 < p < 0.01; ***p < 0.001; ns p > 0.05
a = data for 1992–93 omitted

control; ii) the natural drought period Na:Cl = 0.77 experimental, Na:Cl = 0.76 control; and iii) the post-natural drought period Na:Cl = 1.00 experimental, Na:Cl = 0.98 control wetlands.

The apparent absence of a concentration effect for Ca can be explained from observing the temporal trends in Ca over the course of the study (Fig. 2j). Figure 2j shows clearly that Ca concentrations were enhanced in the experimental wetland during the initial simulated drought period in 1992, but reveals a trend towards a gradual decline in concentrations relative to the control wetland thereafter. These results suggest that the supply of Ca in the mire is limited and successive droughts gradually depleted the availability of this cation in the peat water. However, any one or a combination of mechanisms may be involved. Along with the obvious reduction of Ca^{2+} inputs to the experimental wetland by the removal of streamflow recharge during simulated drought periods, availability of Ca^{2+} in the peat water may have been reduced by physical changes in the peat in response to drying.

Table 2 shows the similarity of the concentrations of Cl⁻ in the control and experimental wetlands during the post-simulated drought periods, this indicates that the observed 'concentration effect' in the experimental wetland during the simulated drought periods disappeared soon after the start of rewetting.

As described above, concentrations of Fe in the experimental wetland, tended to be much lower relative to the control, and the differences between the two wetlands increased during drought periods (including natural drought). A similar response to drought was apparent for DOC. The means for SO_4 , similar during drought, were significantly greater in the experimental wetland during the post drought (autumn-winter) periods. Post-natural drought SO_4 levels in the control were similar to mean levels in the experimental wetland post-simulated drought (3.6 cf. 3.3; t-test $p = 0.06$ or $p > 0.05$). However, DOC levels in the control were higher during the natural drought than those in the experimental wetland during simulated droughts (11.9 cf. 5.4; t-test $p < 0.01$). The latter may reflect the effects of the timing of the natural drought compared to the simulated drought(s) on DOC cycling in the wetland.

Microbial processes are likely to contribute to some of the differences in DOC concentrations in the two wetlands. In the anaerobic (low redox potential) conditions normally found in wetlands, a greater proportion of end products of metabolism include low molecular weight organic solutes, such as aldehydes and ketones (Ponnanperuma, 1972; Freeman *et al.*, 1993b), whereas in more aerobic (low-water table) conditions, microbial metabolism is more likely to favour oxidative, inorganic carbon (CO_2) end products.

Iron and DOC concentrations were positively correlated in the wetlands ($r = 0.788$, $P = < 0.001$ control; $r = 0.739$, $P = < 0.001$ experimental). This, and the very seasonal

trends in hydrochemistry of DOC and Fe in the mire, with peak concentrations in the summer, strongly support the view that the solubility of Fe in organic-rich waters is dependent on (in addition to pH and redox potential) the relative abundance of natural organic ligands, and that much of the Fe is present in solution as dissolved/colloidal Fe-organo compounds (Vaughan *et al.*, 1993; Heikkinen, 1994). It is also interesting to note that the concentrations of Fe (and DOC) in the control following the natural summer drought in 1995 did not show a decline similar to that observed in the experimental wetland following simulated drought (Figs 2d & 2e). Assuming that these observations are not mainly consequences of any inherent differences in Fe content between the two areas of wetland, this suggests that the timing of a drought may be critical in determining the overall effects on this solute. Simulated drought was initiated early in the summer in the experimental wetland, before the natural cyclic peak of DOC production in the mire. If simulated drought had an inhibitory effect on bio-mediated production of DOC, then it is likely that the major factor determining the solubility of Fe in the experimental wetland during simulated drought was the supply of natural organic ligands in the peat-water. The natural drought of 1995, however, affected the wetlands later in the summer, after the peak cycle of DOC production in the mire had begun. This suggests that redox effects were likely to be more important in determining the solubility of Fe-organo compounds in the control wetland following the natural drought. It is known that Fe(II) complexed to organic matter is stabilised against oxidation compared to free Fe^{2+} , and that, once formed, these compounds are removed only slowly from solution by oxidation and precipitation (Theis & Singer, 1975). This scenario might explain the lack of a decline in Fe and DOC concentrations in the control following the natural drought, compared with those in the experimental wetland following drought simulation.

As described above, sulphate concentrations in the peat water also showed strong natural seasonal trends in the mire, with peaks occurring during autumn-winter and troughs during summer (Fig. 2f). Summer troughs probably resulted from a number of contributory factors, which may have included increased assimilatory uptake of SO_4 by wetland vegetation and soil microbes and dissimilatory uptake by sulphate reducing bacteria during the growing season (Urban *et al.*, 1989). Sulphur cycling in wetlands, however, is known to be complex and sulphur mineralisation and oxidation rates in the wetlands are also likely to have increased during the summer, possibly leading to a dynamic cycle of oxidation and reduction in the mire (Urban *et al.*, 1989). On balance, however, and in the absence of drought conditions in the control, demand for pore-water SO_4 by assimilatory and/or dissimilatory uptake must have been sufficiently large to offset any additional release of SO_4 to pore-water by mineralisation/oxidation during the summer.

In contrast, natural autumn-winter peaks in SO_4 in the pore-water probably reflected increased release of SO_4 from bio-senescence during the autumn, coupled with increased S deposition, especially that of marine origin, during the winter months (DOE, 1990) (the influence of the latter may have been further enhanced by the expectation that rates of internal S-cycling and retention in the mire were likely to be inhibited by low temperatures during the winter). Moreover, additional SO_4 is likely to have been mobilised during autumn-winter emanating from reoxidation of reduced-S species during dynamic S-cycling during the summer, and subsequently 'washed off' from the peat surfaces during rewetting (Ponnamperuma, 1972). Sulphatase activity in the experimental wetland increased following simulated drought (Freeman *et al.*, 1997), which suggests that an increased rate of mineralisation of organic-S might have contributed to the increased SO_4 abundance following drought. Although the scope of the present study does not provide for detailed information on the mechanisms of SO_4 release, it seems likely that these two mechanisms may be of some importance following drought conditions; indeed, the former has been proposed previously by a number of researchers to explain autumnal SO_4 pulses in wetland drainage waters following dry periods (Gorham *et al.*, 1984; Bayley *et al.*, 1986; LaZerte, 1993). Whichever mechanism(s) is responsible, the present results reveal a significant enhancement of the natural autumn-winter peaks in pore-water SO_4 concentrations in the experimental wetland, relative to the control, following successive simulated droughts (Table 2 & Fig. 2e). The autumn-winter peaks in SO_4 concentrations in the control wetland following the natural drought in 1995 were of similar magnitude to those induced by simulated drought in the experimental wetland in the previous 3 yrs. This is both supportive of the basis of the original experiment, *i.e.* that the hydrological manipulation succeeded in simulating actual drought conditions in the mire, and that the observations following the natural (and simulated) drought(s) are true drought/rewet effects and not simply consequences of natural annual fluctuations reflecting differences in annual S deposition, or inherent differences between the control and experimental patches of wetland.

Hydronium accompanied SO_4 released to the peat water in the winter, with a sharp decrease in pH observed during these periods (Fig. 2g), and with very little additional release of base cations being detected. This was as expected for a base-poor wetland in an area of moderately-high acid S deposition (wet deposition: *c.* 0.9–1.2 g S m⁻² yr⁻¹) (DOE, 1990), and may have wider consequences in terms of the water quality of surface waters draining upland catchments in Wales following very dry summers. The possibility exists that periodic acid pulses may occur during large rainfall events following rewetting, when runoff from surface peat would be expected to increase.

Other factors which may lead to periodic acid episodes include the occurrences of large, marine-derived, salt

events. Large concentrations of neutral salts impacting the wetlands, from occult, dry and wet deposition sources, can lead to short-term changes in peat water chemistry (Chapman, 1994). The main effects are a lowering of pH and a change in the Na:Cl molar ratio (lower) in the peat water as a result of ion exchange of Na^+ for H^+ on the exchange sites on the peat surface (as described earlier). One such event was observed during a period of exceptionally high rainfall in Dec-93. Comparison of Figs 2g & 2h shows that a large peak in chloride concentrations in both wetlands (Cl^- values >9 mg/l) was accompanied by a sharp fall in pH. Figures 2h & 2k reveal a fall in the Na:Cl molar ratio, from a value of 1.15 immediately preceding the salt event, to a value of 0.68 during the event itself.

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