

Effects of Short-Term Drying and Irrigation on Electron Flow in Mesocosms of a Northern Bog and an Alpine Fen

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Methane emissions and element mobility in wetlands are controlled by soil moisture and redox conditions. We manipulated soil moisture by weekly drying and irrigation of mesocosms of peat from a bog and iron and sulfur rich fen. Water table changed more strongly in the decomposed fen peat (~11 cm) than in the fibric bog peat (~5 cm), where impacts on redox processes were larger due to larger change in air filled porosity. Methanogenesis was partly decoupled from acetogenesis and acetate accumulated up to 5.6 mmol L⁻¹ in the fen peat after sulfate was depleted. Irrigation and drying led to rapid redox-cycles with sulfate, hydrogen sulfide, nitrate, and methane being produced and consumed on the scale of days, contributing substantially to the total electron flow and suggesting short-term resilience of the microbial community to intermittent aeration. Anaerobic CO₂ production was partly balanced by methanogenesis (0–34%), acetate fermentation (0–86%), and sulfate reduction (1–30%) in the bog peat. In the fen peat unknown electron acceptors and aerenchymatic oxygen influx apparently drove respiration. The results suggest that regular rainfall and subsequent drying may lead to local oxidation–reduction cycles that substantially influence electron flow in electron acceptor poor wetlands.

Introduction

Peatlands play a significant role in global methane budgets (1) and the sequestration, mobilization and transformation of major elements (e.g., S), nutrients (e.g., N and P) and trace elements (e.g., mercury, arsenic, lead, copper, and cadmium) (2–5). The variability in elemental cycling is partly caused by spatiotemporal gradients in soil moisture and redox conditions near the peatland surface, which are controlled by soil structure and transport properties, water balance, and vegetation cover (6). Superimposed on such gradients are biogeochemical microstructures, particularly in the

rhizosphere. This pattern encourages accumulation of iron and trace metals near local redox interfaces (7) and a resilience of respiration pathways against smaller changes in soil moisture content (8). Permanently water logged conditions and depletion of nitrate, sulfate, and ferric iron often lead to hydrogenotrophic and acetoclastic methanogenesis predominating terminal electron flow (9) due to slowness of electron acceptor supply from the unsaturated zone and inactivation of mineral surfaces. Also acetate and other short-chained fatty acids were reported as end-products of anaerobic decomposition (10, 11).

Even when pools of electron acceptors are small, methanogenesis often only accounts for a fraction of anaerobic respiration in peat soils (2, 12, 13). This finding has partly been attributed to a renewal of electron acceptors by oxygen release from aerenchymatic roots (14), the production of additional CO₂ by fermentation processes (13), the microbial utilization of oxidizing capacity stored in humic substances (15, 16), and the impact of periodic drought (8). It has become evident that deep and persistent decline in soil moisture and oxygen intrusion associated with summer drought induces oxidation of reduced iron, sulfur, nitrogen, and humic moieties (8, 11, 15). Subsequently the electron acceptors released can drive anaerobic respiration and lowered rates of methanogenesis for time periods of weeks to months (8, 17). More subtle changes in soil moisture due to intermittent rainfall have mostly been neglected as a driver for oxidation–reduction cycles. Two common observations argue for their importance. First, they are frequent and continuously superimpose water table changes of some centimeters on seasonal trends of some tens of centimeters (6). Second, most of anaerobic respiration was concentrated in a thin layer around the water table in studies that estimated respiration in intact soils (8, 18). This metabolically active layer would be affected by smaller but frequent fluctuations in water table and the periodic presence of oxygen.

We tested the hypothesis that intermittent rainfall could potentially induce local and short-term oxidation–reduction cycles that sustain nitrate, iron, and sulfate reduction and alter the electron flow balance in peat soils. To this end, we conducted a mesocosm experiment with peat and vegetation from an ombrotrophic bog, and an iron and sulfur rich mountain fen. We chose this approach because electron flow is difficult to quantify in the field and because this way we could analyze redox dynamics under two differing irrigation regimes. To test the hypothesis we quantified soil moisture levels, soil and pore water chemistry, and gas concentrations in high spatial and temporal resolution. From these data we calculated production and consumption of acetate, inorganic terminal electron acceptors, and CH₄ in the peat, and analyzed the impact of daily and intermittent irrigation and of differing soil physical properties on redox dynamics.

Materials and Methods

Site Description and Sampling and Treatment. Peat cores were collected from two contrasting peatlands. Mer Bleue (MB) is an acidic, ombrotrophic bog in Eastern Ontario that is dominated by mosses and shrubs, with a mean annual air temperature of 5.8 °C (19). The second site, an alpine fen, was located near Niwot Ridge (NR) in the Green Lakes Valley in the Colorado Front Range (Supporting Information (SI) Figure 1s). NR is dominated by grasses and herbs with a mean annual air temperature of –1 °C (20). Cores were collected in plastic containers, 30 cm in diameter and depth, with intact vegetation from hollows in MB and a lawn in NR. Water table was below sampling depth at both sites the day

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of sampling. Niwot Ridge peat had higher bulk density (0.2–0.6 g cm⁻³ NR, 0.02–0.04 g cm⁻³ MB), and lower porosity (0.6–0.8 NR, > 0.9 MB). The cores were transported to the laboratory at the University of Colorado and stored under artificial light at about 20 °C. A schematic of the mesocosm setup is given in SI Figure 2s.

Within two weeks the water table was adjusted to a level of 20 cm below surface by adding irrigate similar in composition to precipitation at the MB site (see SI for composition). For a period of 40 days all cores were irrigated daily to replace water lost via transpiration, resulting in minimal water table fluctuations of ±1 cm (MB) and ±2 cm (NR). From day 40 to 71, the cores were treated differently. In two “control” cores, C-MB and C-NR, the initial irrigation regime was maintained. In the “treatment” cores, F-MB and F-NR, we irrigated only on days 46 and 58 (“irrigation events”) to simulate natural intervals between rain events. The average of water table position was kept at 20 cm by adjusting the amount of irrigate. Daily irrigation added 2.4 (MB) and 1.9 (NR) L m⁻² d⁻¹ of water, 0.06 (MB) and 0.05 (NR) mmol m⁻² d⁻¹ of SO₄²⁻, and 0.10 (MB) and 0.07 (NR) mmol m⁻² d⁻¹ of NO₃⁻. Irrigation events amounted to 0.88 (MB) and 0.62 (NR) mmol m⁻² SO₄²⁻ and 1.36 and 0.96 mmol m⁻² (NR) NO₃⁻. This experimental design allowed for a spatiotemporally highly detailed analysis of redox dynamics in each core, albeit at the expense of a statistical analysis of treatment effects, which we considered to be less important in the context of this study.

Concentration of Gases, Solutes, and Solid Phase Constituents. Water content was measured in 5 depths of F-MB and F-NR using calibrated function domain reflectometry probes (FDR, ECH₂O EC-5, Decagon Devices). Air filled porosity was calculated as the difference between total porosity measured at the end of incubations in subsamples and the measured water content. Soil gas was sampled from horizontally installed silicone tubes modified after Kammann et al. (21) at depths of 3, 7, 11, 15, 17, 19, 21, 25, and 27 cm. Tubes were filled with N₂ after sampling and CO₂ and CH₄ were measured within 30 min on a gas chromatograph with flame ionization detector (FID) and CO₂ methanizer (8610C SRI Instruments, U.S.). At identical depths, Rhizon soil solution samplers (pore size ~0.16 μm, length 10 cm, diameter 3 mm) were installed and sampled 2–4 times a week. Values of pH were measured with a glass electrode; hydrogen sulfide with a voltammetric microelectrode, and dissolved iron concentration with the 2', 2'-bipyridine method (22). Sulfate, nitrate, chloride, and acetate were measured from frozen samples by ion chromatography (IC; Metrohm; Metrosep Anion Dual 3 column, 0.8 mL min⁻¹ with chemical suppression). Solid phase samples were freeze-dried; reactive iron in the solid phase was measured after 24 h of cold extraction with 1 M HCl (23), using the phenantroline method. Fe(III) was calculated as the difference between Fe(tot) and Fe(II). The method of Fossing and Jorgensen (24) was used to measure total reduced inorganic sulfur (TRIS: Σ FeS₂, FeS, S⁰).

Calculations. Pore water concentration of DIC and CH₄ were calculated from measured concentrations in the gas phase, using Henry's law constants corrected for temperature ($K_{CO_2} = 0.0389 \text{ mol L}^{-1} \text{ atm}^{-1}$, $K_{CH_4} = 0.0014 \text{ mol L}^{-1} \text{ atm}^{-1}$ (25); pH was used to calculate DIC speciation (26)).

Turnover rates (R_N) of CO₂, CH₄, iron, sulfate, and acetate were calculated from the change in storage of the corresponding dissolved species ($\Delta S/\Delta t$), diffusion coefficients in peat (D_p) and the concentration gradients at the lower and upper boundaries of the corresponding layer ($\Delta C/\Delta x$), applying eq 1. Diffusion coefficients were corrected for porosity with $D = D_{H_2O} \times \varphi^{-2}$ and for temperature (27); see SI Table 1s for coefficients used.

$$R_N = \frac{\Delta S}{\Delta t} + \left[D_p \frac{\Delta C_{\text{upper}}}{\Delta x} \right]_{\text{upper}} z^{-1} - \left[D_p \frac{\Delta C_{\text{lower}}}{\Delta x} \right]_{\text{lower}} z^{-1} \quad (1)$$

For the calculation of electron flow we assumed that (1) CO₂ is produced from C-species of oxidation state 0 (e.g., acetate, ethanol, glucose; represented by <CH₂O>); (2) nitrate is reduced to N₂ (⁵/₄ mol CO₂ per mol nitrate); (3) Fe(III) is reduced to Fe²⁺ (¹/₄ mol CO₂ per mol iron); (4) sulfate is completely reduced to H₂S, leading to 2 mol CO₂ per mol sulfate reduced; (5) 2 <CH₂O> are converted into CH₄ and CO₂ by fermentation and methanogenesis; (6) 1 mol CO₂ is produced per mol acetate built, the highest CO₂ yield of common fermentation processes (28). This “additional” CO₂ is only unaccounted for by processes 2–5 if the equivalent quantities of more reduced fermentation products, such as butyrate, propionate and H₂, are not utilized by 2–5.

EAs added with the irrigate were subtracted from net production in the unsaturated zone. The boundary between saturated and unsaturated zone was set to the water table for MB and to 18 cm depth for NR according to reducing conditions and abundant presence of Fe²⁺ below. Net reduction rates calculated from solute concentration were considered for nitrate, iron and sulfate. These assumptions are conservative; CO₂ production is rather underestimated and maximum CO₂ yield was assumed for each process.

Concentrations over time were plotted by contour plots; Kriging was used for gridding with anisotropy ratio of 2 as time and depth are not comparable and results were plausible (Surfer 8, Golden Software).

Results

Water Content, Movement, And Air Filled Porosity. The drying-rewetting cycles caused water table changes of about 5 cm in the F-MB peat and 11 cm the F-NR peat. Air filled porosity (afp) generally decreased with depth from >82 to 92% (F-MB) and from 14 to 36% (F-NR) in the unsaturated zone to values of <0.01 (F-MB) and 0 to 9% (F-NR) in the saturated zone (Figure 1). In C-MB afp sharply increased from the water table to about 20% at one centimeter above the water table. In contrast, in C-NR afp increased more gradually, through the 10 cm overlying the water table. Drying and irrigation substantially changed afp by 10–30% at 15–20 cm depth in MB, and at 10 cm in F-NR, whereas above and below effects of drying and irrigation on afp were small in this peat. In 15 cm depth, about 4 cm above average water table level, afp increased from 0 to 5% only to about 10% when water table dropped to 25 cm and more (Figures 1 and 2). In the denser and more fine-porous peat from Niwot Ridge, water table changed more and afp less in comparison to MB peat. Only irrigation after drying lead to a substantial transport of water down into the saturated zone, especially in F-MB, as indicated by increases in chloride concentrations (SI Figure 3s).

Dissolved Carbon Species. Concentrations of DIC and CH₄ rapidly increased after initial flooding to 1000–1500 μmol L⁻¹ in the MB and 10 000–14 000 in the NR peats (Figure 2). The potential for anaerobic respiration was thus much larger in NR and similar among the two cores from each site. In agreement with this finding, CO₂ production below the water table, calculated from eq 1, reached maxima of 10.5 mmol m⁻² d⁻¹ in C-MB, 16.4 mmol m⁻² d⁻¹ in F-MB, 115 mmol m⁻² d⁻¹ in C-NR and 112 mmol m⁻² d⁻¹ in F-NR. Methane concentrations increased initially and with depth from <0.5 μmol L⁻¹ up to 100 μmol L⁻¹ in MB peats and up to 370 μmol L⁻¹ in NR peats. There was some apparent methane consumption in C-MB in the second half of the experiment.

F-MB and F-NR reacted quite differently to drying and irrigation. The small water table change in F-MB coincided with distinct decreases in DIC and CH₄ at 15–20 cm depth

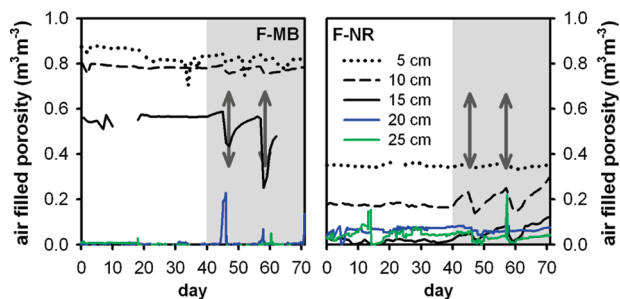


FIGURE 1. Air filled porosity in Mer Bleue (MB, left) and Niwot Ridge (NR, right) mesocosms in different depths over time. Gray fields indicate the period of water table fluctuations. Irrigation events are marked with arrows.

during drying and increases after irrigation. Whereas, the unsaturated peat in F-NR continued to support high concentrations of both gases. Some change in both CO_2 and CH_4 was visible only at around 15 cm depth and changes in CH_4 occurred deeper in the peat during the second and third slightly longer dry periods (Figure 2). Thus, unlike the MB peats, anaerobic respiration in NR peats was at least temporally disconnected from the position of the water table, which is in agreement with the small changes in afp and restricted oxygen transport.

Concentration of DOC reached $>1000 \mu\text{mol C L}^{-1}$ (MB) and $>25\,000 \mu\text{mol C L}^{-1}$ (NR) in the saturated zone, broadly increased with time, and peaked in the surface layer of MB, or where acetate accumulated in NR (SI Figure 4s and Figure 2). Irrigation and drying had no strong impact on DOC concentration. Acetate was not detected in the unsaturated zone of MB and C-NR cores, but it accumulated to high concentrations below the water table. In C-MB, acetate concentration initially reached $430 \mu\text{mol L}^{-1}$ and then diminished in association with faster methanogenesis to less than $5 \mu\text{mol L}^{-1}$. In F-MB, this effect was weaker and acetate concentrations peaked at $>1000 \mu\text{mol L}^{-1}$. In C-NR, acetate accumulated only after sulfate was depleted (Figure 2) and net production of acetate persisted for 10 days longer than in MB, building up to $5680 \mu\text{mol L}^{-1}$. In F-NR, net production of acetate also occurred, reaching $4500 \mu\text{mol L}^{-1}$ at depths of 17–19 cm. Acetate was then depleted during drying periods in F-NR. The sharpest decrease occurred simultaneously with CH_4 depletion during the last dry period.

Dissolved Nitrogen, Sulfur, And Iron. In the saturated zone of all mesocosms nitrate (NO_3) was generally below detection limit. Only in F-MB did nitrate increase distinctly with irrigation, reaching levels $>10 \mu\text{mol L}^{-1}$, which were subsequently depleted within two days (Figure 2). In the unsaturated zone, nitrate concentrations reached up to $40 \mu\text{mol L}^{-1}$ in C-MB and $30 \mu\text{mol L}^{-1}$ in F-MB. In the unsaturated zone of the NR peats nitrate was much higher, with concentrations up to $>1100 \mu\text{mol L}^{-1}$ in C-NR and $830 \mu\text{mol L}^{-1}$ in F-NR. The apparent effect of irrigation events was to slow denitrification or dilute nitrate concentrations. Corresponding nitrification rates reached $1.4 \text{ mmol m}^{-2}\text{d}^{-1}$ (C-NR) and $2.2 \text{ mmol m}^{-2}\text{d}^{-1}$ (F-NR). Nitrate was reduced below 18 cm with up to $1.1 \text{ mmol m}^{-2}\text{d}^{-1}$ neglecting plant uptake. Nitrate turnover thus mostly took place in the unsaturated zone.

Sulfate (SO_4) was initially abundant in all peat cores at $8\text{--}117 \mu\text{mol L}^{-1}$ in MB and $10\text{--}680 \mu\text{mol L}^{-1}$ in NR. In the saturated zone, SO_4 was depleted within two weeks in MB and in a layer at about 20 cm depth in F-NR, which corresponded to acetate accumulation (Figure 2). Sulfate depletion occurred more slowly elsewhere in NR cores. Corresponding sulfate reduction rates in the saturated zone rapidly declined from 0.23 to $0.58 \text{ mmol m}^{-2}\text{d}^{-1}$ to $<\pm 0.06 \text{ mmol m}^{-2}\text{d}^{-1}$ in MB cores. In the C-NR and F-NR cores rates

reached $1.4 \text{ mmol m}^{-2}\text{d}^{-1}$ and $1.1 \text{ mmol m}^{-2}\text{d}^{-1}$, respectively, and declined more slowly than in MB cores. Depletion of sulfate coincided with vigorous methane production, particularly in F-NR (Figure 2).

In the shallow unsaturated zone of all cores, SO_4 accumulated over time to levels of $150\text{--}250 \mu\text{mol L}^{-1}$ (MB) and $750\text{--}900 \mu\text{mol L}^{-1}$ (NR). With the exception of irrigation events in MB, daily watering did not appear to transport sulfate downward to the water table, or sulfate was already reduced in the unsaturated zone. Irrigation of F-MB on days 46 and 58 resulted in SO_4 production, with some addition by irrigation, and subsequent depletion within 1–4 days. Apparent sulfate production in F-MB reached $2.3\text{--}3.0 \text{ mmol m}^{-2}\text{d}^{-1}$ in the saturated zone. During these periods sulfide was immediately and distinctly produced in the saturated zone of F-MB and accumulated to $8\text{--}11 \mu\text{mol L}^{-1}$ (Figure 2), apparently as a direct consequence of sulfate supply. A sulfate reducing potential was thus maintained despite sulfate depletion and drying and activated by rewetting and sulfate supply. In the F-NR core no such dynamics occurred. In NR cores, H_2S was mostly present in the deepest layers at concentrations of $<5\text{--}20 \mu\text{mol L}^{-1}$, and with a tendency toward depletion over time.

Dissolved Fe^{3+} concentration was generally negligible and Fe^{2+} much lower in MB than in NR peat, reaching $<50 \mu\text{mol L}^{-1}$ in MB and $30\text{--}600 \mu\text{mol L}^{-1}$ in NR cores (SI Figure 4s). Concentration changed little over time and peaked near 30 cm (MB and F-NR) and 20 cm (NR), extending into the unsaturated zone in F-NR. Iron turnover alternated between production and removal at $\pm 1.5 \text{ mmol e-equiv. m}^{-2}\text{d}^{-1}$ in NR, was negligible in the iron poor MB peat, and occurred concurrently with sulfate reduction and later also with methanogenesis in the NR peat. Similar to the other redox-sensitive solutes, water table change in F-NR had little impact on ferrous iron concentration (SI Figure 4s).

Electron Flow of Inorganic Electron Acceptors and Impact of Drying and Irrigation. The magnitude and dynamics of the electron flow in the saturated zone are illustrated in Figure 3. In both peats, reduction of electron acceptors was generally smaller than $10 \text{ mmol e-equiv. m}^{-2}\text{d}^{-1}$ and sulfate reduction was most important with smaller and variable contributions of iron and nitrate reduction. In MB peat inorganic electron acceptors were rapidly depleted within two weeks (Figure 3). The NR peat sustained faster electron acceptor reduction longer; but reduction rates also generally declined under daily watering to $<5 \text{ mmol e-equiv. m}^{-2}\text{d}^{-1}$. The exception to this trend was the apparent nitrification-denitrification dynamics in C-NR in the last 20 days of the experiment. The similar magnitude of rates among the two mesocosms from each site before drying and rewetting suggests that subsequent differences in electron flow were caused by treatment.

Short-term drying and irrigation induced a renewal of electron flow in MB peat. Sulfur oxidation and to a minor extent seepage “produced” $20\text{--}30 \text{ mmol e-equiv. m}^{-2}\text{d}^{-1}$ of sulfate and minor amounts of nitrate, and subsequently net nitrate and sulfate reduction rebounded to $8\text{--}11 \text{ mmol e-equiv. m}^{-2}\text{d}^{-1}$. In contrast, in C-MB no such process dynamics occurred. In the F-NR core, for which the soil physical characteristics limit seepage and aeration, the redox dynamics were much smaller despite the strong water table draw-down. Nonetheless, the decreasing trend of electron flow was interrupted and ferric iron, nitrate and sulfate were produced during drying and consumed thereafter, restoring the electron flow to initial levels.

Production of CO_2 was not balanced against net electron acceptor consumption, acetogenesis and methanogenesis (Figure 4). In MB peat the proportion decreased with time to less than 35% and in the NR peat, only up to 16% were matched. Thus, consumption of unknown electron acceptors

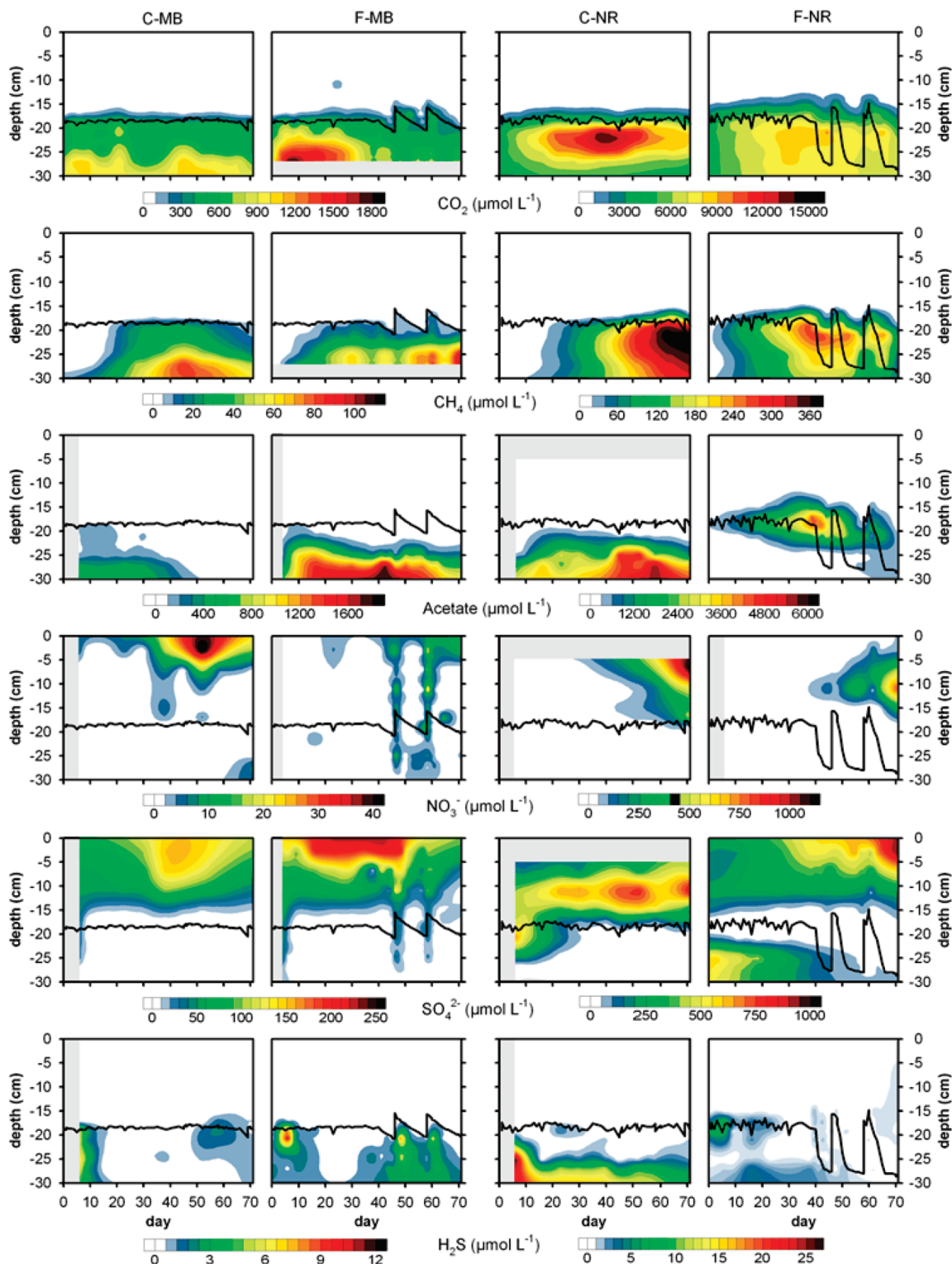


FIGURE 2. Concentration of solutes in soil solution from Mer Bleue (MB) bog and Niwot Ridge (NR) fen peat (C-: control; F-: induced fluctuations). The black line represents average water table level. Light gray areas indicate times or depths for which no data was available.

strongly dominated respiration especially in NR cores. The CH_4 : CO_2 ratio increased over time in all but the C-MB core. Initially acetogenesis potentially generated more CO_2 than other processes in all peats and also later potentially remained important in the NR cores.

Inorganic Iron and Sulfur Contents. The MB peat was much lower in TRIS and iron contents compared to NR peat (SI Figure 5s, Table 2s). In MB peat, TRIS content reached a maximum of $1.4 \mu\text{mol g}^{-1}$ and in NR $14.5\text{--}22.5 \mu\text{mol g}^{-1}$.

S^0 content was everywhere below 0.3 nmol g^{-1} except for an accumulation of $1.1\text{--}6.2 \text{ nmol g}^{-1}$ at 21 cm depth in NR. Reactive ferrous and ferric iron content was also much lower in MB than in NR cores; Fe(II) content increased from $2.0 \mu\text{mol g}^{-1}$ to $35\text{--}46 \mu\text{mol g}^{-1}$ and Fe(III) depleted with depth at levels of $1\text{--}7 \mu\text{mol g}^{-1}$. In the NR cores, Fe(II) content increased from $40\text{--}50 \mu\text{mol g}^{-1}$ to $115 \mu\text{mol g}^{-1}$ in F-NR up to $>250 \mu\text{mol g}^{-1}$ in C-NR near the water table. Fe(III) content increased with depth up to $>800 \mu\text{mol g}^{-1}$ in C-NR. TRIS and

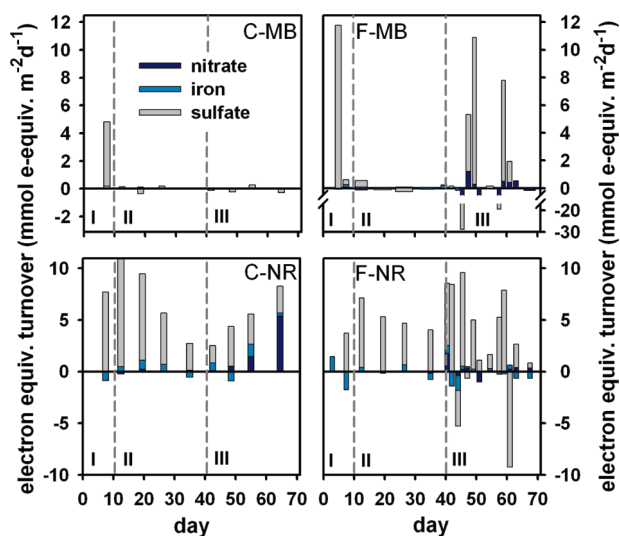


FIGURE 3. Turnover rates of electron acceptors in soil solution of peat cores below 20 cm (MB, Mer Bleue bog) and below 18 cm (NR, Niwot Ridge fen). Positive values represent reduction, negative values production of electron acceptors.

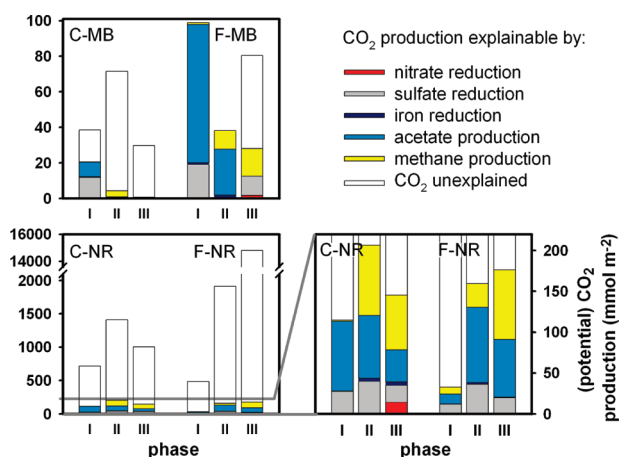


FIGURE 4. Cumulative CO_2 production attributed to different processes in peat cores of Mer Bleue bog (MB) and Niwot Ridge fen (NR). Phase I: days 1–10, phase II: days 11–40, both with constant water table level. Phase III: days 41–71 with constant water table in controls (C) and water table fluctuations induced in F-cores. Production relates to the layers below the water table in MB and below 18 cm in NR cores. Note different scales of the y-axes.

reactive iron content in additionally incubated small peat cores, treated analogously, did not respond to water table drawdown (see SI Figure 6s).

Discussion

The electron flow balance showed that CO_2 production was not fully accounted for by specific processes in both peats (Figure 4), which has emerged as a general feature in such environments. Up to 76% could be explained mostly by methane production in an intermediate fen studied by Keller and Bridgman (9), and in bog peat at least 48% remained unexplained. More than 90% remained unexplained in bog peat studied by Vile et al. (13); similar results have been obtained for Mer Bleue peats using different methodologies and for a northern temperate fen (8). As suggested by Vile and colleagues and documented for an ombrotrophic bog by Duddleston et al. (10), acetogenesis potentially contributed to anaerobic CO_2 production (Figure 4) assuming that some reduced fermentation products, such as butyrate, propionate,

ethanol, and H_2 accumulated with acetate. The temporary accumulation of acetate corroborates earlier work on anaerobic electron flow in peats under transient conditions (11, 29). As in the later study accumulation of acetate was apparently linked to depletion of sulfate, particularly in F-MB, and acetoclastic methanogenesis being comparatively slow. The persistent finding of excess anaerobic CO_2 production in peat soils could thus be potentially resolved by accumulation of fermentation products, such as ethanol, butyrate and propionate, which we did not analyze, reduction of additional electron acceptors, such as humic substances (15), and by root-conduit supported supply of oxygen into the saturated zone creating local redox interfaces (30). A hint for an accumulation of other fermentation products than acetate is found in the preceding and concurrent accumulation of DOC compared to acetate in the F-NR mesocosm (SI Figure 4s, and Figure 2). Root conduit transport of oxygen, however, is the most likely explanation for the large gap in the electron flow balance of the NR mesocosms, which had a high density of sedges capable of such transport, and for the difference in the budget compared to MB, which was devoid of grasses.

More importantly, the study demonstrates that frequently occurring small fluctuations in soil moisture and water table, i.e., shifts in local redox interfaces, can have a substantial impact on the anaerobic electron flow in peat soils. The results thus expand earlier work documenting such effects for seasonal change in soil moisture and water table (8, 17, 31, 32). The rapid decline from a net sulfate reduction of 5–10 $\text{mmol e-equiv. m}^{-2}\text{d}^{-1}$ after initial flooding in the MB mesocosms to values near 0 was reversed by sulfate production in the pore water of 20–30 $\text{mmol e-equiv. m}^{-2}\text{d}^{-1}$ in F-MB during drying and the subsequent net reduction of sulfate within days (Figure 3). The addition of sulfate with the irrigate during daily irrigation amounted to about 0.4 $\text{mmol e-equiv. m}^{-2}\text{d}^{-1}$ and the large irrigation events supplied 7 $\text{mmol e-equiv. m}^{-2}\text{d}^{-1}$, suggesting that most of the sulfate stemmed from oxidation of reduced inorganic or organic sulfur.

Periodic drying and rainfall could thus be important for electron flow in peatlands. The short-term rates of oxidation and reduction of sulfur found here are on a similar order of magnitude as the reported *in situ* anaerobic respiration, methanogenesis, and sulfate reduction. Keeping lower *in situ* soil temperatures in mind, rates of below-water table respiration and methanogenesis were found to be concentrated near the water table and estimated at 10–20 $\text{mmol e-equiv. m}^{-2}\text{d}^{-1}$ (CO_2) and 1–4 $\text{mmol e-equiv. m}^{-2}\text{d}^{-1}$ (CH_4) in the Mer Bleue peatland (refs 15, 18 and references therein). Potential *in situ* sulfate reduction rates using a hydrologic push–pull methodology were 1.2–7.5 $\text{mmol e-equiv. m}^{-2}\text{d}^{-1}$ (33) at this site. Studies based on ^{35}S -radiotracer application at other sulfate poor sites reported similar rates (34). Compared to sulfate reducing bacteria methanogens are little competitive for acetate and hydrogen for thermodynamic and kinetic reasons (28) and repeated sulfate availability may thus reduce rates of methane production and emission, although we cannot provide direct evidence for such a consequence in this study.

It can also be speculated that the short-term and local redox cycles identified may partly sustain the large impact of sulfate deposition on cumulative methane emissions reported from ecosystem manipulation experiments and studies investigating gradients of long-term atmospheric sulfate deposition on bogs (34, 35). These authors found that each sulfate molecule deposited needed to be reduced several times to cause the identified effect on methane emissions, which is in agreement with high rates of gross sulfate reduction reported from radiotracer experiments (34). So far, explanations have focused on anaerobic recycling of sulfur, e.g., by humic substances (15), but short-term redox

cycles along shifting redox interfaces may contribute to the effectiveness of sulfate deposition.

The comparison between the bog (MB) and fen (NR) mesocosms illustrates that the impact of drying and rewetting strongly depends on soil physical characteristics that control the transport of gases. In the bog soil the impact on redox processes (Figures 2) and electron flow of terminal electron acceptors (Figure 3) was much greater than in the fen soil, despite the greater response of water table in the F-NR core, and 2 orders of magnitude larger contents of reduced inorganic sulfur, reactive ferrous iron, and ferric iron (SI Table 2s). The underlying reason for the difference in electron flow dynamics is found in the insensitivity of air filled porosity to drying and irrigation in the fen peat (Figure 1), which obviously remained too low to allow for effective oxygen transport into larger depths and the degassing of dissolved gases (Figure 2). Even under such "adverse" conditions some intensification of the electron flow dynamics appeared to occur with irrigation and drying in the NR peat (Figure 3). The disconnection between water table and redox processes in the fen peat adds evidence to more recent doubts (36) about the water table being a good proxy for the interface between aerobic and anaerobic regimes in minerotrophic wetland systems with dense soils.

Acknowledgments

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Supporting Information Available

Additional material including five figures and two tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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