The influence of degree of peat decomposition on phosphorus binding forms in fens

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This article is dedicated to the memory of our very good friend and colleague, Dr Silke Velty, 07 April 1973 – 14 October 2007.

SUMMARY

Re-wetting of drained fens can release phosphorus, introducing a eutrophication risk for associated aquatic ecosystems. Characterisation of the different forms of organic and inorganic bound phosphorus in the peat is an important step towards the development of tools for assessing the level of risk attached to individual re-wetting projects. In the work reported here, a sequential extraction (fractionation) method was used to distinguish the following P binding forms:

1. labile P, detected by NH₄Cl extraction;
2. redox-sensitive P, detected by Na₂S₂O₄/NaHCO₃ extraction;
3. P adsorbed to metal oxides, detected by HCl extraction;
4. P bound to humic substances, detected by NaOH extraction; and
5. organic and refractory bound P, detected using H₂SO⁴ and H₂O₂.

Special attention was paid to the degree of decomposition (DPD) of the peat, and metal concentrations were measured in selected fractions. Higher P concentrations were found in completely humified than in little humified peat for all fractions except the NH₄Cl (labile P) fraction, where P content increased as DPD decreased. As only 1% of total phosphorus (TP) was present as labile P, the results indicate that the decisive horizons for nutrient release after re-wetting are those that are completely humified due to pedogenetic changes. The principal metal sorption partner for P was Fe.

KEY WORDS: fen restoration, humification, peat soil, re-wetting, sequential extraction.

INTRODUCTION

In north-eastern Germany, the drainage of huge areas of fen (sensu Joosten & Clarke 2002) over several decades means that their natural functions as accumulators, buffers, transformers and filters for nutrients and water have been impaired. Fundamental changes in the hydrology, chemistry, biochemistry, physics and biology of the peat are apparent. Aerobic conditions have resulted in oxidative peat decomposition, with concomitant emission of CO₂ to the atmosphere. Possible consequences are peat mineralisation and transformation of organically bound phosphorus (P) into redox-sensitive inorganic Fe(III) oxohydroxide-bound P (Gelbrecht & Koppisch 2001, Zak et al. 2004). The porosity, water capacity, hydraulic conductivity and wettability of the peat have all been reduced (Zeitz 2003) and the peat body is characterised by structural damage (Lehrkamp 1989, Succow & Jeschke 1990, Velty et al. 2006, Zeitz & Velty 2002) such as aggregation in the peat shrinkage horizon (Figure 1) with adherent shrinkage cracks (Figure 2).

The regeneration of fens is now promoted both economically and politically, for example by the Kyoto Protocol (UNFCC 1998) and the European Water Framework Directive (EU 2000). Many degraded fens have been re-wetted and there are plans to re-wet more in the near future. Re-wetting leads to saturated conditions which prevent peat decomposition and may initiate new peat growth. Re-wetting of degraded fens is often accompanied by enhanced release of P due to changes in the redox potential of P-adherent chemical elements such as Fe (Paludan 1995, Gelbrecht & Koppisch 2001, Gelbrecht et al. 2003). Thus, in managing degraded fens, special account must be taken of the potential for supplementation of nutrient outputs to adjacent aquatic ecosystems. Partitioning, mineralisation, immobilisation, transport and uptake of P are well-known individual processes that govern P dynamics and whose effects on surface water eutrophication have been studied worldwide (Bar-Yosef 2003).

Total phosphorus (TP) concentrations in natural and uninfluenced waters are mostly below 0.1 mg l⁻¹ (Rump 1998). In re-wetted fen sites Rupp et al.
(2004) report soluble reactive P (SRP) concentrations up to 0.36 mg l\(^{-1}\) in surface water whilst Gelbrecht & Zak (2004) measured SRP concentrations up to 18.9 mg l\(^{-1}\) in pore water.

In order to obtain more detailed information on the P pool that could be released after re-wetting of fens, it is important to assess accumulated P in the peat. Sequential extraction of P from peat soil samples provides information about its potential mobility under different environmental conditions; and the determination of P binding forms helps to clarify mechanisms of P release likely to result from re-wetting so that P release potentials may be estimated prospectively.

Conventional investigation methods such as the Calcium-Acetate-Lactate-Digestion or the Double-Lactate-Digestion (VDLUFA 1991, Scheffer & Schachtshabel 2002) are used for the determination of plant-available P. The accuracy of these methods is sufficient for the evaluation of agricultural fertiliser requirements, but no information about soil-chemical complexes is obtained because the recorded P fraction cannot be related plausibly to the binding forms. The first sequential extraction methods for soils were developed e.g. by Dean (1938), Chang & Jackson (1957), Smith (1965) and Hedley et al. (1982) and these procedures have been adapted for the analysis of P in lake sediments e.g. by Hieltjes & Lijklema (1980), Pettersson (1986) and Psenner et al. (1988). In the sequential extraction after Chang & Jackson (1957) which has been applied, modified and simplified worldwide (Tiessen & Moir 1993, Guppy et al. 2000, Tyler 2002), organic P is detected only as the difference between TP and the sum of all inorganic P forms (Pagel et al. 1982, Barbanti et al. 1994).

For fens, there is no specific sequential extraction method that allows differentiation of P binding forms, and the processes of P shifting and P release are still incompletely understood. This situation creates difficulties in estimating the risk of re-wetting for the environment. More studies on the influence of the degree of peat decomposition (DPD) on P release are also needed before a general risk assessment scheme for peat substrates can be devised.

In the work described here, we tested the hypothesis that DPD influences the P binding forms in fens. We determined inorganic and organic P binding forms by sequential extraction and related this to DPD. We also determined the content of metals as potential sorption partners for P.
METHODS

Peat and degree of decomposition

Representative peat samples (n=16) with different DPD were taken from a fen in the Peene Valley (Mecklenburg-Western Pomerania, Germany). Sample selection was based on von Post’s humification scale, which involves visual estimation of the colour and turbidity of the water that can be extracted by squeezing the peat through the fingers. As a rule, the clearer (without residuum) the water, the less humified is the peat (von Post 1924, von Post & Granlund 1926, Hämäläinen 1991). Degree of decomposition (humification) is expressed in terms of a ten-class scale on which higher numbers indicate stronger peat decomposition (Table 1).

Table 1. Degree of peat decomposition after von Post, and number of peat samples analysed.

<table>
<thead>
<tr>
<th>Degree of decomposition after von Post</th>
<th>Level of humification</th>
<th>Number of peat samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>H 1</td>
<td>completely/virtually unhumified</td>
<td></td>
</tr>
<tr>
<td>H 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H 3</td>
<td>little/poorly humified</td>
<td>6</td>
</tr>
<tr>
<td>H 4</td>
<td>fairly humified</td>
<td>2</td>
</tr>
<tr>
<td>H 5</td>
<td>quite well-/well humified</td>
<td>2</td>
</tr>
<tr>
<td>H 6</td>
<td>almost completely/completely humified</td>
<td>4</td>
</tr>
</tbody>
</table>

Whilst von Post’s method for estimation of DPD is a subjective means for rapid field determination of the degree of humification, it is indispensable in this context and should complement rather than be displaced by “modern” procedures.

Sequential extraction of phosphorus

Knowledge of the P forms in soils has been derived largely by chemical fractionation based on the ability of selective chemical reagents to dissolve specific types of organic and inorganic compounds.

For the present study, the sequential extraction method of Psenner et al. (1984), originally used for the detection of P binding forms in lake sediments (Jensen & Thamdrup 1993, Hupfer 1995, Paludan 1995, Lewandowski 2002), was adapted to take account of the special properties of peat.

The fractionation was carried out on replicate field-fresh peat samples as soon as possible after collection, since drying induces oxidation of the peat and leads to irreversible changes in its fractional composition.

A 5 g sub-sample of each peat sample was placed in a 25 ml centrifuge tube and extracted sequentially into five fractions. At each stage, bound P was assumed to be removed selectively from specific types of compounds contained in the peat (Table 2 and Figure 3).

The bio-availability of the prevalent P binding forms decreases with each extraction step (Pettersson 1986). For this reason, stable organic and refractory bound P was determined as “Rest-P” (residue of the NaOH fraction) in the final extraction step, which involved washing with deionised water, decanting, drying, grinding and taking a 20 mg sample for H2SO4/H2O2 digestion.

In order to verify the P content of the fractions, it was necessary also to determine TP for each peat sample by H2SO4/H2O2 digestion (10 mg of dry peat) (Zwirnmann et al. 1999, DIN EN 1189).

Table 2. Fractionation scheme showing the five extraction steps, the extraction solvent and P binding form (BD = Bidithionite, SRP = soluble reactive phosphorus, NRP = non-reactive phosphorus, TP = total phosphorus).

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Extraction solvent</th>
<th>P binding form</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH4Cl-SRP</td>
<td>1 M NH4Cl</td>
<td>labile, loosely bound or adsorbed P; immediately available</td>
</tr>
<tr>
<td>BD-TP</td>
<td>0.1 M NaHCO3-Na2S2O4-Solution</td>
<td>redox-sensitive P, mainly from Fe(III)- and Mn(IV)-oxyhydroxide surfaces</td>
</tr>
<tr>
<td>HCl-SRP</td>
<td>0.5 M HCl</td>
<td>P adsorbed to metal oxides (Al-, Fe- and Mn-bound P); apatite-P and P bound in carbonates</td>
</tr>
<tr>
<td>HCl-NRP</td>
<td></td>
<td>acid labile organic P</td>
</tr>
<tr>
<td>NaOH-TP</td>
<td>1 M NaOH</td>
<td>humic substance bound P and poly-P</td>
</tr>
<tr>
<td>Rest-P</td>
<td>TP detection</td>
<td>organic and refractory bound P</td>
</tr>
</tbody>
</table>
Figure 3. Procedure of the modified PSENNER-Fractionation (centrifuge 5 min at 10000·g; filtration with 0.45 µm CA-Filter, Whatman).
Gasparatos & Haidouti (2001) compared different methods for the detection of TP in soils and found no significant differences between the concentrations of TP extracted by digestion in HClO₄, aqua regia and H₂SO₄/H₂O₂.

P concentrations in the extracts and TP were detected photometrically (at λmax=680 nm) using the Molybdenum Blue Method (Murphy & Riley 1962).

The concentrations of labile P, redox-sensitive P, P adsorbed to metal oxides and P bound to humic substances are presented in this paper. Rest-P and TP are not discussed because these fractions contain stable P that is not immediately available.

### Analysis of metals

Fe, Al, Mn and Ca were determined in selected fractions using an Atomic Absorption Spectrometer (Perkin-Elmer 3300 with flame). Ca was detected mainly as soluble calcium(hydrogen)carbonate within the NH₄Cl fraction; Fe and Mn were determined in the BD fraction; and Al, Ca, Fe and Mn in the HCl-SRP-fraction (Table 3). No metals were measured in the NaOH fraction or in Rest-P because the P here was bound organically and therefore refractory. Total metal concentrations for each sample were also determined.

### RESULTS

The relationships between the P concentration in each fraction and DPD are shown in Figure 4. Redox-sensitive P data are presented for all 16 peat samples (Figure 4b), but only 12 data points are shown for the other P binding forms due to methodological changes. Regression analysis (calculation of R²) was not carried out because the class variable DPD is discontinuous.

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### Table 3. Scheme of extractions for metal analyses.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>P binding form</th>
<th>Detected metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄Cl-SRP</td>
<td>labile, loosely bound or adsorbed P; immediately available</td>
<td>Ca</td>
</tr>
<tr>
<td>BD-TP</td>
<td>redox-sensitive P, mainly from Fe(III) and Mn(IV) oxhydroxide surfaces</td>
<td>Fe, Mn</td>
</tr>
<tr>
<td>HCl-SRP</td>
<td>P adsorbed to metal oxides (Al-, Fe- and Mn-bound P); apatite-P and P bound in carbonates</td>
<td>Al, Ca, Fe, Mn</td>
</tr>
</tbody>
</table>
Phosphorus fractionation
The concentration of labile P was lowest (NH₄Cl-SRP below 0.5 µg g DM⁻¹) in the completely humified (H 10) peat horizon, and increased with decreasing DPD (Figure 4a). The highest concentration (5.5 µg P g DM⁻¹) was found in a little humified (H 3) sample.

The content of redox-sensitive P was higher than that of labile P and increased with increasing DPD, ranging from 20.7 µg P g DM⁻¹ in little humified (H 3) peat to 434 µg P g DM⁻¹ in completely humified (H 10) peat (Figure 4b).

The largest concentrations of metal oxide bound P (HCl-SRP: 347 µg P g DM⁻¹; H 3: 27.7 µg P g DM⁻¹) and acid labile organic P (HCl-NRP: 159.2 µg P g DM⁻¹; H 3: 11.2 µg P g DM⁻¹) were found in the completely humified (H 10) peat sample. The content of P again increased with increasing DPD in this fraction (Figure 4c).

The concentration of humic substance bound P (NaOH-TP) increased from 152 µg P g DM⁻¹ in little humified (H 3) peat up to 587 µg P g DM⁻¹ in completely humified (H 10) peat (Figure 4d).

Metals
No relationships were found between DPD and Al:P, Ca:P or Mn:P. However, a statistically significant linear relationship (R²=0.85) was found between the concentrations of redox-sensitive P and Fe, the P content increasing with increasing Fe content (Figure 5a). The Fe content of the BD fraction increased with DPD, from 0.64 µmol Fe g DM⁻¹ at H 3 to 116.6 µmol Fe g DM⁻¹ at H 10 (Figure 5b); and the Fe content of the HCl fraction increased from 6.3 µmol Fe g DM⁻¹ at H 3 to 246.1 µmol Fe g DM⁻¹ at H 10 (Figure 6).

**DISCUSSION**

**Applicability of methods**
Sequential extraction methods were developed to better quantify the (clustered) bio-availability of different pollutants and trace elements associated with soils and sediments in a rapid and simplified way. They generally employ strong solvents and reactions, in contrast to the weak solvents and slow reactions of the natural processes they simulate. As a result, they cannot be used to identify discrete compounds because of deviations from natural physicochemical conditions and have been described as “operational” due to e.g. re-adsorptions, relocations (Lewandowski 2002) and overlaps between the fractions (Martin 1987, Martin et al. 1987).
highest labile P value in the NH₄Cl fraction is low (0.016 % at H 10, 1.25 % at H 3), and the fraction of TP that is present as labile P is very low (0.016 % at H 10, 1.25 % at H 3). This could explain the reverse P distribution in the NH₄Cl fraction as compared to labile P. The relationship is governed by the strong binding of inorganic P to Fe(III)- and Mn(IV)-oxhydroxides. The reductive dissolution of these compounds is likely to be a significant mechanism for P release into adjacent ecosystems when degraded fens are re-wetted, and can be simulated on the basis of the data for this fraction. The principal forms of organic P are inositol phosphates, phospholipids and nucleic acids or their degradation products, whilst sugar phosphates and phosphoproteins occur as organic P trace compounds (Anderson 1975, Harrison 1987, Stevenson 1986).

Peat with high humification has the largest content of P bound to humic substances, which is not immediately available (NaOH-P 42.7 % at H 10, 33.3 % at H 3). Larger P contents are found in the surface horizons of fens because they are more humified and enriched with metal oxides (HCl-P) and humic substances (NaOH-P) (Figure 4d). This relationship can be explained by the fact that humic substances are formed gradually during humification, and so are present at lower concentrations in little humified than in completely humified peat (Koppisch 2001). Due to the concomitant mineralisation, organic P from dead plant material in the process of decomposition and P from fertilisers is permanently fixed to these newly-formed humic substances, to organic decomposition products, and to metal oxides. At the same time, the peat is enriched by P due to humification.

Phosphorus adsorbed to metal oxides and acid-labile organic phosphorus
The concentration of HCl-SRP and HCl-NRP varied (Figure 4c). The ratio of labile organic P (HCl-NRP) to HCl-SRP was higher in little humified (H 3, H 4) than in completely humified (H 10) peat due to the low concentrations of P binding partners such as Fe, Mn, Al and Ca at H 3. In completely humified horizons, a large fraction of TP was adsorbed to metal oxides and acid labile organic P (HCl-TP) (33.4 % at H 10 compared with 9.5 % at H 3), and this could be released by re-wetting.

Phosphorus bound to humic substances
Organically bound P comprises 25-65 % of TP in mineral soils and 80 % in peat soils (Harrison 1987, Stevenson 1986, Scheffer & Schachtschabel 2002). The principal forms of organic P are inositol phosphates, phospholipids and nucleic acids or their degradation products, whilst sugar phosphates and phosphoproteins occur as organic P trace compounds (Anderson 1975, Harrison 1987, Stevenson 1986).

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Metals
The BD fraction simulates the reduction of Fe(III) to Fe(II) with concomitant release of P during re-wetting of fens. The duration of P release is unclear, but may persist for many years. We found high BD-TP contents in peat soil samples nine years after re-wetting, with the implication that large quantities of Fe were still available in oxidised form after this period of time.

Mn(IV) oxides can be neglected as P binding partners due to the occurrence of only minor concentrations in the BD extract. The results indicate that the predominant P binding mechanism involves Fe.
CONCLUSIONS

1. The results of sequential extraction indicate that only labile P, redox-sensitive P and part of the metal oxide-bound P could be released from the fen peat substrate by re-wetting.
2. Only 1% of the total phosphorus (TP) is present in labile form, and so presents no risk for increased nutrient release into adjacent ecosystems after re-wetting of fens.
3. High potential for release of phosphorus may exist in well and completely humified fen peat horizons with high Fe(III)-oxyhydroxide contents. If oxidised Fe remains after re-wetting, P may be released from these horizons over many years.
4. Phosphorus that is bound to humic substances and Rest-P can be disregarded as sources of nutrient release after re-wetting because these P binding forms are stable, organically bound and refractory, and thus not immediately available.
5. When re-wetting a drained fen, well humified horizons have to be taken into account because they have been changed pedogenetically.
6. The results of the P fractionation can be interpreted in terms of a qualified correlation with parallel detection of metals in the same extraction solvent (Hupfer 1995). Fe, Al, Mn and Ca are supposed to be potential sorption partners for P. As a rule, the content of P-binding metals in mineral soils and in peat substrates is higher than the content of P, so that all P may be bound to these elements (Tischner 2000). The solution properties of the sorption partners in the different extraction solvents differ sufficiently from one another to provide an indication of P release potential on re-wetting. No relationships of P with Al, Ca, Mn or DPD were found, so that P binding predominantly to Fe is indicated for peat samples from the locality investigated.

ACKNOWLEDGEMENTS

We thank Jörg Gelbrecht, Dominik Zak and the staff of the Central Chemical Laboratory, Leibniz Institute for Fresh Water Ecology and Fishery (IGB) for support in carrying out the chemical analyses and for interesting discussions. Louise Dunn made improvements to the text. The research was funded by the scholarship programme of the Deutsche Bundesstiftung Umwelt (DBU). This paper is based on a presentation by Sabine Jordan at the Fifth European Conference on Ecological Restoration held at Greifswald, Germany, in August 2006.

REFERENCES


