Biogeochemistry **10**: 81–104, 1990

Methane production and sulfate reduction in two Appalachian peatlands

R. KELMAN WIEDER,[1] JOSEPH B. YAVITT[2,3] & GERALD E. LANG[2]
[1]Department of Biology, Villanova University, Villanova, PA 19085, [2]Department of Biology, West Virginia University, Morgantown, WV 26506-6057, USA ([3]present address: Department of Natural Resources, Fernow Hall, Cornell University, Ithaca, NY 14853, USA)

Accepted 18 January 1990

Key words: Appalachian Mountains, bogs, carbon dioxide, methane, peat, sulfate reduction

Abstract. Anaerobic carbon mineralization was evaluated over a 1-year period in two *Sphagnum*-dominated peatlands, Big Run Bog, West Virginia, and Buckle's Bog, Maryland. In the top 35 cm of peat, mean rates of methane production, anaerobic carbon dioxide production, and sulfate reduction at Big Run Bog were 63, 406 and 146 μmol $L^{-1} d^{-1}$, respectively, and at Buckle's Bog were 18, 486 and 104 μmol $L^{-1} d^{-1}$. Annual anaerobic carbon mineralization to methane and carbon dioxide at Big Run Bog and Buckle's Bog was 52.8 and 57.2 mol m^{-2}, respectively. Rates of methane production were similar to rates reported for other freshwater peatlands, but methane production accounted for only 11.7 and 2.8%, respectively, of the total anaerobic carbon mineralization at these two sites. Carbon dioxide production, resulting substantially from sulfate reduction, dominated anaerobic carbon mineralization. Considerable sulfate reduction despite low instantaneous dissolved sulfate concentrations (typically < 300 μmol L^{-1} of substrate) was apparently fueled by oxidation and rapid turnover of the reduced inorganic sulfur pool.

The coincidence of high sulfate inputs to the Big Run Bog and Buckle's Bog watersheds through acid precipitation with the unexpected importance of sulfate reduction leads us to suggest a new hypothesis: peatlands not receiving high sulfate loading should exhibit low rates of anaerobic decomposition, and a predominance of methane production over sulfate reduction; however, if such peatlands become subjected to high rates of sulfur deposition, sulfate reduction may be enhanced as an anaerobic mineralization pathway with attendant effects on carbon balance and peat accumulation.

Introduction

Peatland ecosystems cover about 450 million ha of the earth's land surface (Kivinen & Pakarinen 1981) and may play important roles in the global cycling of carbon, serving as significant carbon reservoirs and as potential sources or sinks for atmospheric carbon (Miller 1981; Harriss et al. 1985; Trabalka 1985; Sebacher et al. 1986; Matthews & Fung 1987; Moore & Knowles 1987). Peat accumulates on the landscape until a balance is reached between annual organic matter production via photosynthesis at the surface of a wetland and annual organic matter mineralization, both aerobic and anaerobic, throughout an entire peat column. Using a mathematical modeling approach, Clymo (1984) concluded that peat accumulation was most directly influenced by two factors, input of organic matter into the anaerobic zone of the peat and the rate of anaerobic decomposition of organic matter (anaerobic carbon mineralization).

Thermodynamic and kinetic considerations suggest that since freshwater peatland ecosystems systems typically have low dissolved sulfate concentrations (cf. Gorham et al. 1985), anaerobic carbon mineralization should be dominated by methanogenesis, with sulfate reducing bacteria limited by low sulfate supply (e.g. Mechalas 1974; Kristjansson et al. 1982; Ingvorsen et al. 1984). In our previous studies of anaerobic decomposition processes at Big Run Bog, West Virginia, both methane and carbon dioxide have been generated under anaerobic conditions (Yavitt et al. 1987, 1988). Some of the carbon dioxide apparently was generated from sulfate reduction, since rates of sulfate reduction were similar to those reported for coastal marine sediments, despite low instantaneous dissolved sulfate concentrations in the peat (Wieder & Lang 1988). In contrast to the much more abundant boreal peatland ecosystems, Big Run Bog is situated in a region that receives considerable atmospheric sulfur input via acid precipitation (approximately $18.2\,kg\,ha^{-1}\,yr^{-1}$ or $57\,mmol\,m^{-2}\,yr^{-1}$ of SO_4^{2-}–S in wet deposition alone; Wieder et al. 1987). Although attempts have been made to assess the potential links between global climatic change and carbon balance in peatlands (Miller et al. 1981; Trabalka 1985), the potential impacts of high atmospheric sulfur deposition on carbon balance in peatlands has received little attention (cf. Gorham et al. 1984).

In light of the simultaneous occurrence of methane production and sulfate reduction in Big Run Bog peat, this study was initiated to quantitatively characterize the annual cycle of both methane production and sulfate reduction in two Appalachian peatlands, with an objective of estimating annual carbon mineralization through these two anaerobic pathways.

Study sites

Two Appalachian peatlands, Big Run Bog, West Virginia (39°07′N, 79°35′W, and Buckle's Bog, Maryland (39°35′N, 79°22′W) were chosen for study. Both peatlands are dominated by *Sphagnum* and *Polytrichum* mosses. At each of these two peatlands, a relatively shallow deposit (maximum depth of about 225 cm) of relatively highly decomposed peat has developed over about 13 000 years (Maxwell & Davis 1972; Watts 1979; Wieder 1985).

Big Run Bog is a 15 ha peatland situated at about 980 m above sea level. Big Run Bog is physiographically a minerotrophic fen, receiving inputs of water and nutrients in runoff from the 276 ha of mixed deciduous–coniferous forest surrounding the wetland. Despite its minerotrophic status, water chemistry and peat chemistry at Big Run Bog are similar to water and peat chemistry typical of ombrotrophic bogs (Wieder 1985). For example, surface water pH is about 4.0, dissolved Ca^{2+} concentrations are less than $1\,mg\,L^{-1}$, and the dominant cation and anion are H^+ and SO_4^{2-}, respectively.

Sampling at Big Run Bog was restricted to *Sphagnum–Eriophorum virginicum* plant community in which *Sphagnum* mosses cover over 90% of the surface of the peat. Major vascular plant species include *Eriophorum virginicum*, *Rhynchospra alba*, *Solidago uliginosa*, and *Rubus hispidus* (cover values of 17, 14, 5, and

31%, respectively); upright shrubs and trees are minor components of the vegetation (Wieder et al. 1981; Walbridge 1982). For the present study, on each of the sampling dates, the water table at Big Run Bog was within 5 cm the peat surface.

Buckle's Bog is a 27 ha peatland situated at an elevation of about 815 m above sea level. Only 68 ha of mostly forested watershed surrounds Buckle's Bog. Limited published data for Buckle's Bog indicate that its water chemistry is similar to water chemistry at Big Run Bog (Yavitt et al. 1988). The proportionately smaller area of upland watershed surrounding Buckle's Bog relative to that surrounding Big Run Bog is reflected in lower concentrations of Fe and Al in the top 20 cm of peat (101 and 109 μmol g^{-1}, respectively at Buckle's Bog as compared to 300 and 159 μmol g^{-1}, respectively in Big Run Bog peat; Wieder & Lang 1986). Sampling at Buckle's Bog was restricted to a plant community in which *Sphagnum* species formed a continuous cover, but in which small-statured shrub cover, mainly *Vaccinium* spp. and *Pyrus arbutifolia*, was somewhat higher than at Big Run Bog. For the present study, on each of the sampling dates, the water table at Buckle's Bog was at or below 35 cm, and thus was considerably lower than at Big Run Bog. Although the peat at Buckle's Bog was never completely saturated, it was always quite moist.

Regional climate in the vicinity of these two peatlands has been described in considerable detail (Weedfall & Dickerson 1965; Wieder 1982; Wieder & Lang 1984; Wieder 1985). Mean annual temperature is 7.9 °C, with a minimum monthly mean of −3.2 °C in January and a maximum monthly mean of 18.3 °C in July. The average frost-free season (number of days between 0 °C frosts) is 97. Mean annual precipitation averages 133 cm and is fairly evenly distributed throughout the year. Annual snowfall averages 305 cm, and at least 2.5 cm of snow is on the ground for an average of 70 days. On an annual basis, precipitation exceeds potential evapotranspiration, but typically at least one month between April and October exhibits a calculated water deficit (i.e. potential evapotranspiration exceeded precipitation). Such episodic dry periods are associated with transient water table drawdowns at both Big Run Bog and Buckle's Bog (personal observations).

Methods

Peat collection

Two intact peat cores (10 cm diameter × 35 cm deep) were taken from each peatland on each of 8 sampling dates during 1986–1987 using PVC cylinders with sharpened bottom edges. Our core sampling was conducted in areas in which *Sphagnum* cover was nearly 100% and herbaceous and woody species were of minimal importance. Whereas in the top 5–10 cm of the peat decaying portions of *Sphagnum* plants were recognizable and some herbaceous roots were present, deeper peat was amorphous. Cores were inserted into the peat after

using a sharp bread knife to make a cylindrical incision through the surface peat; the PVC cylinders were easily pushed into the peat with apparently minimal compaction of the entrained peat. After insertion, partial excavation of the peat outside of the PVC cylinder allowed a No. 15 rubber stopper to be placed over the bottom of the PVC cylinder so that the entire core could be lifted from the peatland. Entire peat cores were maintained in the capped cylinders during transport to the laboratory on the day of collection.

In addition, on each sampling date, a sample of interstitial water was collected from a well permanently placed at a depth of about 15 cm below the water table of each peatland. The interstitial water samples were transported to the laboratory in air-tight plastic containers with no headspace.

Methane production and carbon dioxide production

Upon return to the laboratory, under a stream of O_2-free N_2, 5 cm thick slices of peat were successively extruded from a cylinder. Avoiding large pieces of woody material (roots or buried stems), three replicate 75 cm^3 subsamples of peat were taken from alternate slices (i.e. 0–5, 10–15, 20–25 and 30–35 cm below the peat surface). Each subsample of peat was placed into a 250 mL Erlenmeyer flask and field-collected interstitial water was added to give a final peat-water volume of 125 mL. We used peatland interstitial water to make the slurries because distilled water would have diluted the native dissolved SO_4^{2-} concentration. Because at our two field sites SO_4^{2-} pool size does not change dramatically with depth (this study, Wieder 1985), we used interstitial water collected from a single depth at each site in the slurries for anaerobic methane and carbon dioxide production. Each Erlenmeyer flask was capped with an aluminum-crimped stopper and the headspace was flushed with helium. The flasks were incubated at the temperature of the peat as measured in the field at the 20 cm depth on the date of collection. At 24–48 h intervals over a 9 day period, a 0.5 mL gas sample was taken from the headspace in each flask; methane and carbon dioxide in the sample were separated with a 152 mm × 3 mm column packed with Poropak Q and detected by flame ionization and thermal conductivity, respectively, on a Varian Model 6000 gas chromatograph (helium gas carrier; 30 mL min^{-1} flow rate). Since concentrations of methane and carbon dioxide in the headspace of each flask generally increased linearly over time, the slopes of linear regressions of gas concentration in the headspace over time were used as estimated of rates of production of each gas (cf. Yavitt et al. 1987, 1988). Because carbon dioxide is a soluble gas, when calculating carbon dioxide production, an empirically determined partition coefficient was used to correct for carbon dioxide accumulation in the water phase (Yavitt et al. 1990).

Sulfate reduction

Rates of dissimilatory sulfate reduction were measured using ^{35}S–SO_4^{2-} incubations. Three replicate subsamples of peat (4–8 g wet mass each; avoiding large

pieces of woody material) were taken from every 5 cm depth interval from the field-collected cores, and under a continuous stream of O_2-free N_2, each was placed individually onto pieces of aluminum foil, injected with 10 μL of a solution containing about 1 μCi of carrier-free $Na_2{}^{35}SO_4$, and wrapped in the foil. The foil packets were placed into a glass bottle which was purged with O_2-free N_2, stoppered, and incubated for 1 h at the peat temperature measured in the field at the 20 cm depth on the date of peat collection. Incubations were terminated by placing the flasks into a -10 °C freezer. Previous studies verified that rates of sulfate reduction were linear over the 1 h incubation period and that radiolabel-injected samples frozen at time 0 exhibited no sulfate reduction activity (Wieder & Lang 1988).

The fate of the added $^{35}SO_4^{2-}$ in the incubated peat samples was determined using Cr^{2+}-reduction in a Johnson–Nishita apparatus, by which inorganic reduced sulfur ($H_2S + S^0 + FeS + FeS_2$) is quantitatively and specifically converted to H_2S, which is trapped in zinc acetate and quantified by iodometric titration (cf. Zhabina & Volkov 1978; Howarth & Jorgensen 1984; Wieder et al. 1985; Canfield et al. 1986; Wieder & Lang 1988). Prior to carrying out the iodometric titration, duplicate 1 mL aliquots of the zinc acetate trapping solution were added to 10 mL of Aquassure for determination of ^{35}S activity by liquid scintillation (quenching was negligible). This protocol allowed for the determination of both the total reduced inorganic sulfur pool and the reduced inorganic ^{35}S in a single peat sample.

Following Cr^{2+}-reduction, the peat was rinsed to remove unreacted $^{35}SO_4^{2-}$ which was quantified by liquid scintillation using appropriate quench correction. Mean percent recovery ($n = 639$) of the added label in the combined reduced inorganic ^{35}S and the unreacted $^{35}SO_4^{2-}$ fractions was 89.5 $\pm$ 1.0 (standard error). Even in short-term incubations, a small percentage of the added label (typically 10–20% in Big Run Bog peat) can become incorporated into organic sulfur fractions, either as ester sulfate or carbon bonded sulfur (Rudd et al. 1986; Wieder & Lang 1988; H. Spratt, pers. comm.). In the studies reported here, recoveries of less than 100% resulted at least in part from our not quantifying incorporation of added label into these two organic sulfur fractions.

To calculate the dissolved sulfate pool size, a separate subsample from each 5 cm slice of peat was pressure filtered through a 0.2 μm membrane, weighed, oven-dried at 50 °C, and reweighed, allowing for the calculation of the water content of the peat. The filtrate was retained for analysis of SO_4^{2-} on a Dionex Model 2010 Ion Chromatograph. The SO_4^{2-} pool size (in μmol L^{-1} of peat substrate) needed to calculate sulfate reduction rates was determined using the SO_4^{2-} concentration, the water content of the peat and the bulk density of the peat. Bulk densities for Big Run Bog peat in the 0–10, 10–20, 20–30, and 30–40 cm depth intervals are 0.04, 0.05, 0.07, and 0.09 g (dry mass) cm^{-3}, respectively (Wieder 1985), and for Buckle's Bog peat in the 0–5, 5–10, 10–15, 15–20, 20–25, 25–30, and 30–35 cm depth intervals are 0.06, 0.09, 0.15, 0.16, 0.17, 0.20, and 0.16 g cm^{-3}, respectively.

Sulfate reduction rate was calculated as the proportion of the added $^{35}SO_4^{2-}$ recovered as reduced inorganic sulfur times the initial dissolved sulfate pool size times a factor of 1.06 to account for discrimination against the heavier ^{35}S isotope by sulfate reducing bacteria (Mountfort et al. 1980).

In addition to measuring sulfate reduction as a function of depth throughout an annual cycle, a separate experiment was conducted to test whether or not sulfate reduction rate is limited by sulfate availability. Using subsamples of surface (0–5 cm; water content of 95% w/w) and subsurface (30–35 cm; water content of 86% w/w) peat collected from Big Run Bog on November 5, 1986, the instantaneous dissolved SO_4^{2-} pool size was augmented by adding 500 μL of a Na_2SO_4 solution (0, 2.6, 5.2, 10.4, 20.8, or 41.6 mmol L^{-1}; 3 replicates per SO_4^{2-} augmentation level) to each 3–6 g wet mass. Subseqeuntly, each subsample was injected with approximately 1 μCi of carrier-free $Na_2{}^{35}SO_4$ incubated for 1 h at 19 °C, total reduced ^{35}S, unreacted $^{35}SO_4^{2-}$, and the sulfate reduction rate determined as described above. In these studies, percent recovery of the added label as reduced inorganic ^{35}S plus unreacted $^{35}SO_4^{2-}$ was 92.1 $\pm$ 3.2 (mean $\pm$ standard error).

Cautionary notes regarding methodology

Three aspects of our procedures merit clarification and comment. First, it is difficult, if not impossible, to collect a completely undisturbed peat core. Disturbances related to core collection and preparation of samples can result in measured rates of anaerobic processes that may be quite different from *in situ* rates (cf. Kelly & Chynoweth 1980). After considerable experimentation, we adopted a coring technique that we feel caused minimal disturbance and was maximally effective in preserving any vertical stratification present in the peat deposit, as well as the native water content, bulk density, and chemical conditions of the peat at a particular depth.

Second, our measurements of anaerobic methane and carbon dioxide production (but not sulfate reduction) were made on anaerobic slurries in which peatland interstitial water was added to peat samples from each depth. To evaluate the potential effects of slurrying on anaerobic methane and carbon dioxide production, subsamples of surface (0–5 cm) or subsurface (15–20 cm) peat, collected from Big Run Bog in March 1987 were placed into 125 mL flasks without adding interstitial water (12 replicates per depth) or as slurries with added interstitial water (12 replicates per depth). The headspaces of the flasks were purged with He and incubated. Initially and after 2, 8, and 12 h, 3 replicate flasks for each treatment were killed (acid/formalin addition) and shaken vigorously to strip methane and carbon dioxide, the concentrations of which in the headspace were measured as described above. Slurrying had no significant effect either on methane production or on anaerobic carbon dioxide production (comparison of slopes of regressions in Fig. 1 by analysis of covariance $p > .05$; see Yavitt et al. 1990). The displacement of the slurried curves to lower concentrations of

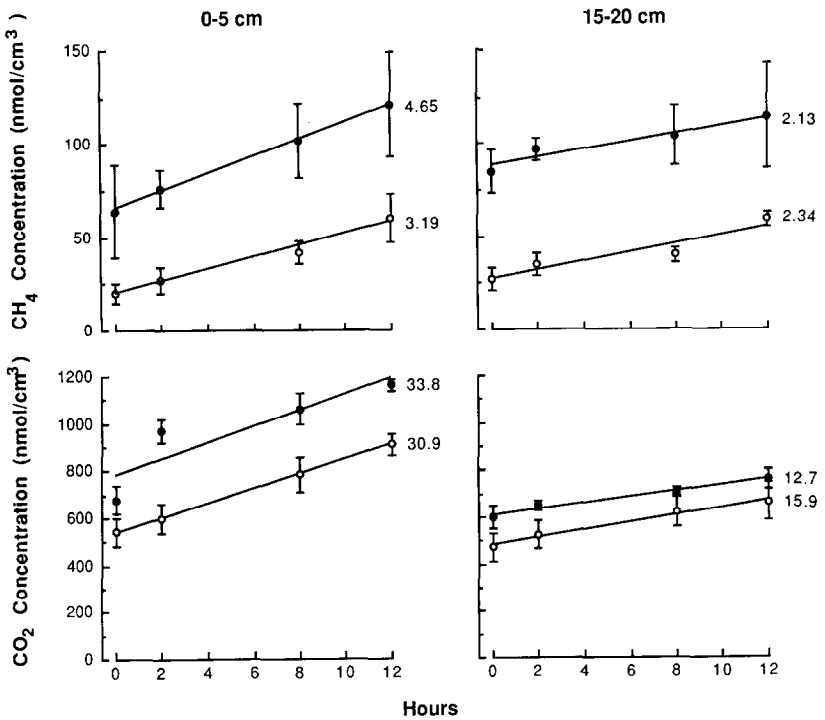

Fig. 1. Comparison of rates of accumulation of methane and carbon dioxide in the headspaces of flasks under non-slurried (●) and slurried (○) conditions. Each data point represents the mean ± standard error for 3 replicate determinations. Values to the right of each plotted linear regression line are the slopes, corresponding to the rates of methane or carbon dioxide production in nmol $cm^{-3} h^{-1}$.

methane and carbon dioxide throughout the 12 h period (Fig. 1) resulted from initial losses of methane and carbon dioxide from degassing of the peat during preparation of the slurries. In the present study, we opted to use slurries to allow for a more direct comparison with our previous studies of anaerobic carbon metabolism in Big Run Bog and Buckle's Bog peat, conducted using slurried peat (see Yavitt et al. 1987, 1988). Difficulties with measuring anaerobic carbon metabolism, including a discussion of the use of slurries, have been thoroughly reviewed elsewhere (Jones & Simon 1984).

Finally, in the flasks for measurement of anaerobic methane and carbon dioxide production, we purged the headspace with helium, thereby effectively preventing any possibility of methane oxidation. Previous measurements of the magnitude of potential methane oxidation in peat from both Big Run Bog and Buckle's Bog indicate that the values reported in this paper for methane production may overestimate net methane production by as much as 18–22% (Yavitt et al. 1988).

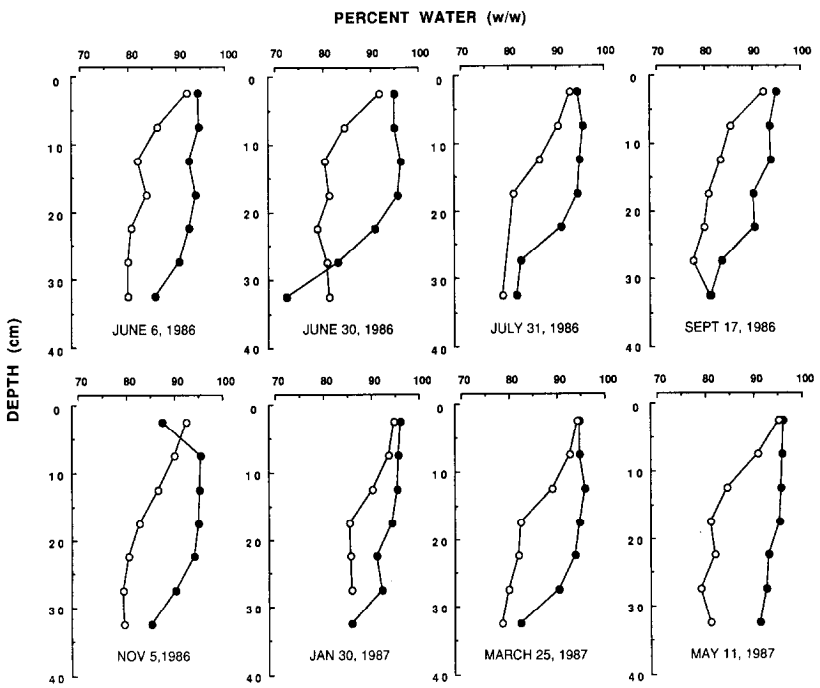

Fig. 2. Water contents (percent w/w) of peat from Big Run Bog (●) and from Buckle's Bog (○); values are means of 2 determinations (1 per depth in each of 2 cores).

Results

Water content

Peat from Big Run Bog was generally wetter than peat from Buckle's Bog, with mean (± standard error) water contents (percent, w/w) averaged across all dates and all depths of 91.3 ± 0.6 (n = 112) and 84.4 ± 0.6 (n = 104), respectively. At both sites there was a general trend of decreasing water content of the peat with increasing depth, although this trend was more pronounced in Buckle's Bog peat than in Big Run Bog peat (Fig. 2).

Methane production

At Big Run Bog, rates of methane production in individual peat samples ranged from 0–336 μmol $L^{-1} d^{-1}$, with an overall mean (n = 191) of 63 μmol $L^{-1} d^{-1}$ (Fig. 3). Methane production varied seasonally and with depth. In January and March, when peat temperatures were 4 °C or less, consistently low rates of methane production were found throughout the top 35 cm of peat. In contrast, from June through September when peat temperatures were 15 °C or greater,

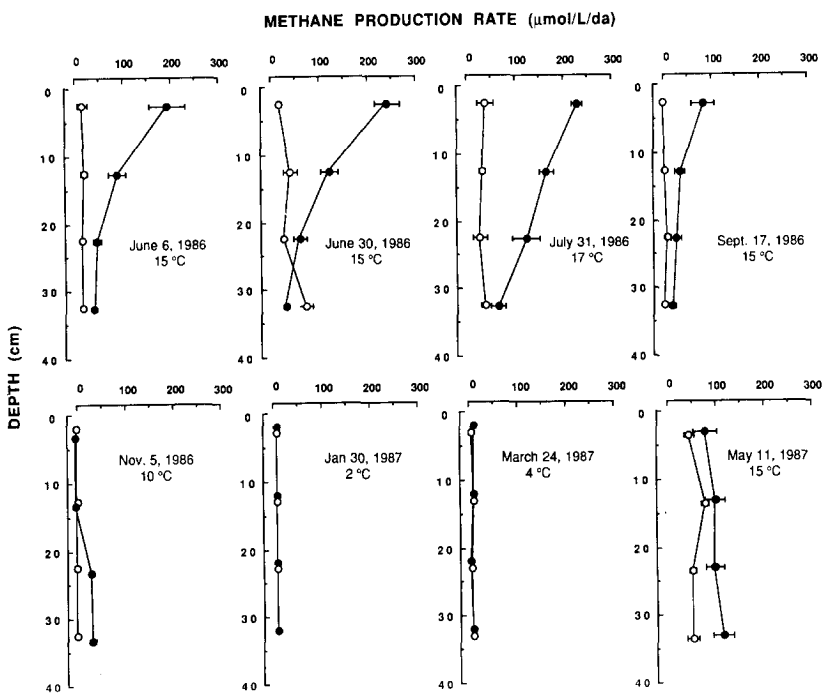

Fig. 3. Methane production in peat from Big Run Bog (●) and from Buckle's Bog (○); values are means of 6 determinations (3 per depth in each of 2 cores) ± standard errors. Peat temperatures at a depth of 20 cm, measured on each sampling date, are also given.

rates of methane production were highest in surface peat and decreased with increasing depth. At Buckle's Bog, rates of methane production in individual peat samples ranged from 0–154 μmol $L^{-1} d^{-1}$, with an overall mean (n = 202) of 18 μmol $L^{-1} d^{-1}$ (Fig. 3). In contrast to the spatial and temporal changes in methane production observed for Big Run Bog peat, at Buckle's Bog rates of methane production were fairly uniform throughout the top 35 cm of peat and did not exhibit as strong a seasonality associated with changes in peat temperature.

Total annual methane production within the top 35 cm of Big Run Bog peat was 6.2 ± 1.2 mol m^{-2} (mean ± range; see Fig. 4 for explanation of how the range was estimated for the annual integrated values), with daily integrated rates ranging from 0.2 mmol m^{-2} on 30 January to 52.0 mmol m^{-2} on 31 July (Fig. 4). In Buckle's Bog peat, total annual methane production in the top 35 cm of peat was 1.6 ± 0.5 mol m^{-2}, with daily integrated rates ranging from 0 mmol m^{-2} on 5 November to 15.6 mmol m^{-2} on 11 May (Fig. 4). At Big Run Bog and Buckle's Bog, 87 and 96%, respectively, of the total annual methane production occurred during the relatively warm 6-month period between 25 March and 17 September.

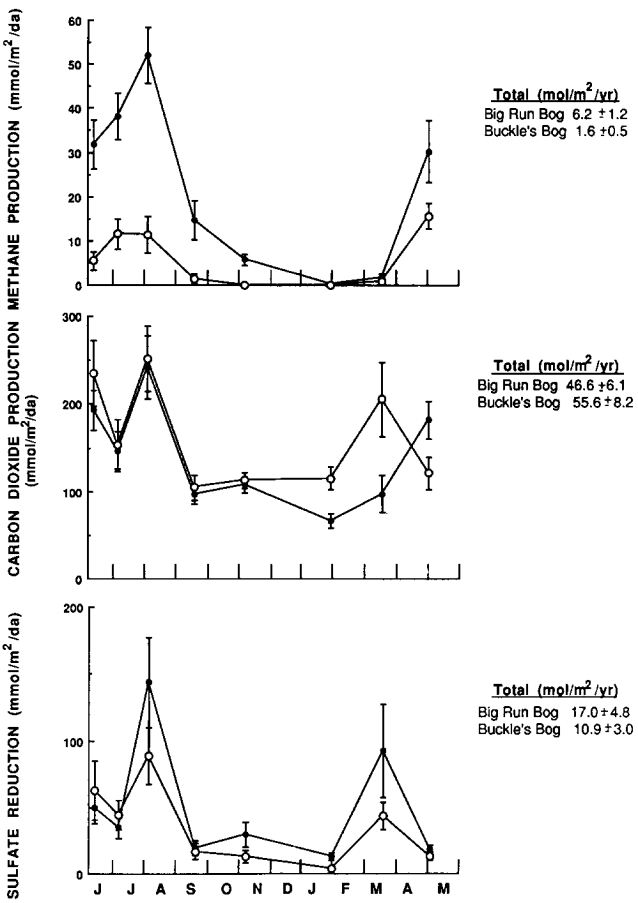

Fig. 4. Depth-integrated rates of methane production, carbon dioxide production, and sulfate reduction in the top 35 cm of peat at Big Run Bog (●) and Buckle's Bog (○). Depth-integrated values were calculated by integrating the mean rates for each process (Figs. 3, 5, or 6) across all depths; vertical bars above and below each value represent ranges, calculated by integrating the means plus one standard error and the means minus one standard error (Figs. 3, 5, 6) across all depths for each date. Total annual rates were calculated by integrating the values plotted in this figure across all dates; ranges for the total annual rates were calculated by integrating the maximum or minimum depth-integrated values, represented by the vertical bars, across all dates.

Carbon dioxide production

In contrast to methane production, rates of carbon dioxide production were similar at the two sites (Fig. 5). At Big Run Bog, rates of carbon dioxide production in individual peat samples ranged from 72–1238 μmol $L^{-1} d^{-1}$, with an overall mean (n = 191) of 406 μmol $L^{-1} d^{-1}$. At Buckle's Bog rates of carbon dioxide production in individual peat samples ranged from 86–2030 μmol $L^{-1} d^{-1}$, with an overall mean (n = 202) of 486 μmol $L^{-1} d^{-1}$. In peat

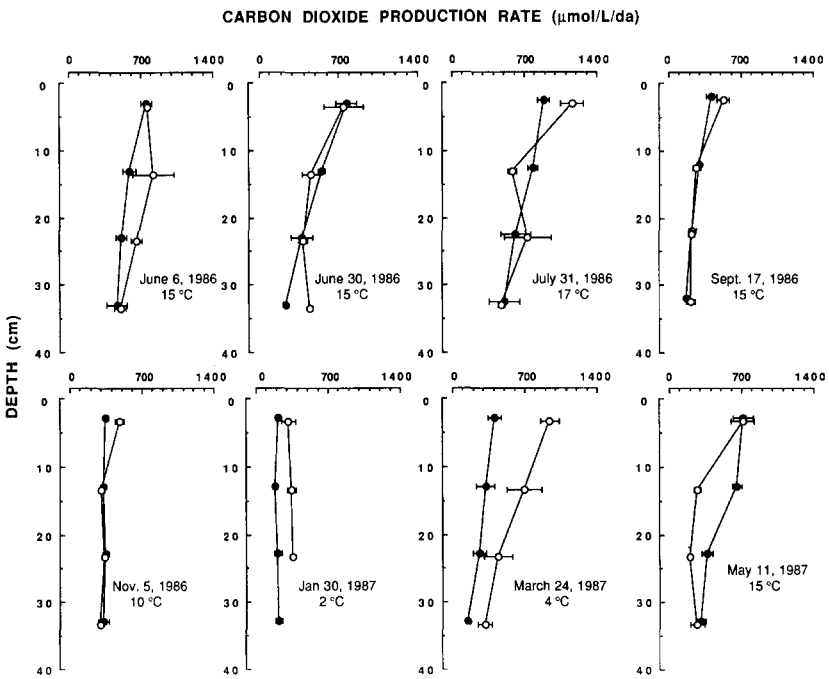

Fig. 5. Carbon dioxide production in peat from Big Run Bog (●) and from Buckle's Bog (○); format is as in Fig. 3.

from each site, rates of carbon dioxide production often were greatest in surface peat and gradually decreased with depth. Seasonal variation in carbon dioxide production related to peat temperature was not nearly as evident as was seasonal variation in methane production.

At Big Run Bog, daily integrated rates of carbon dioxide production ranged from 66.7 mmol m^{-2} on 31 January to 241.3 mmol m^{-2} on 31 July, whereas at Buckle's Bog, daily integrated rates of carbon dioxide production ranged from 104.5 mmol m^{-2} on 17 September to 251.6 mmol m^{-2} on 31 July (Fig. 4). On an annual basis, total carbon dioxide production in the top 35 cm of peat was 46.6 ± 6.1 and 55.6 ± 8.2 mol m^{-2} (mean ± range) at Big Run Bog and Buckle's Bog, respectively. At these two sites, 64 and 58%, respectively, of the total amount carbon dioxide production occurred during the relatively warm 6-month period between 25 March and 17 September.

Sulfate reduction and pool sizes of sulfur fractions

In general, rates of sulfate reduction were similar at the two sites (Fig. 6). Rates of sulfate reduction in individual peat samples from Big Run Bog ranged from 2.5–1568 μmol L^{-1} d^{-1}, with an overall mean (n = 333) of 146 μmol L^{-1} d^{-1}, whereas rates of sulfate reduction in individual peat samples from Buckle's Bog ranged from 0.2–1883 μmol L^{-1} d^{-1}, with an overall mean (n = 306) of

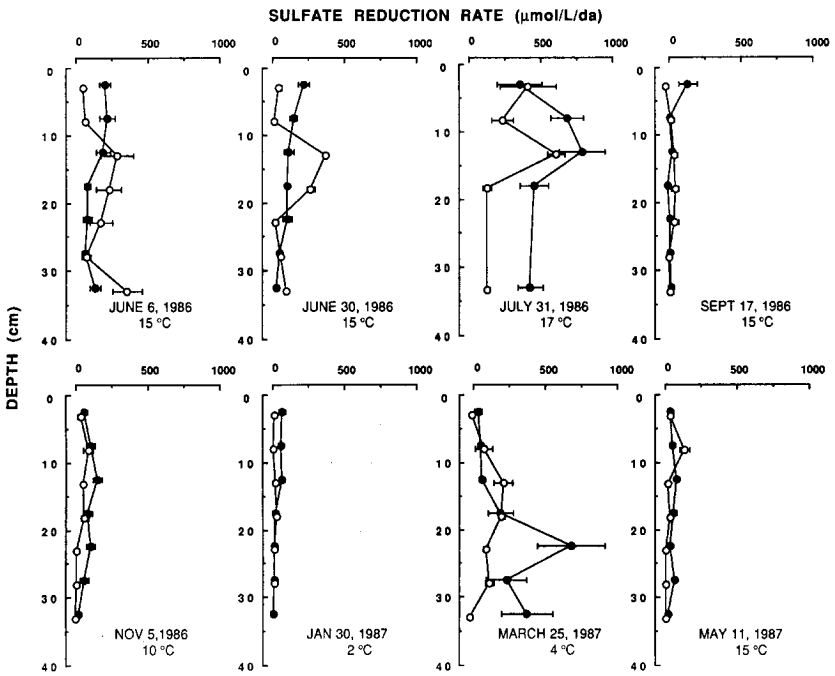

Fig. 6. Sulfate reduction in peat from Big Run Bog (●) and Buckle's Bog (○); format is as in Fig. 3.

104 mmol L^{-1} d^{-1}. Although changes in the rates of sulfate reduction with depth were not consistent among all sampling dates, it was often the case that the highest rates of sulfate reduction were obtained at a depth between 10 and 25 cm.

At Big Run Bog and Buckle's Bog, daily integrated rates of sulfate reduction in the top 35 cm of peat ranged from minimum values of 12.7 and 3.5 mmol m^{-2}, respectively, on 31 January to maximum values of 143.3 and 88.3 mmol m^{-2}, respectively, on 31 July (Fig. 4). Total annual sulfate reduction in the top 35 cm of peat at the two sites was 17.0 ± 4.8 and 10.9 ± 3.0 mol m^{-2} (mean ± range), respectively, with 66 and 75%, respectively, of the total occurring between 25 March and 17 September.

Dissolved sulfate concentrations were generally more uniform, both as a function of depth and over time, at Big Run Bog than at Buckle's Bog (Fig. 7). The overall mean dissolved sulfate concentration was greater at Buckle's Bog (125 μmol L^{-1} of substrate) than at Big Run Bog (66.9 μmol L^{-1} of substrate), mainly because on some of the sampling dates (most notably 30 June) dissolved sulfate concentrations were considerably higher in Buckle's Bog peat than in Big Run Bog peat. Concentrations of total reduced inorganic sulfur (S^0 + FeS_2 + FeS + H_2S) were similar in peat from the two sites, with overall means in Big Run Bog peat and Buckle's Bog peat of 1.35 mmol L^{-1} and 1.40 mmol L^{-1},

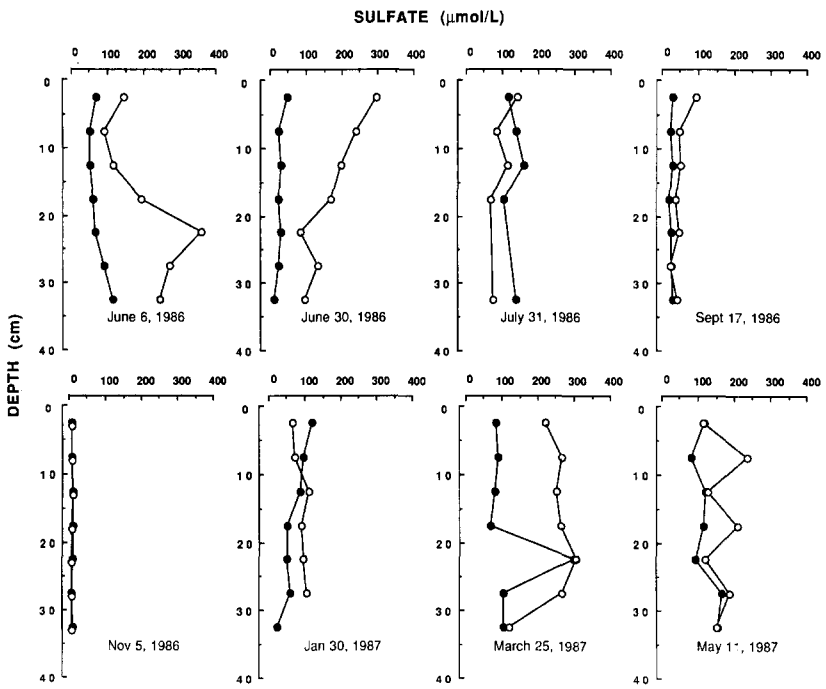

Fig. 7. Dissolved sulfate pool sizes in peat from Big Run Bog (●) and from Buckle's Bog (○); values are the means of 2 determinations (1 per depth in each of 2 cores).

respectively (Fig. 8). Concentrations of reduced inorganic sulfur were fairly uniform both as a function of depth and over time, although at Buckle's Bog there tended to be a peak in total reduced inorganic sulfur concentrations between 5 and 15 cm below the peat surface.

Discussion

Anaerobic carbon mineralization

Rates of methane production obtained in peat from Big Run Bog and Buckle's Bog (Figs. 3, 4) are similar to rates previously reported for these two sites (Yavitt et al. 1987, 1988), as well as to rates reported for *Sphagnum*-dominated wetlands in Minnesota (Williams & Crawford 1984), Wisconsin (Goodwin & Zeikus 1987), and Sweden (Svensson 1984), or for rice paddies (Holzapfel-Pschorn et al. 1985).

Although seasonal variation in methane production was evident in peat from both Big Run Bog and Buckle's Bog, marked enhancement of methane production in Big Run Bog surface peat during the warmer months of the year (Fig. 3) resulted in a total annual methane production in Big Run Bog peat that was 3.9 times greater than in Buckle's Bog peat. Other studies have also reported low

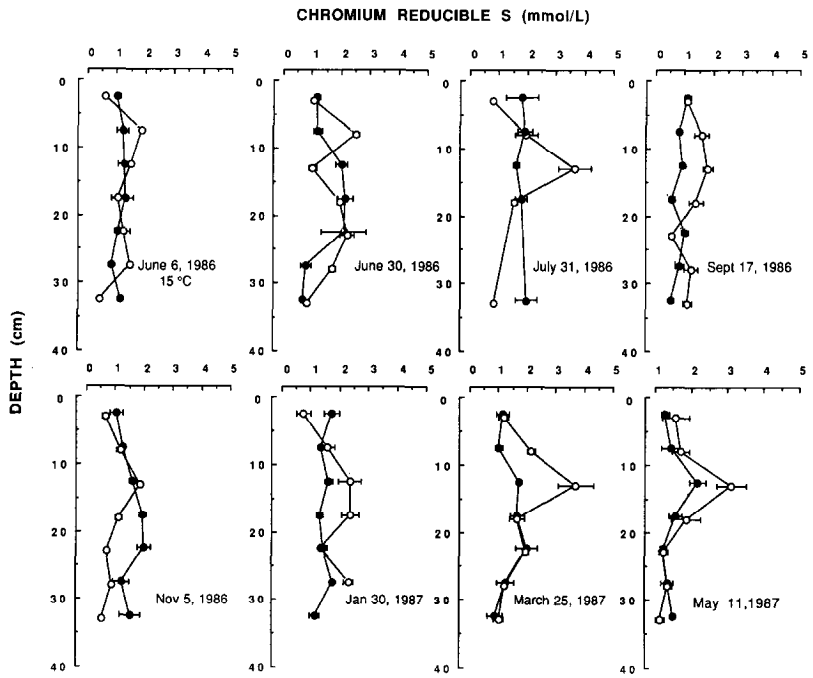

Fig. 8. Reduced inorganic sulfur pool sizes in peat from Big Run Bog (●) and from Buckle's Bog (○); values are the means of 6 determinations (3 per depth in each of 2 cores), ± standard errors.

temperature inhibition of methane production in surface peat (Williams & Crawford 1984; Svensson 1984), whereas methane production in deeper peat is typically much less responsive to temperature (Williams & Crawford 1984; DeLaune et al. 1986; Yavitt et al. 1987).

Although the seasonal and depth patterns in methane production in Big Run Bog peat are consistent with results from previous studies of methane production in freshwater wetlands, the lack of any substantial enhancement of methane production during the warmer months in Buckle's Bog surface peat (Fig. 3) is unusual. Differences between the two peatland sites should be minimal with regard to either macroclimatic conditions or the chemical quality of the organic peat since both peat deposits are derived predominantly from *Sphagnum* mosses. One difference between the two sites, however, is that Buckle's Bog peat has a consistently lower water content than Big Run Bog peat, especially near the surface (Fig. 2). Although experimental studies are needed to more definitively assess factors contributing to differences in methane production between Big Run Bog and Buckle's Bog, our observations suggest that methanogenic bacteria may be sensitive to the field moisture content of peat. A positive correlation between methane production and the field moisture content of peat has also been reported by Svensson & Rosswall (1984). It is notable that, as in our study, the methane production data reported by Svensson & Rosswall (1984) were

obtained using slurry techniques which tend to minimize or eliminate any preexisting differences among peat samples in field moisture contents.

Probably because of the prevailing view that anaerobic carbon mineralization in freshwater wetland systems should be dominated by methane production, relatively little attention has focused on either sulfate reduction or carbon dioxide production generated by anaerobic processes in peatland ecosystems. Rates of sulfate reduction in Big Run Bog peat and Buckle's Bog peat are similar to rates previously reported for Big Run Bog peat (Wieder & Lang 1988), but are generally higher than rates reported for *Sphagnum* peat from the New Jersey Pinelands where the highest daily rates (43 μmol L^{-1} of peat) were obtained in the spring (Spratt et al. 1987). Other studies have used $^{35}SO_4^{2-}$ to evaluate aspects of sulfur cycling in peatland ecosystems (Behr 1985; Brown 1985; Brown & MacQueen 1985), but these studies have not estimated rates of dissimilatory sulfate reduction.

Although both sulfate reduction and carbon dioxide production exhibited marked seasonal variation (Fig. 4), in contrast to methane production, variation in rates of sulfate reduction (Fig. 6) and in rates of carbon dioxide production (Fig. 5) were similar at Big Run Bog and Buckle's Bog, as were annual rates for each process at these two sites. Thus, whatever factor or factors contributed to low methane production at Buckle's Bog relative to Big Run Bog did not have parallel effects on either sulfate reduction or carbon dioxide production.

At both Big Run Bog and Buckle's Bog, sulfate reduction rate was positively correlated with sulfate pool size (Spearman's rho values of 0.591, $n = 333$ and 0.330, $n = 305$, for the two sites respectively, $p \leqslant 0.05$; correlations are between sulfate reduction rate and sulfate pool size for each replicate determination, regardless of either depth or sampling date) suggesting that sulfate reduction may have been sulfate limited. However, in Big Run Bog peat augmentation of the sulfate pool in short-term laboratory incubations failed to stimulate sulfate reduction in either surface (one-sided test, Spearman's rho = 0.317, $p = 0.10$) or subsurface (one-sided test, Spearman's rho = -0.746, $p = 0.9998$) peat (Fig. 9). The ultimate source of sulfate to these peatlands is atmospheric deposition, either directly incident or entering the peatlands in runoff from the surrounding upland portions of the watersheds, but the magnitude of sulfate reduction in these two peatlands far exceeds the level of atmospheric sulfate deposition. Annual sulfate deposition in the Big Run Bog watershed is 57 mmol m^{-2} (Wieder et al. 1987) whereas total annual sulfate reduction in the top 35 cm of peat at Big Run Bog is 17 020 mmol m^{-2}. At both of these two peatland sites, the maintenance of moderately high rates of sulfate reduction in spite of relatively low dissolved sulfate concentrations is made possible through the continual replenishment of the dissolved sulfate pool by sulfide oxidation.

Despite the unexpectedly high rates of sulfate reduction in Big Run Bog and Buckle's Bog peat, the reduced inorganic sulfur endproducts of sulfate reduction apparently do not accumulate to any substantial extent in the peat. Concentrations of reduced inorganic sulfur do not vary much over time in either Big

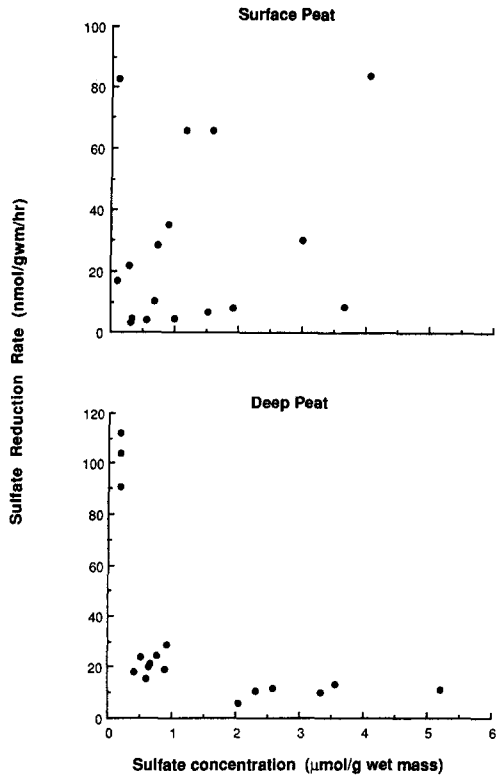

Fig. 9. Effect of experimental augmentation of the dissolved sulfate pool size on sulfate reduction rate. Each data point represents a single determination.

Run Bog peat or Buckle's Bog peat (Fig. 8). The mean turnover times of the reduced inorganic sulfur pool (pool size divided by sulfate reduction rate) in Big Run Bog peat and Buckle's Bog peat are 38 and 96 days, respectively. Not only does the reduced inorganic sulfur pool turn over rapidly, but also the dissolved sulfate pool turns over rapidly (mean turnover times of 1.5 and 5.8 days, respectively), thereby supporting moderately high rates of sulfate reduction in peat with a low instantaneous dissolved sulfate concentration (cf. Wieder & Lang 1988).

Simple diffusion of oxygen from the atmosphere into the waterlogged peat is almost certainly insufficient to support the rates of sulfide oxidation inferred from our data. In freshwater peatlands like Big Run Bog and Buckle's Bog, however, it is not necessarily the case that oxygen is the electron acceptor for the oxidation of reduced inorganic sulfur. We have previously presented experimental evidence for anaerobic (i.e. anoxic) oxidation of FeS and FeS_2 in subsurface peat from Big Run Bog (Wieder & Lang 1988). Oxidation of hydrogen sulfide and iron sulfides by soluble oxidized iron or manganese ions or by iron and/or manganese oxyhydroxides has been widely reported (e.g. Garrels & Thompson

1960; Singer & Stumm 1970; Burdige & Nealson 1986; Moses et al. 1987; Aller & Rude 1988). In the top 20 cm of peat from Big Run Bog and Buckle's Bog, we have measured concentrations of iron oxides (oxalate- plus dithionite-extractable iron) of 62 and 41 μmol g^{-1}, respectively, and of manganese oxides of 0.4 and 1.3 μmol g^{-1}, respectively (Wieder & Lang 1986).

Accepting this scenario, however, it is still the case that at some point oxygen is needed to regenerate the oxidized iron and manganese electron acceptors. At sites like Big Run Bog and Buckle's Bog, several mechanisms may play a role in supplying oxygen to the deeper, usually anaerobic peat layers. Vascular plant roots can provide a chronic, low level supply of oxygen to otherwise seemingly anoxic peat (Armstrong 1979). Water table drawdowns can provide intermittent periods of oxygenation of the peat. Finally, relatively rapid flushing of the wetland with oxygenated water in association with major precipitation events could provide not only oxygen but also inputs of dissolved iron from the upland portions of the watersheds surrounding these wetlands.

As in Big Run Bog and Buckle's Bog, in salt marshes annual rates of sulfur accumulation in peat are much lower than annual sulfate reduction (cf. Howarth & Teal 1980; King 1988). Apparently, much of the reduced inorganic sulfur produced from sulfate reduction is also reoxidized (Giblin & Howarth 1984, Feitjel 1986; Giblin 1988; Luther & Church 1988), although neither the precise mechanism nor the organisms responsible are well understood.

In many ecosystems, the co-occurrence of sulfate reduction and methane production has been characterized by spatially and/or temporally separated zones of maximum activity established through competitive interactions between sulfate reducing and methanogenic bacteria (see Ward & Winfrey 1985 for a review). Such was not the case at either Big Run Bog or Buckle's Bog. Neither spatial nor temporal separation of sulfate reduction and methane production was consistently evident at Big Run Bog or at Buckle's Bog (Figs. 3, 4, 6), suggesting that these two processes were not strongly affected by competition for common substrates. Previous studies with Big Run Bog peat indicated that experimental augmentation of the dissolved sulfate pool (up to a concentration of 5.0 mM) sometimes, but not always, resulted in a decrease in methane production, especially in surface peat (Yavitt et al. 1987). Moreover, when sulfate augmentation did result in a decrease in methane production, a concomitant increase in carbon dioxide production was not always obtained, as would be expected if sulfate reducers were stimulated and were outcompeting methane producers. In the present study sulfate reduction rates and methane production rates were not significantly negatively correlated at either Big Run Bog or Buckle's Bog (Spearman's rho values of 0.312, $n = 64$ and 0.272, $n = 59$, respectively; $p > 0.05$, one-sided test; correlations are between the means of the 3 sulfate reduction determinations per depth per date and the means of the 3 methane production determinations per depth per date). Moreover, as previously stated, our rates of methane production are similar to those reported for other *Sphagnum* peatlands. Although our arguments are mainly circumstantial and further experimental studies on the interactions between sulfate reducers and methanogens are warranted, at this point it appears that at least for

Table 1. Tentative carbon budgets for Big Run Bog and Buckle's Bog. All values are in mol $m^{-2} yr^{-1}$ of carbon. See text for assumptions and derivations of estimated values.

	Both sites	
Net primary production:		
Aboveground	39.2	
Belowground	22.3	
Total	61.5	
Aerobic carbon mineralization of:		
Aboveground net primary production	27.4–35.2	
Belowground net primary production	0	
Total	27.4–35.2	
Input to anaerobic zone from:		
Aboveground net primary production	3.9–11.7	
Belowground net primary production	22.3	
Total	26.2–34.0	
Anaerobic carbon mineralization	*Big Run Bog*	*Buckle's Bog*
CH_4 production	6.2	1.6
CO_2 production	46.6	55.6
From methanogenesis	6.2	1.6
From sulfate reduction	34.0	21.8
From other processes	6.4	32.2
Total	52.8	57.2

these two peatlands, the unexpectedly high rates of sulfate reduction are not occurring at the expense of methane production.

Carbon balance and peat accumulation

Clymo (1984) argued that peat accumulation depends mainly on two factors, the rate of input of organic matter into the anaerobic zone and the rate of organic matter decomposition in the anaerobic zone (anerobic carbon mineralization). Neither net primary production nor aerobic decomposition *per se* are nearly as important in affecting rates of peat accumulation, although it is these two processes combined that determine the quantity of organic matter that passes from the aerobic surface zone into the underlying anaerobic zone. Using the conceptual framework provided by Clymo (1984), the rates of anaerobic carbon mineralization presented in this paper are put in the context of carbon balance at Big Run Bog and Buckle's Bog (Table 1). Although in the synthesis in Table 1, rates of methane production, carbon dioxide production, and sulfate reduction are presented as single annual values, our intent is to emphasize the interpretation of the information summarized in Table 1, rather than the actual annualized values themselves. Moreover, it must be emphasized that we have measured rates of anaerobic methane and carbon dioxide production in peat, not rates of emission of these gases to the atmosphere. As such, our data are not interpreted in terms of atmospheric carbon cycling.

At Big Run Bog, annual aboveground net primary production in terms of carbon (assuming that plant material is 45% carbon) is 39.2 mol m^{-2}, with 43% of that production contributed by mosses and the remainder by herbaceous species and shrubs (Wieder et al. 1989). We did not measure aerobic decomposition or the rate of input of organic matter into the anaerobic zone. However, a litterbag study conducted at Cranesville Swamp, a peatland less than 20 km from Buckle's Bog, obtained rates of leaf decomposition that were similar to rates obtained in other northern peatland ecosystems (Lang & McDonald 1982). Assuming that only 10–30% of the annual aboveground net primary production becomes available for anaerobic carbon mineralization via transfer into the anaerobic zone (Heal et al. 1975; Moore et al. 1975; Parkarinen 1975; Clymo 1984), the annual input of carbon into the anaerobic zone is estimated as 3.9–11.7 mol m^{-2}.

Belowground production of the herbaceous species and shrubs has not been quantified at either Big Run Bog or Buckle's Bog, and the few published estimates of belowground production in *Sphagnum* peatlands vary widely (see Wieder et al. 1989). As a rough estimate, we have assumed that belowground production at our sites is equivalent to aboveground production of the herbaceous and shrub species. We further assume that all of the belowground net primary production becomes available for anaerobic decomposition. Finally, we apply the estimates for Big Run Bog to Buckle's Bog since both are typical representatives of Appalachian *Sphagnum*-dominated peatland ecosystems.

Integration over time of the methane production plus carbon dioxide production curves (Fig. 4) gives estimates of total annual anaerobic carbon mineralization in the top 35 cm of peat at Big Run Bog and Buckle's Bog of 52.8 and 57.2 mol m^{-2}, respectively. Sulfate reduction accounted for 64 and 38%, respectively, of total anaerobic carbon mineralization, assuming that two moles of carbon dioxide are produced from each mole of sulfate reduced (Fenchel & Blackburn 1979). Contrary to prevailing concepts of anaerobic decomposition in freshwater peatlands, methanogenesis accounted for only 23.5 and 5.6%, respectively, of the total anaerobic carbon mineralization at these two sites, assuming one mole of carbon dioxide is produced along with each mole of methane. Especially at Big Run Bog, anaerobic carbon dioxide production, resulting substantially from sulfate reduction, dominated anaerobic carbon mineralization. The input of sulfur via acid precipitation by itself is insufficient to support the total annual sulfate reduction and attendant carbon mineralization observed at our two sites. Rather, it is the apparent spiraling effect whereby a single sulfur atom may be alternately reduced and oxidized several times before leaving a peatland, that allows sulfate reduction to be more important than atmospheric sulfur deposition might suggest.

The summary in Table 1 suggests that in the absence of sulfate reduction, the carbon balance at both Big Run Bog and Buckle's Bog would more than likely be either at a steady-state or in a condition of peat accumulation, i.e. inputs of carbon into the anaerobic zone would be equal to or greater than anaerobic carbon mineralization. However, under extant conditions, it appears that annual anaerobic carbon mineralization at both Big Run Bog and Buckle's Bog

exceeds annual input of carbon into the anaerobic zone, placing the peat deposits into a present state of negative carbon balance, so that these peat deposits are being degraded rather than accumulating.

A new hypothesis and areas for future study

Traditional concepts hold that in low sulfate freshwater wetlands, anaerobic decomposition should be dominated by methanogenesis rather than sulfate reduction, the latter process being limited by an inadequate supply of dissolved sulfate. When sulfate concentration becomes sufficiently high, sulfate reduction should proceed at the expense of methanogenesis since thermodynamically and kinetically sulfate reducers outcompete methanogens for organic carbon substrates. These traditonal concepts do not hold for Big Run Bog and Buckle's Bog. In contrast, anaerobic carbon mineralization is dominated by sulfate reduction rather than methanogenesis, sulfate reduction proceeds at quite low dissolved sulfate concentrations and is not stimulated by experimental augmentation of the dissolved sulfate pool, and there is little evidence that sulfate reduction occurs at the expense of methane production.

It remains to be seen, however, whether or not our findings for Big Run Bog and Buckle's Bog are generalizable to all *Sphagnum*-dominated peatland ecosystems. Because of their geographic location, our two study sites along with other Appalachian *Sphagnum* peatlands receive considerably greater inputs of sulfate via the recent phenomenon of acid precipitation than do the vast majority of North American peatlands. The coincidence of high sulfate inputs to the Big Run Bog and Buckle's Bog watersheds with the unexpected importance of sulfate reduction and a very dynamic cycling of sulfur through alternating oxidation and reduction within the peatlands themselves leads us to suggest a new hypothesis: anaerobic decomposition processes in peatlands not receiving high sulfate loading should exhibit low rates of anaerobic decomposition in general, and a predominance of methane production over sulfate reduction; however, if such peatlands become subjected to increased atmospheric sulfur deposition, sulfate reduction may be enhanced as an anaerobic mineralization pathway with attendant effects on carbon balance and peat accumulation.

The data presented in this paper are inadequate to unequivocally support or refute this hypothesis. It would be particularly informative to know the relative contributions of anaerobic production, carbon dioxide production, and sulfate reduction to anaerobic carbon mineralization at Big Run Bog and at Buckle's Bog prior to the advent of high sulfur deposition in acid precipitation. Since such information cannot be directly obtained, an alternative approach would be to measure depth-integrated rates of anaerobic methane production, carbon dioxide production, and sulfate reduction over an annual cycle in a *Sphagnum* peatland that historically has received low inputs of sulfate from precipitation. An even stronger test of the hypothesis would be to conduct such measurements along with a field experimental manipulation in which sulfate additions were made to a peatland with historically low sulfate inputs.

On a finer scale of resolution, additional questions remain regarding the nature of the electron acceptors that participate in the oxidation of the reduced inorganic sulfur. Our data from Big Run Bog and Buckle's Bog indicate a rapid turnover of the reduced inorganic sulfur pool, even under supposedly anaerobic conditions, and we suggested that oxidized Fe and/or Mn, nitrate or even oxygen may be candidates as electron acceptors in the oxidation process. To sustain the rapid cycling of sulfur between oxidized and reduced inorganic forms, the electron acceptors participating in reduced inorganic sulfur oxidation must be constantly supplied to these peatlands and/or must be regenerated within the peatlands by themselves cycling through oxidation/reduction reactions. Although acid precipitation has resulted in a considerable increase in sulfur deposition to sites like Big Run Bog and Buckle's Bog, acid precipitation has almost certainly not concomitantly increased the supply of electron acceptors that may mediate reduced inorganic sulfur oxidation. Thus, under our hypothesis that the dynamic sulfur cycle observed at our two study sites is somehow linked to high sulfur input through acid precipitation, a major gap in our knowledge is represented by an inadequate understanding of the biogeochemical roles of these electron acceptors both prior to and subsequent to high sulfur input.

Acknowledgements

We thank V.A. Granus, A.L. Tarleton, M.A. Kichak, and M. Nardi for laboratory assistance. This work was supported by grants from the National Science Foundation (BSR-8215731 and BSR-8516700) and from the National Aeronautics and Space Administration (NAGW-842).

References

Aller RC & Rude PD (1988) Complete oxidation of solid phase sulfides by Mn and bacteria in anoxic marine sediments. Geochim. Cosmoshim. Acta 52: 751–765

Armstrong W (1979) Aeration in higher plants. Adv. Bot. Research 7: 225–332

Behr RA (1985) Sulfur dynamics in an experimentally acidified mire in north-western Ontario. M.S. Thesis, University of Manitoba

Burdige DJ & Nealson KH (1986) Chemical and microbiological studies of sulfide-mediated manganese reduction. Geomicrobiol. J. 4: 361–387

Brown KA (1985) Sulphur distribution and metabolism in waterlogged peat. Soil Biol. Biochem. 17: 131–140

Brown KA & MacQueen JG (1986) Sulphate uptake from surface water by peat. Soil Biol. Biochem. 17: 411–420

Canfield DE, Raiswell R, Westrich JT, Reaves CM & Berner RA (1986) The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. Chemical Geol. 54: 149–155

Clymo RS (1984) The limits to peat bog growth. Phil. Trans. Royal Soc. London, Series B 303: 605–654

DeLaune RD, Smith CJ & Patrick WH Jr. (1986) Methane production in Mississippi River deltaic plain peat. Organic Geochem. 9: 193–197

Feijtel TCJ (1986) Biogeochemical cycling of metals in Barataria Basin, Ph.D. Dissertation, Louisiana State University, Baton Rouge

Fenchel T & Blackburn TH (1979) Bacteria and Mineral Cycling. Academic Press, New York

Garrels RM & Thompson ME (1960) Oxidation of pyrite by iron sulfate solutions. Amer. J. Sci. 258: 57–67

Giblin AE (1988) Pyrite formation during early diagenesis. Geomicrobiol. J. 6: 77–97

Giblin AE & Howarth RW (1984) Porewater evidence for a dynamic sedimentary iron cycle in salt marshes. Limnol. Oceanogr. 29: 47–63

Goodwin S & Zeikus JG (1987) Ecophysiological adaptations of anaereobic bacteria to low pH: analysis of anaerobic digestion in acid bog sediments. Appl. Environ. Microbiol. 53: 57–64

Gorham E, Eisenreich SE, Ford J & Santelmann MV (1985) The chemistry of bog waters. In: Stumm W (Ed) Chemical Processes in Lakes (pp 339–363). John Wiley and Sons, New York

Gorham E, Bayley SE & Schindler DW (1984) Ecological effects of acid deposition upon peatlands: a neglected field in 'acid rain' research. Can. J. Fish. Aquat. Sci. 41: 1256–1268

Harriss RC, Gorham E, Sebacher DI, Bartlett KB & Flebbe PA (1985) Methane flux from northern peatlands. Nature 315: 652–653

Heal OW, Jones HE & Whittaker JB (1975) Moor House, U.K. In: Rosswall T & Heal OW (Eds) Structure and Function of Tundra Ecosystems. Ecol. Bull. (Stockholm) 20: 295–320

Holzapfel-Pschorn A, Conrad R & Seiler W (1985) Production, oxidation and emission of methane in rice padies. FEMS Microbiol. Ecol. 31: 343–351

Howarth RW & Teal JM (1980) Energy flow in a salt marsh ecosystem: The role of reduced inorganic sulfur compounds. Amer. Nat. 116: 862–872

Howarth RW & Jorgensen BB (1984) Formation of ^{35}S-labelled elemental sulfur and pyrite in coastal marine sediments (Limfjorden and Ksying Fjord, Denmark) during short-term $^{35}SO_4^{2-}$ incubations. Geochim. Cosmochim. Acta 48: 1807–1818

Ingvorsen K, Zehnder AJB & Jorgensen BB (1984) Kinetics of sulfate and acetate uptake by *Desulfovibrio postgatei*. Appl. Environ. Microbiol. 47: 403–408

Jones JG & Simon BM (1984) Measure of microbial turnover of carbon in anoxic freshwater sediments: cautionary comments. J. Microbiol. Meth. 3: 47–55

Kelly CA & Chynoweth DP (1980) Comparison of *in situ* and *in vitro* rates of methane release in fresh-water sediments. Appl. Environ. Microbiol. 40: 287–293

King GM (1988) Patterns of sulfate reduction and the sulfur cycle in a South Carolina salt marsh. Limnol. Oceanogr. 33: 376–390

Kivinen E & Pakarinen P (1981) Geographical distribution of peat resources and major peatland complex types in the world. Annales Academiae Scientiarum Fennicae, Series A, III. Geologica-Geographica 132

Kristjansson JK, Schonheit P & Thauer RK (1982) Different K_s values for hydrogen of methanogenic bacteria and sulfate reducing bacteria: an explanation for the apparent inhibition of methanogenesis by sulfate. Archiv fur Microbiol. 131: 278–282

Lang GE & McDonald BR (1982). Loss of mass and elemental changes in decomposing sedge and alder leaves. In: McDonald BR (Ed) Proceedings of the Symposium on Wetlands of the Unglaciated Appalachian Region (pp 31–41). West Virginia University, Morgantown

Luther GW & Church TM (1988) Seasonal cycling of sulfur and iron in pore waters of a Delaware salt marsh. Mar. Chem. 23: 295–309

Matthews E & Fung I (1987) Methane emission from natural wetlands: global distribution, area, and environmental characteristics of sources. Global Biogeochem. Cycles 1: 61–87

Maxwell JA & Davis MB (1972) Pollen evidence of Pleistocene and Holocene vegetation on the Allegheny Plateau, Maryland. Quaternary Res. 2: 506–530

Mechalas BJ (1974) Pathways and environmental requirements for biogenic gas production in the ocean. In: Kaplan IR (Ed) Natural Gases in Marine Sediments (pp 12–25). Plenum Press, New York

Miller PC (Ed) (1981) Carbon balance in northern ecosystems and the potential effect of carbon dioxide induced climatic change, CONF-8003118. U.S. Dept. Energy, Off. Health and Environ. Res., Washington, D.C.

Moore JJ, Dowding P & Healy B (1975) Glenamoy, Ireland. In: Rosewall T & Heal OW (Eds) Structure and Function of Tundra Ecosystems. Ecol. Bull. (Stockholm) 20: 321–343

Moore TR & Knowles R (1987) Methane and carbon dioxide evolution from subarctic fens. Can. J. Soil Sci. 67: 77–81

Moses CO, Nordstrom DK, Herman JS & Mills AL (1987) Aqueous pyrite oxidation by dissolved oxygen and by ferric iron. Geochim. Acta 51: 1561–1571

Mountfort DO, Asher RA, Mays EL & Tiedje JM (1980) Carbon and electron flow in mud and sandflat intertidal sediments at Delaware Inlet, Nelson, New Zealand. Appl. Environ. Microbiol. 39: 686–694

Pakarinen P (1975) Bogs as peat-producing systems. Bull. Int. Peat Soc. 7: 51–54

Rudd JWM, Kelly CA & Furutani A (1986) The role of sulfate reduction in long term accumulation of organic and inorganic sulfur in lake sediments. Limnol. Oceanogr. 31: 1281–1291

Sebacher DI, Harriss RC, Bartlett KB, Sebacher SM & Grice SS (1986) Atmospheric methane sources: Alaska tundra bogs, an alpine fen, and a subarctic boreal marsh. Tellus 38B: 1–10

Singer PC & Stumm W (1970) Acidic mine drainage: the rate-determining step. Science 167: 1121–1123

Spratt HG Jr, Morgan MD & Good RE (1987) Sulfate reduction in peat from a New Jersey Pinelands cedar swamp. Appl. Environ. Microbiol. 53: 1406–1411

Svensson BH (1984) Different temperature optima for methane formation when enrichments from acid peat are supplemented with acetate or hydrogen. Appl. Environ. Microbiol. 48: 389–394

Svensson BH & Rosswall T (1984) *In situ* methane production from acid peat in plant communities with different moisture regimes in a subarctic mire. Oikos 43: 341–350.

Trabalka JR (Ed) (1985) Atmospheric carbon dioxide and the global carbon cycle, DOE/ER-0239. U.S. Dept. of Energy, Off. Energy Res., Carbon Dioxide Research Division, Washington, D.C.

Walbridge MR (1982) Vegetation patterning and community distribution in four high-elevation headwater wetlands in West Virginia. M.S. thesis, West Virginia University, Morgantown

Ward DM & Winfrey MR (1985) Interactions between methanogenic and sulfate-reducing bacteria in sediments. Adv. Aquat. Microbiol. 3: 141–179

Watts WA (1979) Late quaternary vegetation of central Appalachia and the New Jersey coastal plain. Ecol. Monog. 49: 427–469

Weedfall RO & Dickerson WJ (1965) The climate of the Canaan Valley and Blackwater Falls State Park, West Virginia. Climatography of the United States No. 20-46-2. West Virginia Agric. Exp. Stn. Current Rep. 43, West Virginia University, Morgantown

Wieder RK (1982) Biogeochemical relationships in *Sphagnum*-dominated wetlands in West Virginia. Ph.D. dissertation, West Virginia University, Morgantown

Wieder RK (1985) Peat and water chemistry at Big Run Bog, a peatland in the Appalachian Mountains of West Virginia. Biogeochem. 1: 277–302

Wieder RK & Lang GE (1984) Influence of wetlands and coal mining on stream water chemistry. Water, Air, Soil Pollut. 23: 381–396

Wieder RK & Lang GE (1986) Fe, Al, Mn, and S chemistry of *Sphagnum* peat in four peatlands with different metal and sulfur input. Water, Air, Soil Pollut. 29: 309–320

Wieder RK & Lang GE (1988) Cycling of inorganic and organic sulfur in peat from Big Run Bog, West Virginia. Biogeochem. 5: 221–242

Wieder RK, Lang GE & Granus VA (1987) An evaluation of wet chemical methods for quantifying sulfur fractions in freshwater wetland peat. Limnol. Oceanogr. 30: 1109–1115

Wieder RK, McCormick AM & Lang GE (1981) Vegetational analysis of Big Run Bog, a nonglaciated *Sphagnum* bog in West Virginia. Castanea 46: 16–29

Wieder RK, Lang GE & Granus VA (1987) Sulphur transformations in *Sphagnum*-derived peat during incubation. Soil Biol. Biochem. 19: 101–106. pa

Wieder RK, Yavitt JB, Lang GE & Bennett CA (1989) Aboveground net primary production at Big Run Bog, West Virginia. Castanea 45: 209–216

Williams RT & Crawford RL (1984) Methane production in Minnesota peatlands. Appl. Environ. Microbiol. 47: 1226–1271

Yavitt JB, Lang GE & Wieder RK (1987) Control of carbon mineralization to CH_4 and CO_2 in anaerobic, *Sphagnum*-derived peat from Big Run Bog, West Virginia. Biogeochem. 4: 141–157

Yavitt JB, Lang GE & Downey DM (1988) Potential methane production and methane oxidation rates in peatland ecosystems of the Appalachian Mountains, United States. Global Biogeochem. Cycles 2: 253–268

Yavitt JB, Downey DM, Lancaster & Lang GE (1990) Methane consumption in decomposing *Sphagnum*-derived peat. Soil Biol. Biochem (in press)

Zhabina NN & Volkov II (1978) A method for determination of various sulfur compounds in sea sediments and rocks. In: Krumbein WE (Ed) Environmental Biogeochemistry and Geomicrobiology (pp 735–745). Ann Arbor Science Publishers, Ann Arbor, Michigan