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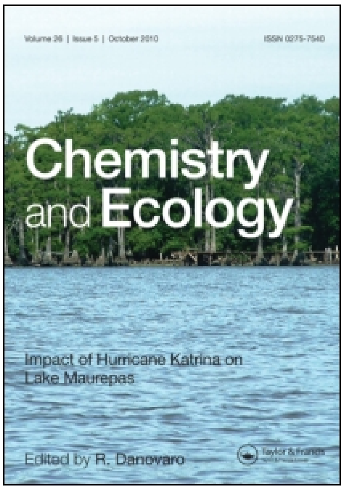

Chemistry and Ecology

Publication details, including instructions for authors and subscription information:
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To cite this Article Skiba, U. and Cresser, M. S.(1991) 'Seasonal Changes in Soil Atmospheric Co_2 Concentrations in Two Upland Catchments and Associated Changes in River Water Chemistry', Chemistry and Ecology, 5: 4, 217 — 225

To link to this Article: DOI: 10.1080/02757549108035251

URL: http://dx.doi.org/10.1080/02757549108035251

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Chemistry and Ecology, 1991, Vol. 5, pp. 217–225

SEASONAL CHANGES IN SOIL ATMOSPHERIC CO_2 CONCENTRATIONS IN TWO UPLAND CATCHMENTS AND ASSOCIATED CHANGES IN RIVER WATER CHEMISTRY

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(Received May 10, 1991 in final form May 21, 1991)

Seasonal changes in river water chemistry and in soil atmospheric CO_2 concentrations at two depths and drainage water solute composition at two upland peaty podzol sites in north east Scotland were monitored over 12 months. The CO_2 concentrations were controlled by changes in soil temperature and moisture status. Highest CO_2 concentrations were observed in late summer 1988 when both soil temperatures and the moisture status of the soils were high. Then maximum CO_2 concentrations of 4% (v/v) were recorded for one of the sites. No significant correlations between seasonal changes in soil CO_2 concentrations and river water solute composition were observed. Nevertheless the field results and laboratory experiments indicated that in upland areas, where soils with acid surface horizons are common, soil CO_2 substantially influences river water chemistry at baseflow, increasing the pH and cation concentration of the soil water draining into the river. The results suggest that transfer of carbon as dissolved CO_2 in drainage water is a significant pathway for CO_2 transfer to the atmosphere.

KEY WORDS Carbon dioxide, river water, soil atmosphere, flux

INTRODUCTION

In soils which are not strongly acidic, a major factor influencing the rate of natural soil acidification is CO_2 concentration in the soil atmosphere. Soil atmospheres often have CO_2 concentrations 10 to 100 times above atmospheric values. In soil, CO_2 is primarily produced by respiration from plant roots and soil organisms, mainly microorganisms (Edwards and Harris, 1977). Soil atmospheric CO_2 either diffuses to the surface, remains trapped in soil pores or dissolves in the soil water. Carbon dioxide is very soluble in water, the following equilibrium reactions occurring:

$$\begin{aligned} CO_2(g) \rightleftharpoons CO_2 \text{ dissolved} &\rightleftharpoons H_2CO_3 \\ &\rightleftharpoons HCO_3^- + H^+ \\ &\rightleftharpoons CO_3^{2-} + 2H^+. \end{aligned}$$

Large amounts of soil atmospheric CO_2 dissolve in water draining through soil, but the soil solution pH is buffered by the composition of the suite of ions occupying the cation exchange complex. When CO_2-enriched soil water drains into a river, much of the CO_2 is released to the atmosphere (the outgassing effect) and consequently the pH of the inflowing water will rise (Cresser and Edwards, 1987). Therefore under baseflow conditions river water may have a pH value 1–2 pH units higher than the soil through which the water has most recently drained, even though the cation exchange properties of such soil may be used to predict the solute composition of water in associated rivers (Billet and Cresser, 1991).

Very little is known, however, about atmospheric CO_2 concentrations in moorland soils. In upland areas of the UK, moorlands cover a large percentage of the water catchments. Changes in soil CO_2 concentrations here can be an important variable in regulation of river water chemistry. To investigate how soil CO_2 concentrations could affect river water chemistry, soil atmospheric CO_2 concentrations were routinely monitored in two upland catchments in north east Scotland, and the chemical ecological consequences considered.

METHODS AND SITE CHARACTERISTICS

The study was conducted in two *Calluna* moorland catchments in the north east of Scotland, at Peatfold (NJ 353 183) and at Glendye (NO 622 835). For both drainage basins extensive information on soil, water and rain chemistries is available (Edwards, 1984). Three $10\,m^2$ plots on west facing slopes at Peatfold and on south facing slopes at Glendye were chosen. The soil type at all sites was a peaty podzol with a 100 to 150 mm thick surface peat horizon. At Peatfold, soils were underlain by quarz-biotite-norite and at Glendye by granite.

Diffusion wells (50 × 15 mm plastic cups) were assembled from disposable, inverted 5-ml syringes, attached at the top to a 500-mm length of nylon tubing (1 mm internal diameter) and protected at the bottom with very fine gauge nylon mesh. The wells were inserted into small prepared boreholes into the eluvial soil horizon at depths of 150 and 300 mm. The holes were then carefully back filled with the soil excavated from the borehole using a metal tube. The above-ground ends of the plastic tubing were sealed with small air-tight plastic end caps. At 3-week intervals (August 1987–September 1988) two 1 ml samples of air were withdrawn using 1 ml disposable plastic syringes. The first sample was discarded as it contained air from the plastic tubing. The second sample was kept in the syringe and was analysed for CO_2 by gas chromatography with a thermal conductivity detector within 5 hr of sampling. Over this period the disposable syringes, as tested with standard mixtures, proved to be airtight. All diffusion wells were replicated 5 times. Also 3 soil samples were collected from each plot (top 200 mm) at each sampling and analysed for moisture content (oven dried at 110°C) and pH (5 g of sieved (2 mm) field-moist soil plus 10 ml 0.01M $CaCl_2$). Soil water from triplicate tension lysimeters at a soil depth of 200 mm and water from the main stream flowing through the catchment were taken and analysed for pH, major cations, anions and total organic carbon by conventional methods (Edwards, 1984). The main stream flowing through each catchment had a flume installed.

To study the effects of soil atmosphere CO_2 concentration upon soil drainage water chemistry, a fertile loam soil (Aberdeen, 80 g) was air-dried, sieved (2 mm) and loosely packed into 100 ml leaching tubes stoppered with pre-washed glass wool. The soil was then wetted to field capacity with artificial rain at pH 4 (Skiba

Table 1 Site characteristics at Peatfold and Glendye, means of 19 analyses (in triplicate for soil analysis) of samples collected at 3-weekly intervals between August 1987 and September 1988.

Site variable	*Glendye*	*Peatfold*
Soil temperature (°C)	7.6	6.8
Soil Moisture (%m/m)	56.6	53.1
Rain pH	4.24	4.57
River pH (at flume)	5.23	6.98
Peat pH ($CaCl_2$)	2.96	3.54
Soil water pH	4.21	5.48

and Cresser, 1986). A gas mixture of 3% CO_2 in air (prepared gravimetrically) was pumped through the leaching tubes at a rate of 15 ml min^{-1} for 1 hour.

RESULTS

Site characteristics for Glendye and Peatfold are summarised in Table 1. Soils and rivers were more acidic and rainfall volume was 1.15 times greater at Glendye than at Peatfold.

Mean annual soil CO_2 concentrations were greater at Glendye than at Peatfold. At Glendye no significant variations in soil CO_2 concentrations were observed between sites or soil depths. A mean annual soil CO_2 concentration of 1.64% was measured. At Peatfold, mean annual soil CO_2 concentrations were significantly greater at 300 mm than at 150 mm soil depth (0.67% CO_2 at 150 mm soil depth and 0.95% CO_2 at 300 mm, $p < 0.05$). For individual sites, these differences, however, were only significant for one site (Table 2). Within-site variations were very large. Soil CO_2 concentrations were significantly greater at site 2 than at the other two sites (Table 2) ($p < 0.001$). Here soil CO_2 concentrations were similar to those observed at Glendye. For site 2 also the soil pH was significantly lower (pH $CaCl_2$ 3.24) than at the remaining sites (pH $CaCl_2$ 3.69). Other variables measured did not, however, differ between sites.

Table 2 Mean annual soil CO_2 concentrations at Peatfold (means of 5 replicates sampled at 3-weekly intervals between August 1987 and September 1988).

	Soil depth		
Site	150 *mm*		300 *mm*
1	0.48	[a]	0.71
2	1.18	n.s.	1.63
3	0.35	n.s.	0.47

[a] $p < 0.01$; n.s. = not significant.

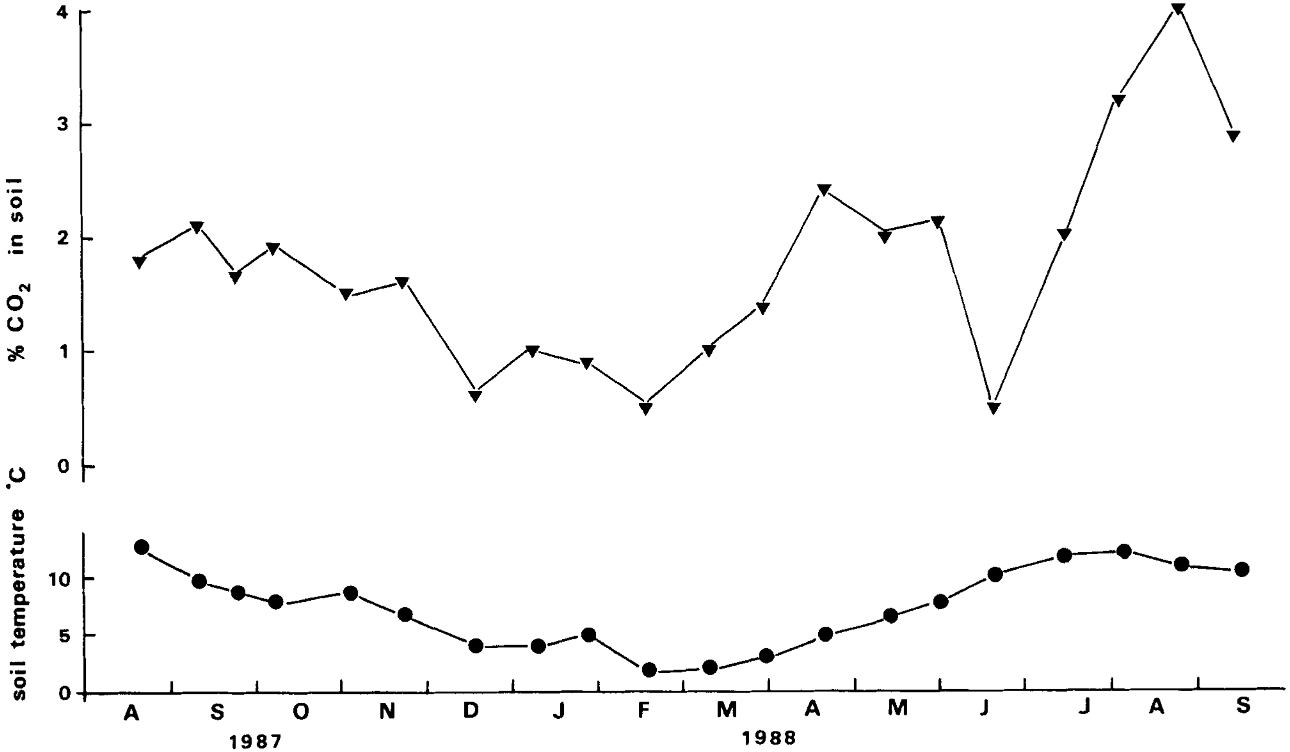

Figure 1 Seasonal variations in soil CO$_2$ concentrations and changes in soil temperature (●) at 150 mm soil depth at Glendye (means of 5 replicates at 3 sites).

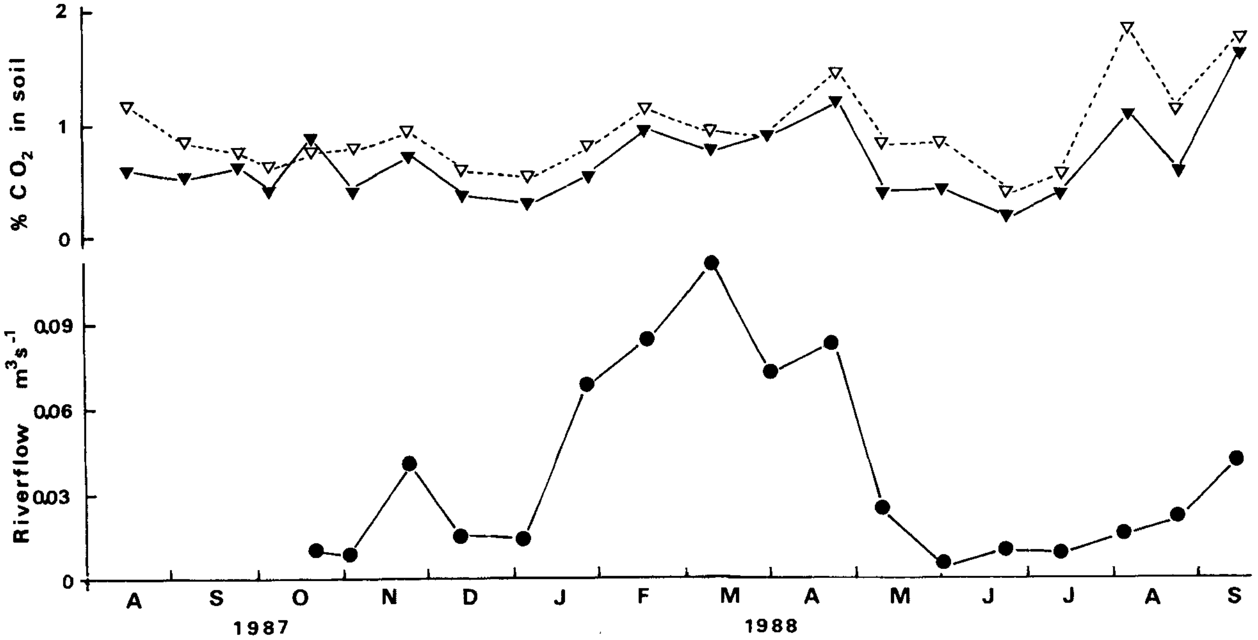

Figure 2 Seasonal variations in soil CO$_2$ concentrations at Peatfold at 150 mm soil depth (▼), at 300 mm soil depth (▽) and associated changes in the rate of riverflow (●) (means of continuous riverflow measurements 3 days prior to CO$_2$ sampling).

Seasonal variations in soil CO_2 concentrations were observed (Figures 1, 2). These correlated significantly between sites and at the two soil depths studied at both Peatfold and Glendye. Seasonal variations at Glendye, however, were different to those at Peatfold. Maximum soil CO_2 concentrations were measured in August/September 1988, when soil temperatures were high. For Glendye, soil CO_2 concentrations correlated significantly with changes in soil temperatures ($r = 0.59$, $n = 21$). As soil temperatures increased, soil CO_2 concentrations increased (Figure 1). At Peatfold, however, significant correlations between soil CO_2 and temperature were not observed. In spite of high soil temperatures, extremely low soil CO_2 concentrations were measured in May, June and July at both catchments (Figures 1 and 2). These months were unusually dry; the moisture content of the soils decreased to 46% at all sites. As the rainfall increased, the soil moisture content increased to 53% and soil CO_2 concentrations rose sharply.

In spite of continuing low soil and air temperatures in January and February, soil CO_2 concentrations increased at all sites at Peatfold (Figure 2). These increases coincided with snow cover. Winter 1987–1988 was milder than usual in north east Scotland with very little snow. No snow was lying when sampling at Glendye, but at Peatfold sampling plots were covered with a thick layer of snow (>300 mm) on two occasions (27/1/88 and 17/2/88).

At Peatfold, from all the parameters measured, seasonal changes in soil CO_2 concentrations at 150 mm depth only correlated significantly with the rate of discharge of the stream flowing through the catchment ($r = 0.520$, $n = 17$) and the total organic carbon content of the river water ($r = 0.734$, $n = 18$). Correlations with soil mositure or rainfall were not significant.

At Glendye, soil CO_2 concentrations also correlated significantly and negatively with soil water pH ($r = -0.649$, $n = 13$) and the calcium concentration of the soil water ($r = 0.563$, $n = 15$). The greater the soil CO_2 concentrations the more acid the soil water and the greater its calcium concentration.

In the laboratory equilibration studies, significantly greater leaching of calcium, magnesium and potassium from small soil columns equilibrated with a high CO_2 concentration (3% CO_2) rather than air (0.03% CO_2) was observed (Table 3). After outgassing, the leachate pH was significantly greater from CO_2-equilibrated soils than from controls.

Table 3 The effect of an elevated soil CO_2 concentration on the chemistry of soil water leaching from a fertile loam soil (means of triplicates).

	Soil water chemistry				
Soil atmosphere	*pH*	*Ca*	*Mg*	*K*	*Na*
3% CO_2	7.63	0.15	0.41	0.47	0.35
	a	a	b	a	n.s.
0.03% CO_2	6.98	0.11	0.27	0.34	0.27

After outgassing, $^a p < 0.05$, $^b p < 0.001$, n.s. not significant.

DISCUSSION

Seasonal changes in soil atmospheric CO_2 concentrations were governed by changes in soil temperature and soil moisture. This was also reported by Volk (1973) for agricultural soils and Fernandez and Kosian (1987) for forest soils. At intermediate temperatures every 10°C increase in temperature doubled the amount of CO_2 evolved (Volk, 1973), as a result of increased microbial activities and root respiration (Alexander, 1977). At Peatfold, the temperature effect on soil CO_2 concentrations was overshadowed by the effect of moisture on soil CO_2. A rise in soil CO_2 with increased moisture was probably a result of physical trapping of much of the CO_2 produced by the filling of a larger proportion of soil pores with water, restricting diffusion of soil gases. Snow cover would have the same effect. Extremely low soil CO_2 conditions were observed during dry periods when the moisture tension of the soil decreased and upward diffusion of soil gases from depth was facilitated. In the upper layers of soil, gas exchange with the atmosphere generally occurs more readily and hence a gradient of soil CO_2 concentrations with soil depth was observed at Peatfold, as for a forest soil (Fernandez and Kosian, 1987) and a sandy loam (Yamaguchi *et al.*, 1967). The correlation between soil CO_2 and river discharge at Peatfold reflects the importance of antecedent soil moisture conditions to both parameters. At Glendye, however, no significant difference between CO_2 concentrations at 150 and 300 mm soil depths were observed. The peats here were always wetter than those at Peatfold (Table 1). Overland flow frequently occurs at Glendye, but not at Peatfold, indicating that Glendye peats are more impermeable and hence allow less gas exchange to occur at the soil/air interface.

At Peatfold, soil CO_2 concentrations did not correlate with soil moisture or rainfall, but did correlate with discharge of the river flowing through the catchment and the total organic carbon content of the river, as mentioned earlier. Both variables reflect changes in rainfall pattern more fully than collected bulk rainfall and soil moisture measurements alone. River discharge was monitored continuously and the response of river water chemistry to changes in rainfall pattern is very rapid, but depends on antecedent soil moisture (Cresser and Edwards, 1987). Total organic carbon concentrations in rivers increase when the bulk of the river water flows through the organic-rich surface horizon of a soil before entering the stream—a situation occurring when high rainfall interacts with an already wet soil. Other relationships between river water chemistry and soil CO_2 concentrations, however, could not be established.

At Glendye a significant relationship between soil CO_2 and the calcium concentration and acidity of the soil water was observed. The soil water collected at 200 mm depth at Glendye was very acid with zero alkalinity and therefore changes in soil CO_2 would not be expected to influence the soil water chemistry. High CO_2 concentrations lower the pH of extracted soil water with more than zero alkalinity and subsequently increase the leaching of cations, as demonstrated for a fertile loam soil (Table 3). Results showed the same trend for mineral soils from Peatfold and Glendye, but differences in cation leaching for soil columns equilibrated with 3% CO_2 or air were not significant. Even in upland soils with acidic surface horizons, in the underlying more alkaline mineral horizons (pH 4.93 for Glendye and pH 5.34 for Peatfold) soil CO_2 fluctuations will influence soil water chemistry. Although at Glenbuchat soil waters were within the CO_2 buffering range, correlations between soil water constituent concentrations and soil CO_2 were not significant. High variability in soil CO_2 concentrations in replicated wells and failure of tension lysimeters to work at dry periods may be responsible for the lack of correlation.

Leachates from 3% CO_2-equilibrated columns of garden soil were more acid (pH 6.3) than those from air-equilibrated columns (pH 6.98). Outgassing, however, reversed the situation (Table 3). The same is expected to happen when rainwater percolates through mineral soil and enters the river as alkaline base-rich water.

The results discussed here suggest that, in uplands, soil CO_2 will influence river water chemistry most when soil temperatures are reasonably high, but the soil remains relatively moist to prevent upward diffusion of soil gases, and also at periods of extensive snowcover. As acid organic surface horizons prevail in uplands, soil CO_2 will only influence river water chemistry at baseflow or when water flows substantially through lower, more alkaline, soil horizons. It is instructive to estimate the carbon flux typically removed from upland soils as CO_2 in drainage water. Taking a typical literature value (Butler, 1982) for Henry's constant of $10^{-1.27}$ (appropriate for 10°C), a constant soil atmosphere CO_2 content of 1% results in a carbon flux of *ca.* 330 kg ha^{-1} yr^{-1} for 500 mm of runoff. A soil atmosphere CO_2 concentration of 3% would result in a carbon flux of 990 kg ha^{-1} yr^{-1}. This represents a significant portion of total dry matter production at such a site, which is *ca.* 6000 kg ha^{-1} yr^{-1} (Smith and Forrest, 1978). It may be important therefore to consider CO_2 outgassing from rivers when evaluating carbon fluxes for terrestrial ecosystems.

ACKNOWLEDGEMENTS

The authors are indebted to the UK Department of Environment for financial support for this work and to the landowners of Glendye and Peatfold for permission to work on their estates.

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