Soil Iron Content as a Predictor of Carbon and Nutrient Mobilization in Rewetted Fens

Willem-Jan Emsens¹ *, Camiel J. S. Aggenbach¹,², Ken Schoutens¹, Alfons J. P. Smolders³,⁴, Dominik Zak⁵,⁶, Rudy van Diggelen¹

¹ Ecosystem Management Research Group, Department of Biology, University of Antwerp, Universiteitsplein 1C, 2610 Wilrijk, Belgium, ² KWR Watercycle Research Institute, P.O. Box 1072, 3430 BB Nieuwegein, The Netherlands, ³ Department of Aquatic Ecology and Environmental Biology, Institute for Wetland and Water Research, Radboud University Nijmegen, Heyendaalseweg 135 1, NL-6525 ED Nijmegen, The Netherlands, ⁴ B-WARE Research Centre, Toernooiveld 1, 6525 ED Nijmegen, the Netherlands, ⁵ Chemical Analytics and Biogeochemistry, Leibniz-Institute of Freshwater Ecology and Inland Fisheries, Müggelseedamm 301, D-12587 Berlin, Germany, ⁶ Department of Bioscience, Aarhus University, Vejlsøvej, 8600 Silkeborg, Denmark

* willem-jan.emsens@uantwerpen.be

Abstract

Rewetted, previously drained fens often remain sources rather than sinks for carbon and nutrients. To date, it is poorly understood which soil characteristics stimulate carbon and nutrient mobilization upon rewetting. Here, we assess the hypothesis that a large pool of iron in the soil negatively affects fen restoration success, as flooding-induced iron reduction (Fe³⁺ to Fe²⁺) causes a disproportionate breakdown of organic matter that is coupled with a release of inorganic compounds. We collected intact soil cores in two iron-poor and two iron-rich drained fens, half of which were subjected to a rewetting treatment while the other half was kept drained. Prolonged drainage led to the mobilization of nitrate (NO₃⁻, > 1 mmol L⁻¹) in all cores, regardless of soil iron content. In the rewetted iron-rich cores, a sharp increase in pore water iron (Fe) concentrations correlated with concentrations of inorganic carbon (TIC, > 13 mmol L⁻¹) and dissolved organic carbon (DOC, > 16 mmol L⁻¹). Additionally, ammonium (NH₄⁺) accumulated up to phytotoxic concentrations of 1 mmol L⁻¹ in the pore water of the rewetted iron-rich cores. Disproportionate mobilization of Fe, TIC, DOC and NH₄⁺ was absent in the rewetted iron-poor cores, indicating a strong interaction between waterlogging and iron-mediated breakdown of organic matter. Concentrations of dissolved phosphorus (P) rose slightly in all cores upon rewetting, but remained low throughout the experiment. Our results suggest that large pools of iron in the top soil of drained fens can hamper the restoration of the fen’s sink-service for ammonium and carbon upon rewetting. We argue that negative effects of iron should be most apparent in fens with fluctuating water levels, as temporary oxygenation allows frequent regeneration of Fe³⁺. We conclude that rewetting of iron-poor fens may be more feasible for restoration.
Introduction

Widespread drainage is compromising the ability of the world’s groundwater-fed peatlands (“fens” hereinafter) to serve as sinks for nutrients and carbon [1,2]. In response to desiccation of organic soils, organic-bound nutrients are mineralized to inorganic mobile compounds [3,4], thereby contributing to pore and surface water eutrophication and loss of typical biodiversity. At the same time, rates of carbon dioxide emission increase upon drainage, which significantly impacts the world’s greenhouse gas budget [2]. Finally, rising concentrations of dissolved organic carbon (DOC) in surface waters adjacent to degraded peatlands have been related to the destabilization of carbon pools within the peat [5,6]. These high DOC loads have become subject to growing international concern as they cause ample environmental problems [7,8].

In response to the aforementioned trends, many countries are installing policies that aim to restore a significant portion of drained fens together with the vital ecosystem services that they provide. Fen restoration primarily focuses on the re-establishment of high groundwater levels, e.g. through ditch blockage. However, reports of excess mobilization of dissolved organic and inorganic carbon, ammonium (NH$_4^+$), and phosphate (PO$_4^{3-}$) into pore and surface water upon rewetting indicate that successful fen restoration is not always guaranteed at least in short-term [3,9]. The apparent difficulty in predicting restoration success by rewetting can be related to the complex and often diverse chemistry of fens: fens, much more than rainwater-fed bogs, vary greatly in cation, nutrient, electron acceptor and organic matter availability as well as pH and alkalinity. To date, all mechanisms and chemical characteristics that affect compound mobilization in drained peat soils are not well understood, which often results in an arbitrary or even random selection of fens that are listed as “suitable” for rewetting.

In this respect, past research has emphasized the importance of high concentrations of iron (Fe) in both soil and flooding water mainly because iron prevents mass mobilization of phosphate and reduced sulfur species into the pore water by providing sorption surfaces for both elements [10,11]. Based on those insights, the rewetting of iron-rich fens could be considered a relatively safe choice. However, potential negative effects of large iron pools in organic soils are usually neglected. In unpolluted fens and wetlands, iron (Fe$^{2+}$-Fe$^{3+}$) forms a dominant reduction-oxidation couple [12,13], and ferric iron often exceeds concentrations of other potential electron acceptors such as SO$_4^{2-}$ or NO$_3^-$. In fact, the “iron-redox wheel”, in which iron alternately shifts between the ferric (Fe$^{3+}$) and ferrous (Fe$^{2+}$) state in fluctuating redox environments, is potentially of major importance for carbon and nutrient cycling as labile organic matter is an electron donor in the microbe-mediated Fe-reduction reaction [13,14,15]. In a peatland that is influenced by Fe-inflow for example, an estimated 72% of anaerobic carbon mineralization is directly coupled with Fe$^{3+}$ reduction, in contrast to only an estimated 7% in an upland bog that lacks Fe inflow [16]. In order for such iron-redox wheel to persist, fluctuating water levels are a prerequisite. In this respect, it is key to realize that human-induced rewetting rarely results in stable water levels year round: wet winters often result in temporarily flooded conditions while occasional long dry summers cause topsoil desiccation, even in “restored” fens [17,18]. This is partly related to irreversible shifts in the local hydrological system [18], as well as to physical alterations in the peat soil like the loss of the oscillation ability due to past drainage [19,20]. These physio-chemical alterations imply that rewetted fens may be relatively vulnerable to iron-induced decomposition.

Besides the direct relationship between iron reduction and decomposition, iron can additionally stimulate organic matter mineralization through indirect pathways. For example, iron promotes the production and activity of the extracellular enzyme phenol oxidase, which catalyzes the oxidation of decomposition-inhibiting phenolics [21,22]. Also, excess production of
alkalinity coupled with Fe reduction raises soil buffering [23,24], thereby indirectly increasing rates of decomposition [25].

As past fen drainage has been shown to concentrate iron in the degraded top soil [23], the potential Fe-related soil reactivity in terms of carbon and nutrient mobilization in degraded fens could be substantially enhanced. The potential magnitude of such effect in natural peat soils has, however, never been documented. In this paper, we investigated if soil iron content is indeed a significant predictor of nutrient and carbon mobilization in drained fens upon rewetting. To test this hypothesis, we comparatively investigated the effects of experimental rewetting on four drained fens that vary in soil iron content.

Materials and Methods

Study areas and soil core collection

We selected four fens in the Pleistocene part of the Netherlands and Belgium that strongly differ in soil iron content: two fens (BM and LH) had relatively low-iron contents in soil (258 and 256 mmol kg\(^{-1}\) soil respectively), while two fens (ES and ZB) were considered iron-rich (537 and 1960 mmol kg\(^{-1}\) respectively, Table 1). All study sites were, historically, characterized by continuous upwelling of base-rich groundwater. Due to differences in geochemistry of the aquifers feeding the fens, the incoming groundwater of locations ES and ZB is relatively iron-enriched whereas the groundwater of BM and LH is relatively iron-poor, which explains the observed differences in total soil iron pools. Over the past century, land use intensification coupled with drainage has led to lowered groundwater levels and thus degradation of the top peaty soil layers at all sites (Von Post Humification Index upper 50 cm > 8). Current vegetation is characterized by a high presence of fen meadow species such as *Caltha palustris*, *Carex panicea*, *Cirsium palustre*, *Galium palustre*, *Juncus spp.*, *Lotus uliginosus*, and *Holcus lanatus* in the herb layer and *Calliergon(ella) spp.*, *Brachythecium spp.* and *Climacium dendroides* in the moss layer. To date, all sites are owned and protected by nature conservation agencies. We were granted permission to collect the peat cores from the following authorities: Staatsbosbeheer (sites BM and ES), Landschap Overijssel (site LH) and Natuurpunt (site ZB).

At the time of soil core collection (early February 2014), groundwater levels averaged 10–20 cm below the fen surface. Within each fen, we chose a central area with a peaty soil layer of > 50 cm thickness. We then collected ten intact replicate soil cores of 45 cm x 12.5 cm

| Parameter | Unit | Bennekomse Meent (BM) | Leijer Hooilanden (LH) | Elperstroom (ES) | Zwarte Beek (ZB) |
|-----------|------|-----------------------|------------------------|-----------------|------------------|
| Coordinates | | 52° 0’25.98"N; 5°35’48.80”E | 52°38’32.71"N; 6°16’37.50”E | 52°52’26.01"N; 6°39’32.96”E | 51° 5’23.91”N; 5°19’10.69”E |
| Bulk density | kg L\(^{-1}\) | 0.13 ± 0.02 | 0.07 ± 0.01 | 0.15 ± 0.05 | 0.27 ± 0.04 |
| OM-content | % | 41.7 ± 7.9 | 81.8 ± 1.4 | 44.6 ± 13.3 | 22.8 ± 3.5 |
| NH\(_4\)Cl-P | mmol kg\(^{-1}\) | 0.018 ± 0.003 | 0.054 ± 0.012 | 0.031 ± 0.021 | 0.019 ± 0.007 |
| BD-P | mmol kg\(^{-1}\) | 1.45 ± 0.55 | 2.72 ± 0.97 | 1.50 ± 0.43 | 1.55 ± 0.7 |
| HCl-P | mmol kg\(^{-1}\) | 2.81 ± 0.54 | 11.16 ± 3.05 | 9.23 ± 3.54 | 50.64 ± 17.85 |
| Total P | mmol kg\(^{-1}\) | 20.15 ± 3.6 | 44.85 ± 7.05 | 29.87 ± 12.81 | 144.8 ± 14.59 |
| HCl-Al | mmol kg\(^{-1}\) | 113.9 ± 23.7 | 128.7 ± 14.5 | 157.4 ± 37.0 | 108.3 ± 18.6 |
| HCl-Ca | mmol kg\(^{-1}\) | 126 ± 34.8 | 189.9 ± 37.3 | 99.1 ± 34.1 | 54.8 ± 11.6 |
| BD-Fe | mmol kg\(^{-1}\) | 31.5 ± 11.8 | 55.5 ± 18.1 | 185.6 ± 84.5 | 294.7 ± 42.2 |
| HCl-Fe | mmol kg\(^{-1}\) | 117.8 ± 29.1 | 174.4 ± 26.8 | 321.7 ± 112.7 | 778.1 ± 159.5 |
| Total Fe | mmol kg\(^{-1}\) | 258 ± 62 | 256 ± 36 | 537 ± 203 | 1960 ± 331 |

doi:10.1371/journal.pone.0153166.t001
Iron as a Predictor of Carbon and Nutrient Mobilization

(diameter x depth) in a 2x4m grid at each location. To extract a core, we manually forced hard-
PVC tubes (diameter = 12.5 cm) of 50 cm length in the peat soil after carefully removing above-
ground vegetation. As the PVC tubes were sharpened at the bottom, it was fairly easy to cut
through the peat without causing compaction. Next, we dug a narrow hole alongside the PVC
tube which allowed us to close the tube’s bottom with a PVC-lid before actually removing the
tube. This allowed us to collect a relatively undisturbed soil core without losing pore water,
which was crucial to minimize peat oxidation during transport. Directly after removal, the top
of the PVC tube was sealed with cling film.

Experimental design and sampling

The 40 cores were placed in an unheated greenhouse where they were sheltered from direct
sunlight. Average temperatures in the greenhouse ranged between 6.5 and 22.9°C
(mean = 13.9 ± 3.8°C) over the course of the experiment, which ran from February through
June 2014. We horizontally inserted 10 cm permanent Rhizon pore water samplers (pore size
0.2 μm, Rhizosphere Research Products, the Netherlands) at three different depths in each
core: 5, 15 and 25 cm below the peat surface. Each Rhizon sampler was connected to a vac-
uum-syringe to allow the anaerobic extraction of pore water. Next, half of the soil cores
received a rewetting treatment (water level at peat surface level), while the other half was
drained (water level = 27 cm below the peat surface). As the water levels at the time of soil core
collection averaged between 10–20 cm below the surface, the experimental water level manipu-
lation not only triggered a rewetting effect but also a (more pronounced) drainage effect. Water
level manipulation was accomplished by placing each PVC tube (perforated at the bottom) in a
separate larger tube that was prefilled with the required amount of stagnant N2-deoxygenized
artificial groundwater containing limited amounts of base minerals but no nutrients (i.e. N and
P) or pollutants (i.e. S) (Fig 1). This in order to mimic rewetting by unpolluted, minerotrophic
groundwater. Characteristics of the artificial groundwater were (means of five samples ± SE,
in μmol L−1): pH = 7.0 ± 0.0, HCO3− = 988 ± 73, Ca2+ = 608 ± 58, K+ = 18 ± 1, Na+ = 199 ± 41,
Mg2+ = 5 ± 1, Cl− = 145 ± 26. In order to allow gas exchange between peat soil and the sur-
rounding atmosphere while preventing plant growth, we made three 3 mm holes in each top
lid. This is sufficient for gas exchange, but hampers plant growth due to light limitation. Water
levels were manually kept stable throughout the duration of the experiment. The design was
full-factorial so that each combination of location (n = 4) x water level treatment (n = 2) was
replicated five times. After initiation of the experiment, we first allowed the cores to stabilize
for four days. On day four, we collected the first set of 120 pore water samples which we con-
sidered the starting point reference (t = 0 days). Next, pore water samples were collected
biweekly and analyzed for pH and electrical conductivity (EC) using portable equipment
(except t = 8 weeks). Pore water samples collected at t = 0, t = 30 and t = 127 were stored air-
tight at 4°C and transported to the lab for further chemical analysis.

Chemical analyses

Total inorganic carbon (TIC) was analyzed in the lab on an Infrared Gas Analyzer (ABB
Advance Optima). Concentrations of NH4+ and NO3− were determined colorimetrically on a
continuous-flow Auto Analyzer system. Pore water subsamples were acidified by adding 0.7 ml
65% suprapure HNO3 per 100 ml sample and were analyzed with inductively coupled plasmas-
pectrometry (ICP, IRIS Intrepid II) for the following elements: Ca2+, Mg2+, K+, Na+, Fe2+, Mn2+,
P2O5, S, and Al. Dissolved organic carbon (DOC) was analyzed using a Shimadzu TOC-VCPH
Total Organic Carbon Analyser (Shimadzu Scientific Instruments, USA). Concentrations of
CH4 and H2S were collected in the headspace of a 12 ml anaerobic glass vacuum tube that was
prefilled with 0.5 ml 4% HCl, to which a subsample of 5 ml pore water was added. CH$_4$ concentrations were measured with a Hewlett-Packard 5890 gas chromatograph (Avondale, California) equipped with a flame-ionization detector and a Porapak Q column (80/100 mesh) operated at 120°C with N$_2$ as carrier gas. H$_2$S concentrations were determined using a Packard 438A gas chromatograph equipped with a Carbopack B HT100 column (40/60 mesh) and a flame photometric detector.

Mineral saturation indices were calculated based on pore water measurements of pH and the following total concentrations of dissolved species: Ca, Mg, Fe, Mn, Na, K, Cl, Al, S, P, C, and N using PhreeqC [26].

Chemical characterization of the soils (Table 1) was done by sequential extractions on fresh soil to determine ammonium-chloride extractable P (NH$_4$Cl-P) (= desorbable P), bicarbonate-dithionite extractable Fe and P (BD-Fe and BD-P (= reductant-soluble Fe and P)) and hydrochloric acid extractable Fe, Al, Ca, and P (HCl-Fe, HCl-Al, HCl-Ca, and HCl-P (= acid-soluble Fe, Al, Ca and P)) [27]. Fe, Al, and Ca concentrations of the chemical extracts (BD and/or HCl) were determined using inductively coupled plasma optical emission spectrometry (ICP-OES)I (Cap 6000 series, Thermo Fischer), and P concentrations of the chemical extracts were determined using the molybdenum blue method after acid digestion [27]. Precision and accuracy were better than 5% for Fe, Al, and Ca analysis and the detection limit was 2, 3 or 4 μM respectively. Total soil Fe and P was determined on ICP-OES after digesting 200 mg of oven-dried and ground soil with 4 mL HNO$_3$ (65%) and 1 mL H$_2$O$_2$ (30%) using a microwave labstation (Milestone srl). Organic matter content (% dry weight) was determined by loss on ignition (4h at 550°C).
Data analyses

We used Linear Mixed-Effect Modeling with REML estimation in SPSS (IBM SPSS Statistics 20) to assess the effects of soil iron content and water level on pore water concentrations of dissolved Fe, carbon (TIC, DOC and CH₄) and macronutrients (NH₄⁺, NO₃⁻, total dissolved P). To this purpose, we made two groups based on soil iron content (treatment = “Iron content”): the two locations with mean soil iron content > 500 mmol kg⁻¹ were classified as iron-rich sites (sites ES and ZB), and the remaining two locations with soil iron content < 500 mmol kg⁻¹ as iron-poor sites (sites BM and LH). For each of these two groups, one half of the replicate cores was fully rewetted while the other half was drained (treatment = “Water level”). This setup resulted in a total of four different groups for data analysis. To correct for random between-site variation as well as for differences in means between sites, we added “Site ID (ES, ZB, BM or LH)” as a random factor nested within the treatment “iron content”. Although we collected data at different points in time, we did not add “Time” as an additional factor in the model for two reasons. First, visual data exploration reveals that the effect of “Time” is merely strengthening (i.e. differences between treatments become more pronounced as time progresses). Second, adding “Time” as a factor to the model would make the model unnecessarily complicated, as this would imply 3-way interactions between “Time”, “Iron content” and “Water level”. Hence, we simplify the Mixed Model by comparing treatment differences both at the start as well as at the end of the experiment (n = 0 and n = 127 days respectively) with tests for 2-way interactions between the fixed factors “Iron content” and “Water level”. We expect that the magnitude of the effect of rewetting (“Water level”) on carbon and nutrient mobilization depends on soil iron content, with higher carbon and nutrient mobilization in the rewetted iron-rich soil cores. For statistical analyses, values of the three pore water subsamples per soil core were averaged to attain column averages as well as to avoid pseudo-replication (S1 Table).

To further verify whether iron reduction is directly coupled with the mobilization of TIC, DOC and NH₄⁺ after rewetting, we used Spearman’s rank correlation to compare the change in concentrations of total dissolved iron (ΔFe) from t = 0 days to t = 127 days with ΔTIC, ΔDOC and ΔNH₄⁺. Correlations were conducted for the 20 rewetted cores and the 20 partly drained cores separately. Significance was accepted at the p < 0.05 level.

Results

pH and conductivity

Pore water pH in the peat columns remained relatively stable between 6.0 and 6.7 for all groups (Fig 2A). Over time, the rewetted soil cores gradually attained higher pH values than the drained soil cores. Highest final pH values were reached in the rewetted iron-rich cores, despite the fact that initial pH values at the start of the experiment were lowest in this group. Rewetting had a significant positive effect on pH values, but no interaction between water level and soil iron content was found (Table 2). Electrical conductivity (EC) in the partly drained soil cores as well as in the rewetted iron-poor soil cores remained between 200 and 600 μS cm⁻¹ (Fig 2B). EC in the rewetted iron-rich soil cores however more than doubled over time, with the strongest increase during the first 70 days after rewetting. After 120 days, EC leveled around values of 1000 μS cm⁻¹. We found a significant interaction effect between water level and iron content with significantly higher EC values in rewetted, iron-rich soil cores (Table 2).

Carbon and nutrient mobilization

At the start of the experiment (t = 0 days) the factors “water level” and “iron content” had no significant effect on pore water concentrations of dissolved Fe, DOC, NH₄⁺ and P (Table 2, Fig
3), indicating that hydrochemical conditions in all four groups were relatively similar. In the iron-poor soil cores, initial concentrations of CH$_4$ were higher, while there was an interaction effect of water level with iron content for concentrations of NO$_3^-$ (Table 2, Fig 4), with slightly higher NO$_3^-$ concentrations in the drained Fe-rich cores (in the order of a few μmolars). Initial concentrations of TIC were slightly higher in all rewetted cores.

At the end of the experiment (t = 127 days), the drained soil cores had responded to desiccation in a similar manner regardless of soil iron content (Fig 3). Prolonged drainage (> 30 days) led to mass mobilization of NO$_3^-$ (> 1 mmol L$^{-1}$) at all locations (Fig 4), and this effect was independent of soil iron content (Table 2).

Experimental rewetting led to a significant increase in pore water concentrations of Fe, TIC, DOC, NH$_4^+$, P and CH$_4$ (Table 2, Fig 3). However, hydrochemical conditions in the rewetted iron-rich soil cores differed markedly from the conditions in the rewetted iron-poor soil cores (Table 2, Fig 3). For the variables Fe, TIC, DOC, and NH$_4^+$, we found strong positive interactions between water regime and soil iron content: concentrations of Fe, TIC, DOC and NH$_4^+$ increased in response to rewetting, but the magnitude of this effect was much stronger in the iron-rich soil cores. Concentrations of both Fe and NH$_4^+$ reached more than 1 mmol L$^{-1}$ in the rewetted iron-rich soil cores, while the accumulation of TIC and DOC had almost doubled compared to the rewetted iron-poor soil cores, reaching final mean concentrations of >13 mmol L$^{-1}$.

![Fig 2. Changes in pore water pH and electrical conductivity (EC) in 40 soil cores. The cores differ in experimental water level treatment (rewetted or desiccated) and initial soil iron content (high or low). Soil cores were classified into 4 groups: rewetted iron-poor fens (n = 10 cores from 2 sites), desiccated iron-poor fens (n = 10 cores from 2 sites), rewetted iron-rich fens (n = 10 cores from 2 sites), and desiccated iron-rich fens (n = 10 cores from 2 sites). Dots represent group means ± SE.](https://doi.org/10.1371/journal.pone.0153166.g002)
and >15 mmol L\(^{-1}\) respectively. Final CH\(_4\) concentrations did not differ between iron-rich and iron-poor soil cores and had increased after rewetting, but we observed a delay in CH\(_4\) accumulation in the rewetted iron-rich soil cores (Fig 3E). Pore water concentrations of total dissolved P increased slightly after rewetting, but in the iron-rich soil cores an initial increase to concentrations of 4.0 \(\mu\)mol L\(^{-1}\) was followed by a gradual decrease to concentrations of 2 \(\mu\)mol L\(^{-1}\) (Fig 3F).

Initial mean (t = 0 days) concentrations of total dissolved sulfur (St) were low in all treatments (<100 \(\mu\)mol L\(^{-1}\), S1 Fig), while concentrations of sulfide remained below detection limit (<0.1 \(\mu\)mol L\(^{-1}\)) throughout the course of the experiment (results not shown).

In addition, the change in concentrations of dissolved Fe throughout the experiment in the rewetted cores (\(\Delta\)Fe) correlated positively with \(\Delta\)TIC (\(\rho = 0.86, \text{df} = 18, p < 0.001, \text{Fig 5A}\)), \(\Delta\)DOC (\(\rho = 0.85, \text{df} = 18, p < 0.001, \text{Fig 5B}\)), and \(\Delta\)NH\(_4^+\) (\(\rho = 0.82, \text{df} = 18, p < 0.001, \text{Fig 5C}\)). In the drained soil cores \(\Delta\)Fe also correlated with \(\Delta\)TIC (\(\rho = 0.69, \text{df} = 18, p < 0.001, \text{Fig 5A}\) and \(\Delta\)DOC (\(\rho = 0.78, \text{df} = 18, p < 0.001, \text{Fig 5B}\)), but not with \(\Delta\)NH\(_4^+\) (\(\rho = 0.08, \text{df} = 18, p = 0.7, \text{Fig 5C}\)).
After 127 days, saturation for siderite (FeCO$_3$) was found in all of the rewetted soil cores, with supersaturation in the iron-rich cores. Supersaturation for rhodochrosite (MnCO$_3$) was found only in a subset of rewetted iron-rich cores, but not in the iron-poor cores. Vivianite (Fe

Fig 3. Iron, nutrient and carbon mobilization. Mobilization of (a) dissolved iron, (b) total inorganic carbon, (c) dissolved organic carbon, (d) ammonium, (e) methane and (f) total dissolved phosphorus over time (t = 0, 30 and 127 days) in the pore water of 40 soil cores that differ in experimental water level treatment (rewetted or desiccated) and initial soil iron content (high or low). Soil cores were classified into 4 groups: rewetted iron-poor fens (n = 10 cores from 2 sites), drained iron-poor fens (n = 10 cores from 2 sites), rewetted iron-rich fens (n = 10 cores from 2 sites), and drained iron-rich fens (n = 10 cores from 2 sites). Dots represent group means ± SE.

doi:10.1371/journal.pone.0153166.g003

Mineral saturation indices

After 127 days, saturation for siderite (FeCO$_3$) was found in all of the rewetted soil cores, with supersaturation in the iron-rich cores. Supersaturation for rhodochrosite (MnCO$_3$) was found only in a subset of rewetted iron-rich cores, but not in the iron-poor cores. Vivianite (Fe
(II)₃(PO₄)₂·8H₂O) precipitation was predicted in some (but not all) of the rewetted iron-rich soil cores. Slight supersaturation for calcite (CaCO₃) was sporadically found in the cores with highest pH values (>6.4), which only occurred in some alkaline layers of the rewetted iron-rich cores of site ES. Ca-P precipitation as hydroxyapatite (Ca₅(PO₄)₃(OH)) was unlikely due to strong undersaturation.

Discussion
Rewetting of drained organic soils unambiguously triggered the mobilization and accumulation of NH₄⁺, TIC and DOC into the pore water, but this rewetting effect was disproportionately stronger in fens with large iron pools, suggesting a strong iron-mediated breakdown of organic matter [14,15]. Concentrations of dissolved P however only rose slightly, and, in the iron-rich cores, had again dropped to low levels at the end of the experiment, indicating a P sink.

Nutrient (P, NO₃⁻ and NH₄⁺) mobilization
Soil desiccation increases mineralization rates of organic matter. In response, organic-bound nutrients are converted into inorganic mobile ions, which is why drainage of wet soils is coupled with eutrophication [4]. In our dataset, this eutrophication effect corresponds with the observed increase in concentrations of NO₃⁻ up to >1 mmol L⁻¹. Conversely, accumulation of NO₃⁻ did not occur in the rewetted soil cores, as no nitrification of ammonium can take place.
under anaerobic conditions. However, although rewetting can be an effective mechanism to prevent aerobic decomposition and accumulation of nitrate in organic soils, rewetting does not necessarily lower nutrient availability in general. Compared to the drained soil cores, we measured slightly higher concentrations of dissolved P and much higher concentrations of ammonium in the rewetted cores. For P, this apparent discrepancy is directly related to the differences in redox-state between both water level treatments. Higher concentrations of dissolved P in the rewetted cores can be linked to anaerobic reduction processes in which organic matter and organic-P are mineralized, as well as to the well-known redox-sensitive dissolution of P from amorphous Fe-(hydr)oxides under anoxic conditions [28, 29, 30]. The latter

---

**Fig 5. Relationship between Iron, TIC, DOC and NH4+.** Correlations between the change in pore water Fe concentrations (ΔFe) and the change in concentrations of (a) total inorganic carbon (ΔTIC), (b) dissolved organic carbon (ΔDOC) and (c) ammonium (ΔNH₄⁺) (in μmol L⁻¹) in 20 rewetted and 20 drained soil cores over 127 days (n = 4 sites).

doi:10.1371/journal.pone.0153166.g005
mechanism is particularly relevant in drained and degraded groundwater-fed fens, in which a large part of the inorganic P pool is already iron-bound [3,23]. Although we had expected a mass release of P in the rewetted iron-poor soils in particular, pore water P concentrations only rose to low concentrations of 1.3 \( \mu \text{mol L}^{-1} \). In the rewetted iron-rich cores, an initial increase in total dissolved P during the first \( t = 30 \text{ d} \) phase of rewetting was soon followed by a decrease in concentrations of dissolved P to 2 \( \mu \text{mol L}^{-1} \). Computed supersaturation for vivianite in some of the rewetted iron-rich cores at the end of the experiment suggests vivianite precipitation under anoxic iron-rich conditions, which can be an effective sink for soluble P but is generally slow to obtain equilibrium [31,32,33]. Additionally, other phases than iron compounds may have controlled the solubility of P in the pore water after rewetting, as P can be resorbed to redox-insensitive compounds such as aluminium oxides [34,35]. It remains unclear to what extent this occurred in our study. Also the role of Ca is not clear, however apatite formation seems to be negligible in our sites. Finally, it should be noted that we measured total P in the pore water and not inorganic P. Therefore, we cannot exclude that part of the P is bound to DOM. Since inorganic P is denoted usually as “bioavailable” we might overestimate the amount of P which is mostly relevant for eutrophication. Concentrations of inorganic P may thus be even lower than the results reported here. These results suggest that pore water P mobilization upon fen rewetting can remain well below eutrophic thresholds, which is in contrast with most studies on fen rewetting [30,36]. We relate this primarily to the low S-loads in our study sites, as sulfates and sulfides enhance internal eutrophication [25].

In contrast to P, \( \text{NH}_4^+ \) concentrations rose to potentially phytotoxic levels (1 mmol L\(^{-1}\)) in the iron-rich rewetted cores, while remaining considerably lower in the rewetted iron-poor cores (< 0.3 mmol L\(^{-1}\)). As inflow and outflow of ammonium as well as plant uptake was absent in our closed experiment, only in situ \( \text{NH}_4^+ \) production/mobilization and transformation/adsorption plays a role. At least two nonexclusive processes must be taken into account in order to explain the observed interaction effect between rewetting and soil iron content on ammonium accumulation. First, a disproportionately high accumulation of \( \text{NH}_4^+ \) in the iron-rich soil cores can be related to the iron-mediated anaerobic breakdown of organic matter, which triggers the conversion of organic-N to inorganic-N and releases \( \text{NH}_4^+ \) into the pore water. Here, reduced nitrification rates prevent \( \text{NH}_4^+ \) transformation [37]. The positive correlations between pore water accumulation of Fe and \( \text{NH}_4^+ \) as well as Fe and TIC in our dataset indeed suggest such iron-mediated breakdown of organic matter coupled with \( \text{NH}_4^+ \) release, as all compounds are products of anaerobic decomposition processes. Second, we explored the possibility that a larger quantity of mineral \( \text{NH}_4^+ \) was, by chance, already adsorbed to the adsorption complex of the two iron-rich fens. Rewetting with artificial groundwater increases competition for soil exchange sites and may stimulate ammonium release from the soil [38]. However, previously collected field data on KCl-extractable \( \text{NH}_4^+ \) at all four study sites indicates that the amount of \( \text{NH}_4^+ \) that can be released from the adsorption complex of one litre of soil equals an estimated 0.98 and 0.97 mmol in the iron-poor sites (site BM and LH respectively) and 1.07 and 0.54 mmol in the iron-rich sites (site ES and ZB respectively). Therefore, the differential response of iron-rich and iron-poor fens is unlikely to be explained by desorption. Finally, nitrate reduction is another well-known mechanism for \( \text{NH}_4^+ \) production [39], and this reaction can be mediated by iron compounds [40]. However, this pathway is unlikely to be important in our experiment as this would require a large pool of nitrate. In our study, initial pore water \( \text{NO}_3^- \) concentrations in the peat cores were only in the order of a few \( \mu \text{molars, while field data on KCl-extractable } \text{NO}_3^- \) suggests values close to or even below detection limit at all study sites.
Carbon (DOC, TIC and CH₄) production
Throughout the experiment, mean pore water DOC concentrations in the drained and rewetted iron-poor soil cores remained within the range of 3.5–9.1 mmol L⁻¹, with slightly elevated concentrations in the latter. In the rewetted iron-rich soil cores however, DOC accumulation reached high mean levels of 16 mmol L⁻¹ (> 192 mg L⁻¹). Such link between iron concentrations and disproportionate DOC mobilization has also been observed in the field [21,41]. We see two nonexclusive reasons for the positive correlation between DOC mobilization and soil iron content in the rewetted soil cores. First, the same mechanism that explains NH₄⁺-mobilization affects DOC mobilization as well, i.e. the iron-mediated decomposition of organic matter. As DOC is a product of decomposition [42], increased rates of litter decomposition (either directly or indirectly) coupled with a large pool of soil iron should stimulate DOC release into the pore water. Second, large quantities of DOM can be adsorbed to Fe(III)(hydro)xides under oxic conditions [43,44], so that Fe(III)-reduction triggers the dissolution of Fe-DOC coagulates. As pointed out in recent research [44], such Fe-DOC coagulation in oxic soil layers serves as a barrier to DOC efflux from semi-terrestrial environments, but such barrier disappears upon rewetting. Although the quantitative contribution of each process to DOC accumulation in rewetted Fe-rich soils cannot be disentangled in our experiment, it is nonetheless clear that large-scale rewetting of drained iron-rich fens (in contrast to iron-poor fens) triggers a strong mobilization of DOC, thereby increasing DOC fluxes towards adjacent water catchments.

In non-calcareous fens (including our study sites), high concentrations of TIC are mainly related to in-situ anaerobic reduction processes coupled with organic matter decomposition [25]. Upon rewetting, hydrogen ions are consumed during anaerobic decomposition while HCO₃⁻ and CO₂ (TIC) are produced, and waterlogged conditions prevent rapid CO₂-degassing towards the atmosphere. In our experiment, excess accumulation of TIC and a sharp rise in pH in the rewetted iron-rich cores, but to a lesser extent in the rewetted iron-poor cores, again points towards iron-induced anaerobic decomposition of organic matter in rewetted soils. For degraded iron-rich fens in particular, a considerable part of TIC production is indeed directly coupled with iron reduction [23]. Likewise, the reduction of nitrates or sulfates also produces TIC and alkalinity [25,45], but given the low mean pore water concentrations of these parameters at the start of the experiment (< 9 μmol L⁻¹ and < 100 μmol L⁻¹ respectively), this is unlikely to explain excess TIC production in our soil cores. It should be noted however that we only measured carbon accumulation in the pore water, but not total carbon fluxes towards the atmosphere. As oxygen is the most favorable electron acceptor, total carbon emissions (in the form of CO₂) are most likely highest in all of the drained cores. Here, the generally rapid degassing of CO₂ in aerated soils prevents CO₂ accumulation in the pore water, so that flux measurements would be needed to estimate actual C loss to the atmosphere.

Organic soils that have been subject to prolonged desiccation generally require a longer time lag before significant CH₄ accumulation, as electron acceptors have had sufficient time to regenerate [46]. Although methanogenesis can occur on a micro-scale despite the presence of energetically favorable electron acceptors, significant CH₄ production is expected to only take place after sequential consumption of these electron acceptors by micro-organisms [21,47]. In our dataset, we observe a clear (an estimated ± 50–100 days) delay in methane accumulation in the rewetted iron-rich cores but not in the iron-poor cores, which, again, suggests that ferric iron is being reduced as an energetically favorable electron acceptor.

Management implications
In the past, it has been emphasized that high concentrations of iron in soil and flooding water are beneficial for the restoration of wet ecosystems as iron prevents mobilization of phosphates...
and sulfides into pore and surface water [10,11,30]. This is particularly relevant in heavily
degraded P-eutrophied or S-polluted wetlands that are characterized by very low soil Fe:S and
Fe:P ratios [3,25]. In unpolluted mesotrophic fens however, the P- and S-binding service of
iron may be of much less importance for the vitality of the fen system. In our experiment for
example, concentrations of sulfide remained below detection limit both in iron-rich and iron-
poor fens, while concentrations of dissolved P never reached eutrophic thresholds. Under such
conditions, positive effects of iron may be overshadowed by negative effects. In this respect,
many restored fens are, despite rewetting, characterized by seasonal fluctutations in water levels
(and thus redox conditions [17,18]), and large pools of accumulated iron in the top soil [23].
Under such conditions, the iron redox cycle in which iron alternately shifts between the ferric
(Fe³⁺) and ferrous (Fe²⁺) state can cause a continuous positive feedback on organic matter
mineralization coupled with nutrient and carbon mobilization [14]. Here, repeated mass mobi-
лизации of TIC, DOC and NH₄⁺ in each rewetting cycle can be expected to impact the function-
ing of the fen ecosystem and downstream systems. Although our data do not allow for an
accurate prediction of how much carbon is released or mineralized with each oxidation/rewet-
ting cycle, we can make a rough estimate based on several assumptions. We assume that a
major part of DOC and TIC in soil water is the product of organic matter decomposition and
associated processes like iron reduction. According to a simplified calculation (e.g. disregarding
CO₂ emissions towards the atmosphere) about 0.8% of total carbon in iron-rich cores and
0.17% of total carbon in iron-poor cores must be dissolved to reach the final mean sum of
DOC and TIC concentrations of 18 mM or 3.5 mM (ΔTIC + ΔDOC), respectively. This esti-
mate is based on i) different organic matter content and dry bulk density for iron-rich soils
(means = 0.326 kg:kg, 0.21 kg L⁻¹) vs. iron-poor soils (means = 0.617 kg:kg, 0.1 kg L⁻¹)
(Table 1), ii) the assumption that one litre of water corresponds roughly with one litre of soil,
and iii) that organic matter has an average C fraction of 0.4 (kg:kg). Accordingly, one litre of
soil of the iron-rich fens holds on average 27 g C and of the iron-poor fens holds on average
25 g C compared to ΔDOC+ΔTIC concentrations of 216 mg C L⁻¹ (18 mM) and 42 mg C L⁻¹
(3.5 mM) in pore water of iron-rich cores vs. in iron-poor cores which equates to percentage
details given above. Therefore, if the goal of a fen rewetting project is to restore a low-produc-
tive fen that provides vital ecosystem services such as long-term carbon sequestration and
nutrient retention, we suggest that the restoration of unpolluted drained iron-poor fens should
deserve priority over the restoration of drained iron-rich fens.

Conclusions
The biogeochemical effects of rewetting on drained fens are often unpredictable and site-depen-
dent, and many rewetted fens remain sources rather than sinks for carbon and nutrients. In our
comparative study, soil cores collected in drained iron-rich fens were characterized by a dispro-
portionate mobilization of Fe, TIC, DOC and NH₄⁺ in the pore water after rewetting, while such
disproportionate mobilization after rewetting was absent in soil cores collected in drained iron-
poor fens. Concentrations of dissolved P remained well below eutrophic thresholds, indicating a
P sink even in rewetted fens. Our results suggest that high iron pools in organic soils interact
with water regime, and rewetting stimulates strong iron-mediated organic matter mineralization
coupled with carbon and inorganic nutrient (NH₄⁺) mobilization. We conclude that fen restora-
tion by rewetting may be more effective in (unpolluted) iron-poor fens.

Supporting Information
S1 Fig. Sulfur mobilization. Mobilization of total dissolved Sulfur (S) over time (t = 0, 30 and
127 days) in the pore water of 40 soil cores that differ in experimental water level treatment
Iron as a Predictor of Carbon and Nutrient Mobilization

(rewetted or drained) and initial soil iron content (high or low). Soil cores were classified into 4 groups: rewetted iron-poor fens (n = 10 cores from 2 sites), drained iron-poor fens (n = 10 cores from 2 sites), rewetted iron-rich fens (n = 10 cores from 2 sites), and drained iron-rich fens (n = 10 cores from 2 sites). Dots represent group means ± SE.

**S1 Table. Dataset with raw data.**

**Acknowledgments**

We thank Staatsbosbeheer, Landschap Overijssel and Natuurpunt for permission to access the study sites. We gratefully acknowledge field support by Guy Emsens. The experiments were conducted in a greenhouse owned by the municipality of Antwerp. This study was financed by the Dutch OBN Research Program (OBN178-BE to university of Antwerp) and the FWO Fund for Scientific Research (11M0414N to WJE).

**Author Contributions**

Conceived and designed the experiments: WJE CJSA AJPS RvD. Performed the experiments: WJE KS. Analyzed the data: WJE. Contributed reagents/materials/analysis tools: WJE CJSA AJPS DZ RvD. Wrote the paper: WJE CJSA AJPS DZ RvD.

**References**

1. Lamers LP, Vile MA, Grootjans AP, Acreman MC, van Diggelen R, Evans MG, et al. (2014) Ecological restoration of rich fens in Europe and North America: from trial and error to an evidence-based approach. Biological Reviews.
2. Kasimir-Klemedtsson A, Klemedtsson L, Berglund K, Martikainen P, Silvola J, Oenema O (1997) Greenhouse gas emissions from farmed organic soils: a review. Soil Use and Management 13: 245–250.
3. Zak D, Gelbrecht J (2007) The mobilisation of phosphorus, organic carbon and ammonium in the initial stage of fen rewetting (a case study from NE Germany). Biogeochemistry 85: 141–151.
4. Olde Venterink H, Davidson TE, Kiehl K, Leonardson L (2002) Impact of drying and re-wetting on N, P and K dynamics in a wetland soil. Plant and Soil 243: 119–130.
5. Freeman C, Fenner N, Ostle NJ, Kang H, Dowrick DJ, Reynolds B, et al. (2004) Export of dissolved organic carbon from peatlands under elevated carbon dioxide levels. Nature 430: 195–198. PMID: 15241411
6. Preston MD, Eimers MC, Watmough SA (2011) Effect of moisture and temperature variation on DOC release from a peatland: Conflicting results from laboratory, field and historical data analysis. Science of the Total Environment 409: 1235–1242. doi:10.1016/j.scitotenv.2010.12.027 PMID: 21237500
7. Holden J (2005) Peatland hydrology and carbon release: why small-scale process matters. Philosophical Transactions of the Royal Society aMathematical Physical and Engineering Sciences 363: 2891–2913.
8. Pastor J, Solin J, Bridgham SD, Updegraff K, Harth C, Weishampel P, et al. (2003) Global warming and the export of dissolved organic carbon from boreal peatlands. Oikos 100: 380–386.
9. Van Dijk J, Stroetenga M, Bos L, Van Bodegom PM, Verhoeven HA, Aerts R (2004) Restoring natural seepage conditions on former agricultural grasslands does not lead to reduction of organic matter decomposition and soil nutrient dynamics. Biogeochemistry 71: 317–337.
10. Geurts JMJ, Smolders AJP, Verhoeven JTA, Roelofs JGM, Lamers LPM (2008) Sediment Fe: PO(4) ratio as a diagnostic and prognostic tool for the restoration of macrophyte biodiversity in fen waters. Freshwater Biology 53: 2101–2116.
11. Smolders AJP, Nijboer RC, Roelofs JGM (1995) Prevention of sulphide accumulation and phosphate mobilization by the addition of iron(II) chloride to a reduced sediment: An enclosure experiment. Freshwater Biology 34: 559–567.
12. Clement JC, Shrestha J, Ehrenfeld JG, Jaffe PR (2005) Ammonium oxidation coupled to dissimilatory reduction of iron under anaerobic conditions in wetland soils. Soil Biology & Biochemistry 37: 2323–2328.

13. Lovley DR (1991) Dissimilatory Fe(III) and Mn(IV) Reduction. Microbiological Reviews 55: 259–287. PMID: 1886521

14. Li YC, Yu S, Strong J, Wang HL (2012) Are the biogeochemical cycles of carbon, nitrogen, sulfur, and phosphorus driven by the "Fe-III-Fe-II redox wheel" in dynamic redox environments? Journal of Soils and Sediments 12: 683–693.

15. Lovley DR, Phillips EJP (1986) Organic-Matter Mineralization with Reduction of Ferric Iron in Anaerobic Sediments. Applied and Environmental Microbiology 51: 683–689. PMID: 16347032

16. Kusel K, Blothe M, Schulz D, Reiche M, Drake HL (2008) Microbial reduction of iron and porewater biogeochemistry in acidic peatlands. Biogeosciences 5: 1537–1549.

17. Richert M, Dietrich O, Koppisch D, Roth S (2000) The influence of rewetting on vegetation development and decomposition in a degraded fen. Restoration Ecology 8: 186–195.

18. Grootjans AP, Adema EB, Bleuten W, Joostn H, Madaras M, Janakova M (2006) Hydrological landscape settings of base-rich fen mires and fen meadows: an overview. Applied Vegetation Science 9: 175–184.

19. Evans MG, Burt TP, Holden J, Adamson JK (1999) Runoff generation and water table fluctuations in blanket peat: evidence from UK data spanning the dry summer of 1995. Journal of Hydrology 221: 141–160.

20. Schlotzhauer SM, Price JS (1999) Soil water flow dynamics in a managed cutover peat field, Quebec: Field and laboratory investigations. Water Resources Research 35: 3675–3683.

21. Fenner N, Williams R, Toberman H, Hughes S, Reynolds B, Freeman C (2011) Decomposition ‘hot-spots’ in a rewetted peatland: implications for water quality and carbon cycling. Hydrobiologia 674: 51–66.

22. Van Bodegom PM, Broekman R, Van Dijk J, Bakker C, Aerts R (2005) Ferrous iron stimulates phenol oxidase activity and organic matter decomposition in waterlogged wetlands. Biogeochemistry 76: 69–83.

23. Aggenbach CJS, Backx H, Emsens WJ, Grootjans AP, Lamers LPM, Smolders AJP, et al. (2013) Do high iron concentrations in rewetted rich fens hamper restoration? Preslia 85: 405–420.

24. Lucassen ECHET, Spierenburg P, Fraaije RGA, Smolders AJP, Roelofs JGM (2009) Alkalinity generation and sediment CO2 uptake influence establishment of Sparganium angustifolium in softwater lakes. Freshwater Biology 54: 2300–2314.

25. Smolders AJP, Lamers LPM, Lucassen ECHET, Van der Velde G, Roelofs JGM (2006) Internal eutrophication: How it works and what to do about it—a review. Chemistry and Ecology 22: 93–111.

26. Parkhurst DL, Appelo CAJ (1999) User’s guide to PHREEQC (version 2)—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: US Geological Survey Water-Resources Investigations Report 99–4259. 312 p.

27. Zak D, Gelbrecht J, Wagner C, Steinberg CEW (2008) Evaluation of phosphorus mobilization potential in rewetted fens by an improved sequential chemical extraction procedure. European Journal of Soil Science 59: 1191–1201.

28. Lucassen ECHET, Smolders AJP, Lamers LPM, Roelofs JGM (2005) Water table fluctuations and groundwater supply are important in preventing phosphate-eutrophication in sulphate-rich fens: Consequences for wetland restoration. Plant and Soil 269: 109–115.

29. Patrick WH, Khalid RA (1974) Phosphate Release and Sorption by Soils and Sediments—Effect of Aerobic and Anaerobic Conditions. Science 186: 53–55. PMID: 17818101

30. Zak D, Wagner C, Payer B, Augustin J, Gelbrecht J (2010) Phosphorus mobilization in rewetted fens: the effect of altered peat properties and implications for their restoration. Ecological Applications 20: 1336–1349. PMID: 20666253

31. Murphy T, Lawson A, Kumagai M, Nalewajko C (2001) Release of phosphorus from sediments in Lake Biwa. Limnology 2: 119–128.

32. Heiberg L, Koch CB, Kjaergaard C, Jensen HS, Hansen HCB (2012) Vivianite Precipitation and Phosphate Sorption following Iron Reduction in Anoxic Soils. Journal of Environmental Quality 41: 938–949. doi: 10.2134/jeq2011.0067 PMID: 22565275

33. Heiberg L, Pedersen TV, Jensen HS, Kjaergaard C, Hansen HCB (2010) A Comparative Study of Phosphate Sorption in Lowland Soils under Oxic and Anoxic Conditions. Journal of Environmental Quality 39: 734–743. doi: 10.2134/jeq2009.0222 PMID: 20176846
34. Walpersdorf E, Koch CB, Heiberg L, O’Connell DW, Kjaergaard C, Bruun Hansen HC (2013) Does vivianite control phosphate solubility in anoxic meadow soils? Geoderma 193: 189–199.

35. Sakadevan K, Bavor HJ (1998) Phosphate adsorption characteristics of soils, slags and zeolite to be used as substrates in constructed wetland systems. Water Research 32: 393–399.

36. van de Riet BP, Hefting MM, Verhoeven JTA (2013) Rewetting Drained Peat Meadows: Risks and Benefits in Terms of Nutrient Release and Greenhouse Gas Exchange. Water Air and Soil Pollution 224.

37. Russow R, Tauchnitz N, Spott O, Mothes S, Bernsdorf S, Meissner R (2013) Nitrate turnover in a peat soil under drained and rewetted conditions: results from a [N-15]nitrate-bromide double-tracer study. Isotopes in Environmental and Health Studies 49: 438–453. doi: 10.1080/10256016.2013.831089 PMID: 24313368

38. Lucassen ECHET, Smolders AJP, Boedeltje G, van den Munckhof PJJ, Roelofs JGM (2006) Groundwater input affecting plant distribution by controlling ammonium and iron availability. Journal of Vegetation Science 17: 425–434.

39. Burgin AJ, Hamilton SK (2007) Have we overemphasized the role of denitrification in aquatic ecosystems? A review of nitrate removal pathways. Frontiers in Ecology and the Environment 5: 89–96.

40. Hansen HCB, Koch CB, NanckeKrogh H, Borggaard OK, Sorensen J (1996) Abiotic nitrate reduction to ammonium: Key role of green rust. Environmental Science & Technology 30: 2053–2056.

41. Hughes S, Reynolds B, Brittain SA, Hudson JA, Freeman C (1998) Temporal trends in bromide release following rewetting of a naturally drained gully mire. Soil Use and Management 14: 248–250.

42. Kalbitz K, Solinger S, Park JH, Michalzik B, Matzner E (2000) Controls on the dynamics of dissolved organic matter in soils: A review. Soil Science 165: 277–304.

43. Lal R, Kimble JM, Follett RF, Stewart BA (1997) Soil processes and the carbon cycle: CRC Press.

44. Riedel T, Zak D, Biester H, Dittmar T (2013) Iron traps terrestrially derived dissolved organic matter at redox interfaces. Proceedings of the National Academy of Sciences of the United States of America 110: 10101–10105. doi: 10.1073/pnas.1221487110 PMID: 23733946

45. Geurts JMJ, Sarneel JMC, Willers BJMC, Roelofs JGM, Verhoeven JTA, Lamers LPM (2009) Interacting effects of sulphate pollution, sulphide toxicity and eutrophication on vegetation development in fens: A mesocosm experiment. Environmental Pollution 157: 2072–2081. doi: 10.1016/j.envpol.2009.02.024 PMID: 19285368

46. Estop-Aragones C, Blodau C (2012) Effects of experimental drying intensity and duration on respiration and methane production recovery in fen peat incubations. Soil Biology & Biochemistry 47: 1–9.

47. Achtinich C, Bak F, Conrad R (1995) Competition for Electron-Donors among Nitrate Reducers, Ferric Iron Reducers, Sulfate Reducers, and Methanogens in Anoxic Paddy Soil. Biology and Fertility of Soils 19: 65–72.