

Assessment of phosphorus associated with Fe and Al (hydr)oxides in sediments and soils

Jiří Jan^{1,2} · Jakub Borovec¹ · Jiří Kopáček¹ · Josef Hejzlar¹

Received: 23 September 2014 / Accepted: 17 March 2015 / Published online: 2 April 2015
© Springer-Verlag Berlin Heidelberg 2015

Abstract

Purpose Numerous extraction procedures have been used to characterize phosphorus (P) forms bound to iron (Fe) and aluminum (Al) (hydr)oxides in soils and sediments. We propose a simple modification of a widely used P fractionation method that more precisely quantifies P associated with active Fe and Al (hydr)oxides, which are mostly responsible for P binding and its potential release to water.

Materials and methods We modified the original sequential extraction [H₂O, bicarbonate-dithionite (BD), NaOH, HCl] by adding short (10-min) extractions with BD and NaOH prior to the respective original steps. The method was verified using (1) dissolution kinetics of Fe and Al minerals of different crystallinity and (2) liberation of P, Fe, and Al from natural samples of soils, sediments, and settling seston, containing different proportions of amorphous and crystalline Fe and Al (hydr)oxides. Extracted P was analyzed for reactive and non-reactive (mostly organic) P forms.

Results and discussion Both mineral and organic P forms associated with Fe and Al were almost completely liberated from the samples during the 10-min BD and NaOH extractions, respectively. Prolonged extraction period caused a

partial P re-adsorption onto the solid phase in some samples. The 10-min extractions were able to dissolve amorphous Fe and Al (hydr)oxides (ferrihydrite, amorphous AlOOH) and a portion of more crystalline Fe and Al minerals, approximately related to their surface area.

Conclusions The additional short extraction steps allow a rapid and more precise quantification of P associated with active Al and Fe (hydr)oxides, and better estimate the amounts of these Fe and Al forms in soils and sediments than the original method. Our simple modification of the traditional method thus provides new and useful information for environmental studies focused on potential P mobility across a solid phase-water interface.

Keywords Aluminum · Iron · Phosphorus · Sediment · Sequential fractionation · Soil

1 Introduction

Most of the phosphorus (P) on Earth is present in the particulate form (P_{part}). P_{part} in water bodies originates from both allochthonous sources, dominated by soil particles transported from the watershed by water and wind erosion, and autochthonous sources, dominated by internal biotic (photosynthetic and bacterial) production and abiotic processes (precipitation and adsorption) (Wetzel 2001). The origin of particles determines their composition and ability to adsorb or release P under changing environmental conditions. The most important binding partners for P in non-calcareous natural systems are iron (Fe) and aluminum (Al), specifically their numerous oxides, hydroxides, and oxyhydroxides, referred to in summary in this study as (hydr)oxides. Fe and Al (hydr)oxides naturally occur in a variety of forms, from amorphous to different degrees of crystallinity, with charge dependent on pH due to

Responsible editor: Brian Kronvang

Electronic supplementary material The online version of this article (doi:10.1007/s11368-015-1119-1) contains supplementary material, which is available to authorized users.

✉ Jakub Borovec
jborovec@hbu.cas.cz

¹ Biology Centre CAS, Institute of Hydrobiology, Na Sádkách 7, 370 05 České Budějovice, Czech Republic

² Faculty of Science, University of South Bohemia, Branišovská 31, 370 05 České Budějovice, Czech Republic

the partial hydrolysis of these metals in aquatic environments. The surface area and positive charge of Fe and Al (hydr)oxides affect their ability to bind phosphate and other anions, including organic molecules in sediments and soils (Kingston et al. 1972; Detenbeck and Brezonik 1991; Kaňa et al. 2001; De Vicente et al. 2008).

Both Fe and Al can be found in the form of free oxides or in association with other particles such as aggregates or coatings. Amorphous or slightly crystalline Fe (hydr)oxides (typically ferrihydrite) are present in environments with changing redox potentials, amorphous Al (hydr)oxides in conditions with changing acidity, while crystalline (hydr)oxides like goethite, hematite, or gibbsite are typical for old, well-weathered soils (Cornell and Schwertmann 2003; Berkowitz et al. 2006).

The importance of distinguishing between P bound to either Fe or Al (hydr)oxides has often been highlighted due to the striking differences in their behavior during biogeochemical transformations (Hansen et al. 2003; Kopáček et al. 2005). Fe and Al (hydr)oxides differ namely in their susceptibility to dissolution during changing environmental conditions. Fluctuating redox potentials affect the stability of ferric (hydr)oxides (Mortimer 1941, 1971) and pH increases above 8 cause the dissolution of Al (and partially also ferric) (hydr)oxides (Lake et al. 2006; Reitzel et al. 2013). Moreover, an increasing number of studies on the ability of sediments to retain or release P are based on various types of P/Al/Fe ratios obtained using various extractions (Rydin and Welch 1999; Rydin et al. 2000; Kopáček et al. 2005; De Vicente et al. 2008; Norton et al. 2008). These studies indicate that the amount of Fe and Al (hydr)oxides in sediments and soils has a direct influence on P mobility and hence on ecosystem structure and function.

Many extraction procedures, ranging from simple one-step extractions to more elaborate schemes involving multiple successive steps, have been used for many decades to characterize the amount of specific “P forms” in particles (Pierzynski 2000). Results of these methods are often difficult to compare, mostly due to their different abilities to dissolve the P-bearing solid phase. Consequently, the development of a method for accurate characterization of particle-associated P and more precise characterization of P-adsorbing phases and their capacity is of crucial importance for predicting the behavior of Ppart, as well as assessing its role in aquatic environments.

A widely used five-step extraction procedure by Psenner and Pucsko (1988) has proven very effective in distinguishing P bound to either Fe or Al (hydr)oxides by using consecutive extraction steps of dithionite buffered by bicarbonate (BD) followed by NaOH solution. The ability of this method to quantify different P, Fe, and Al forms extracted from various types of solids has been evaluated in previous studies (Lukkari et al. 2007; Jan et al. 2013). These studies, however, have indicated that the potential dissolution of more stable crystalline Fe and Al (hydr)oxides together with their active

amorphous forms during the BD and NaOH extractions represents a major disadvantage of this fractionation scheme. The proportion of active Fe and Al (hydr)oxides in the total concentrations of their forms in a sample is important missing information due to their principal role in the P-binding ability of soils and sediments. Active (hydr)oxides have larger specific surface areas than crystalline forms, and, consequently, high P sorption capacity (Lijklema 1980; McLaughlin et al. 1981; Cornell and Schwertmann 2003; De Vicente et al. 2008). They are also more susceptible to reductive dissolution, either by bacteria (Roden and Zachara 1996; Roden 2003) or at higher pH (Kennedy and Cooke 1982). The proportion of amorphous and crystalline minerals varies substantially in particles of different origin, age, and history of redox and pH changes (Cornell and Schwertmann 2003; Jan et al. 2013). For example, the properties of particles and their ability to bind P can substantially change during their transport from watersheds to water bodies and even within water bodies and their sediments. This highlights the importance of a more exact determination of P bound to amorphous Fe and Al (hydr)oxides, as well as better quantification of these active metal forms involved in P cycling in soils and sediments.

The aim of this study was to develop and test a simple modification of the widely used P-fractionation method by Psenner and Pucsko (1988) that would enable distinguishing between P associated with the active (mostly amorphous) forms versus less active (more crystalline) Fe and Al forms. The proposed modification is compatible with the original scheme, but gives better estimates of the active amorphous (hydr)oxides. Such information is important for environmental studies on sediment and soil sorption behavior, as well as for estimates of Fe electron acceptors available for bacterial processes.

2 Materials and methods

2.1 Fe and Al minerals

A variety of laboratory-prepared or commercially obtained Fe and Al minerals were chosen for experimental purposes: Fe (hydr)oxides of different crystallinity including ferrihydrite (Fer), lepidocrocite (Lep), goethite (Goe), and hematite (Hem) and a set of Al (hydr)oxides containing amorphous Al hydrous oxide (AmAl), bayerite (Bay), and gibbsite (Gib), and the silicate mineral kaolinite (Kao). Selected mineral characteristics are given in the Electronic Supplementary Material (1). For more details on mineral preparations and their x-ray analysis, see Jan et al. (2013). All minerals were used in a dry state, ground, and sieved through a 63- μm nylon sieve. The specific surface area of each mineral was determined by multipoint N_2 volumetric BET analysis (Brunauer

et al. 1938) using Autosorb iQ (Quantachrome Instruments, Boynton Beach, FL, USA).

2.2 Natural samples

We used a set of ten natural samples including soils, sediments, and settling seston (collected by sediment traps). Samples differed widely in their origin. Weathered soils and sediments from inlet parts of reservoirs with a high proportion of eroded allochthonous particles were assumed to contain a large proportion of crystalline (hydr)oxides (Cornell and Schwertmann 2003). Sediments sampled near the dam in deep reservoirs and in forest lakes were dominated by particles of autochthonous origin and contained mainly amorphous Fe and Al (hydr)oxides (Borovec J., unpublished data; Kopáček et al. 2001a). For detailed characteristics of the natural samples, see the Electronic Supplementary Material (2). Dry soil samples (provided by the Central Institute for Supervising and Testing in Agriculture, Czech Republic) were homogenized and sieved through a 63- μm nylon sieve prior to analysis. This size fraction includes clay and silt soil particles, which are usually transported from watersheds by erosion and form suspended solids in watercourses and sediments. Sediment samples were collected at several reservoirs in the Czech Republic in September 2011 by a gravity corer. Settling seston was repeatedly collected by sediment traps placed in the water column at a depth of 5 m near the dam of the Řimov Reservoir and exposed for 3-week intervals during winter 2011. Individual samples were freeze-dried and pooled. All natural soil and sediment samples were used for analyses in a freeze-dried state to ensure their long-term compositional stability and the possibility to repeat experiments.

To study the kinetics of the BD extraction, we used the following samples: (1) seston from sediment traps (Seston) as a representative of the non-crystallized material, (2) surface sediment from the Slezská Harta Reservoir with a high content of Fe (hydr)oxides of autochthonous origin and a low content of allochthonous particles (S-auto1), (3) surface sediment from the Ludkovice Reservoir with a high portion of eroded allochthonous particles (S-allo1), and (4) an old cambisol soil as a representative of samples with a high proportion of crystallized Fe (hydr)oxides (Soil1).

To study the kinetics of the NaOH extraction, we used the following samples: (1) sediment from two strongly atmospherically acidified lakes in the Bohemian Forest [Plešné Lake (S-auto2) and Čertovo Lake (S-auto3)]. These lakes receive a high terrestrial export of ionic Al from acidified soils and their sediments have an elevated content of freshly precipitated amorphous Al (Kopáček et al. 2001a, 2007). (2) Sediment of predominantly autochthonous origin (S-auto4) from the dystrophic Hamry Reservoir, with a forested watershed and a low terrestrial export of mineral particles. (3)

Sediment with a high proportion of allochthonous particles (S-allo2) from the Těrlicko Reservoir, with a mostly agricultural watershed. (4) Two soil samples [dystric cambisol (Soil2) and primary pseudogley (Soil3)], representing samples with a dominant proportion of old, crystallized Al (hydr)oxides.

2.3 Dissolution kinetics of Fe and Al minerals during the BD and NaOH extractions

Fe and Al in pure minerals were extracted using buffered dithionite reagent (BD; 0.1 M $\text{Na}_2\text{S}_2\text{O}_4$ +0.1 M NaHCO_3 , pH 7.2, 25 °C) and NaOH (1 M NaOH, 25 °C), respectively, as follows: ten ~20-mg subsamples of minerals were inserted into 50-ml polyethylene tubes and extracted with 40 ml of BD and/or NaOH on a horizontal shaker for time periods ranging from 5 min to 5 h (Fe minerals) and from 5 min to 20 h (Al minerals; see the Electronic Supplementary Material (3)). The BD reagent was prepared from deoxygenated H_2O and extraction tubes were inserted in a glove box under an N_2 atmosphere to prevent deterioration of dithionite by oxygen. After the extraction, samples were centrifuged at ~3000 \times g and extracts filtered through glass-fiber filters (0.4- μm pore size; MN GF-5, Macherey-Nagel, Düren, Germany) and analyzed for Fe or Al concentrations.

2.4 Dissolution kinetics of natural samples during the BD and NaOH extractions

Ten ~0.2-g (dry weight; DW) subsamples of natural samples were inserted into 50-ml polyethylene tubes and extracted with 40 ml of the relevant reagent on a horizontal shaker. Prior to the BD extraction, samples were extracted twice with deoxygenated H_2O for 10 min (each step) and centrifuged (Electronic Supplementary Material (4)). Then, the BD extraction lasted from 5 min to 6 h. Prior to the NaOH extraction, samples were extracted with H_2O as described above, and then with BD for 2 h, with a subsequent 5-min rinse using fresh BD reagent. The NaOH dissolution kinetics were then measured for time periods spanning from 5 min to 16 h. After extraction, samples were centrifuged, filtered, and analyzed for soluble reactive P (SRP), total P (TP), and Fe and Al concentrations as described later. Dissolved non-reactive P (NRP; mainly organically bound P) was calculated as the difference between the TP and SRP concentrations.

2.5 Sequential fractionation

The forms of P, Fe, and Al in sediments, soils, and seston were characterized using the extraction scheme by Psenner and Pucsko (1988, Electronic Supplementary Material (5)), modified as follows (Electronic Supplementary Material (6)): Samples of ~0.2 g DW were sequentially extracted

deoxygenated H₂O (10 min), BD (5 min+2 h), 1 M NaOH (5 min+16 h), and 0.5 M HCl (24 h). After each step, the sample was centrifuged at $\sim 3000\times g$, and the pellet was immediately exposed to fresh extraction solution for an additional 5-min extraction (except for the H₂O fraction; 10 min), centrifuged again, and both extracts were filtered and combined for analyses of SRP, TP, Fe, and Al. For more details on the full extraction scheme and the original extraction method by Psenner and Pucsko (1988), see Electronic Supplementary Material (5) and (6).

Compared to the original method by Psenner and Pucsko (1988), the original BD and NaOH extractions were thus divided into two steps, consisting of short 5-min BD (BD-I) and NaOH (NaOH-I) extractions inserted prior to the original 2-h BD (BD-II) and 16-h NaOH (NaOH-II) extraction steps (Electronic Supplementary Material (6)). The time of the short BD-I and NaOH-I extractions was based on the results of dissolution kinetics (see below) and was set to a total time of 10 min (i.e., two 5-min steps). The second 5-min extraction is also used to completely wash P liberated in the previous step. A similar 5-min washing step was also inserted after the original 24-h extraction step with 0.5 M HCl. Instead of the final step of the scheme by Psenner and Pucsko (1988), i.e., extraction with hot NaOH, we determined the concentrations of residual P, Fe, and Al in freeze-dried solids remaining after the HCl extraction step. All extractions were done in duplicates and their averages were used for subsequent evaluations.

2.6 Surface-specific extraction efficiency of BD and NaOH extractions

Amounts of Fe and Al extractable from minerals during the BD-I and NaOH-I steps were compared with 2- and 16-h extractions (plus additional 5-min extraction), respectively, to provide a surface-specific extraction efficiency. The Fe and Al amounts dissolved during extractions were divided by the surface area of minerals (Electronic Supplementary Material (1)) to show the ability of extractions to dissolve Fe and Al from individual minerals related to their surface area.

2.7 Analysis

Concentrations of TP, Fe, and Al in all samples (solids as well as extracts) were measured colorimetrically after nitric-perchloric acid digestion (Kopáček et al. 2001b). SRP concentrations were determined according to Murphy and Riley (1962), using a flow injection analyzer (Lachat QuikChem 8500; Lachat Instruments, Loveland, CO, USA). Concentrations of dissolved organic carbon (DOC) in extracts were determined using a TOC analyzer (TOC-5000A; Shimadzu, Kyoto, Japan). All analyzed samples had at least five times higher P, Fe, Al, and DOC concentrations than the detection limits of the respective methods, i.e., 0.1, 1, 2, and

20 $\mu\text{mol l}^{-1}$. The TP, SRP, Fe, and Al extracted by individual extraction steps are abbreviated in the text, with each step specified by a subscript (for additional information see the Electronic Supplementary Material (6)).

3 Results

3.1 Dissolution kinetics of Fe and Al minerals and surface extraction efficiency

All of the tested Fe (hydr)oxides were almost completely dissolved during the 5-h BD extraction (Fig. 1). The extraction efficiency differed for the individual Fe (hydr)oxides at the beginning of this step, with 86 % of Fe dissolved from the amorphous ferrihydrite during the first 10 min, but only 56, 32, and 17 % of Fe dissolved from the more crystalline Fe forms (lepidocrocite, goethite, and hematite, respectively) during this period. The differences in the proportion of Fe liberated from individual (hydr)oxides decreased with increasing extraction time, and 69–100 % of Fe was already dissolved after 2 h (Fig. 1). It is also evident that surface-specific extraction efficiencies for Fe in the BD-I step were in a more narrow range than after 2-h extraction (34–115 vs. 39–209 $\mu\text{mol m}^{-2}$; Table 1). This indicates that the short extraction dissolves mostly surface (and potentially active) parts of crystalline (hydr)oxides, while longer extraction steps also dissolve the inactive inner parts of Fe minerals. Similarly, 100 % of Al was

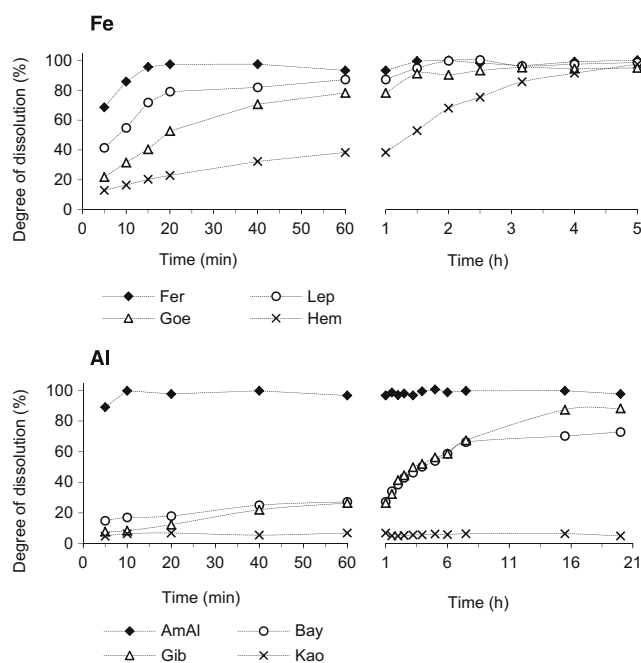


Fig. 1 Kinetics of Fe and Al dissolution during dithionite (BD) and NaOH extractions from Fe and Al minerals, respectively. *Fer* ferrihydrite, *Lep* lepidocrocite, *Goe* goethite, *Hem* hematite, *AmAl* amorphous AlOOH, *Bay* bayerite, *Gib* gibbsite, *Kao* kaolinite. For details, see Electronic Supplementary Material (1)

Table 1 Concentrations of Fe and Al extracted from minerals by dithionite (BD) and NaOH, respectively

| Minerals | BD (5 min+5 min) | | BD (2 h+5 min) | |
|---------------|--|--------------------------------|--|--------------------------------|
| | Concentration Fe (mmol g ⁻¹) | SEE Fe (μmol m ⁻²) | Concentration Fe (mmol g ⁻¹) | SEE Fe (μmol m ⁻²) |
| Ferrihydrite | 8.92 | 33.7 | 10.4 | 39.3 |
| Lepidocrocite | 6.25 | 115 | 11.4 | 209 |
| Goethite | 3.60 | 38.2 | 10.3 | 109 |
| Hematite | 1.93 | 47.9 | 7.95 | 197 |
| | NaOH (5 min+5 min) | | NaOH (16 h+5 min) | |
| | Concentration Al (mmol g ⁻¹) | SEE Al (μmol m ⁻²) | Concentration Al (mmol g ⁻¹) | SEE Al (μmol m ⁻²) |
| Amorph. AlOOH | 11.2 | 50.3 | 11.2 | 50.3 |
| Bayerite | 2.11 | 45.6 | 8.70 | 188 |
| Gibbsite | 1.06 | 88.2 | 11.0 | 917 |
| Kaolinite | 0.80 | 67.5 | 0.80 | 67.5 |

Extractions differed in duration for BD (5 min+5 min vs. 2 h+5 min) and NaOH (5 min+5 min vs. 16 h+5 min). The amount of extracted Fe and Al during these extractions related to the surface area of individual minerals is expressed as the surface-specific extraction efficiency (SEE)

dissolved from amorphous Al (hydr)oxide, while only 17, 8, and 6 % Al were dissolved from bayerite, gibbsite, and kaolinite during the first 10 min of extraction (Fig. 1). Complete dissolution of crystalline bayerite and gibbsite was not reached even after 20 h of extraction. The 16-h step commonly used in extraction schemes was only sufficient to extract 70 and 87 % Al from these two minerals, respectively. Only 6 % of the silicate kaolinite was dissolved after 20 h of extraction (Fig. 1). The results of surface-specific extraction efficiencies of Al minerals were in a more narrow range for all minerals after 10 min than after 16 h of extraction (46–88 vs. 50–917 μmol m⁻²; Table 1).

3.2 Dissolution kinetics of natural samples

More than 95 % of TP that was BD extractable was extracted during the first 10 min (equivalent to the BD-I step) from all tested natural samples (Fig. 2). The proportion of SRP_{BD} in TP_{BD} was uniform during the 6-h extraction and varied from 60 to 100 % for individual minerals. Two samples (S-allo1 and Soil1) exhibited decreasing TP and SRP concentrations with the continuing extraction. Similarly to the BD extraction, >87 % of TP that was NaOH extractable was already extracted during the first 10 min (equivalent to the NaOH-I step) from all samples (Fig. 3). The proportion of SRP_{NaOH} in TP_{NaOH} was also uniform during the whole 16-h extraction, but was lower (35–70 %) than in the BD extraction. The TP_{NaOH} thus contained a higher proportion of NRP than TP_{BD}.

The highest Fe concentrations occurred in the BD extracts from all natural samples after the longest extraction time of 6 h (Fig. 2). More than 90 % of Fe was liberated by the BD extraction during the first 10 min from particles of mostly

autochthonous origin (Seston and S-auto1). In contrast, this short extraction only liberated 62 and 32 % of Fe from samples with a higher proportion of allochthonous particles (S-

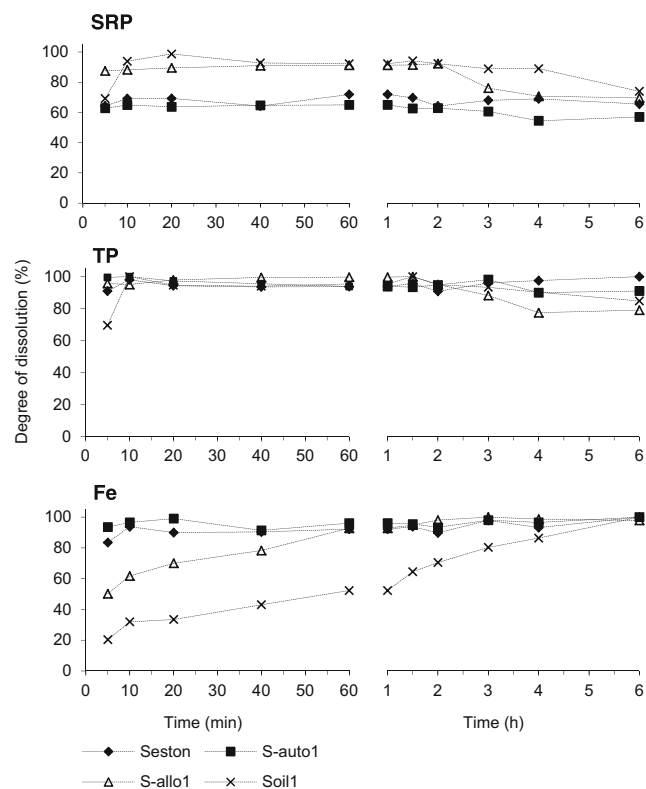


Fig. 2 Kinetics of soluble reactive phosphorus (SRP), total phosphorus (TP), and Fe liberation from natural samples during dithionite (BD) extraction. Data for TP and Fe are related to the respective maximum concentrations observed during this experiment. Data for SRP are shown as a percentage of TP concentrations. For sample abbreviations, see Electronic Supplementary Material (2)

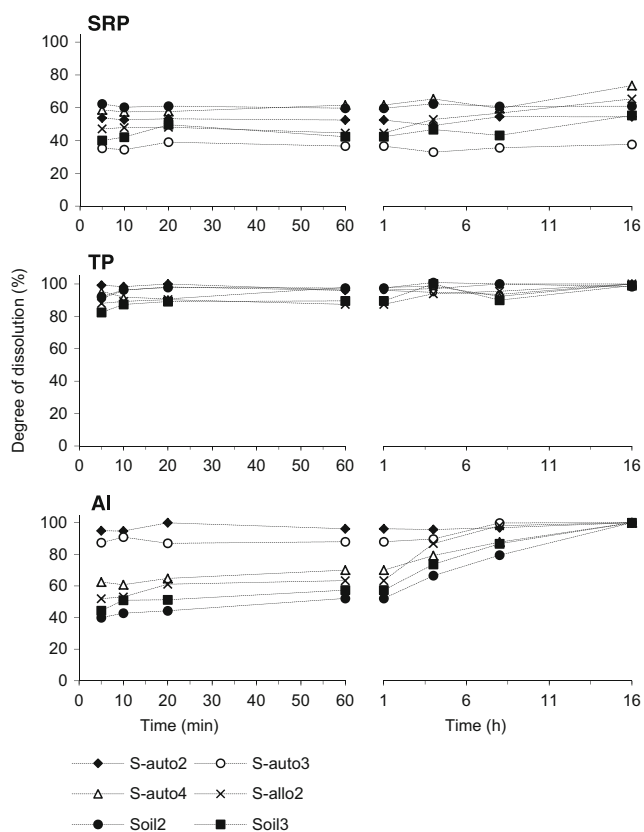


Fig. 3 Kinetics of soluble reactive phosphorus (SRP), total phosphorus (TP), and Al liberation from natural samples during NaOH extraction. Data for TP and Al are related to the respective maximum concentrations observed during this experiment. Data for SRP are shown as a percentage of TP concentrations. For sample abbreviations, see Electronic Supplementary Material (2)

allo1 and Soil1). Concentrations of extracted Fe from S-allo1 and Soil1 then increased with increasing extraction time (e.g., 93 and 52 % after 1 h, and 98 and 71 % after 2 h, respectively). But, even the 6-h BD extraction did not completely dissolve Fe from cambisol Soil1 (Fig. 2).

A pattern analogous to the Fe extraction by BD occurred during the Al extraction by NaOH (Fig. 3). The 10-min NaOH extraction liberated >90 % of Al from particles of mainly autochthonous origin (S-auto2 and S-auto3), but only 43 % from a soil sample (Soil2).

3.3 Sequential fractionation of natural samples

The BD-I step liberated on average (\pm standard deviation) 82 ± 5 % of SRP extracted by both BD-I and BD-II ($SRP_{BD-I+II}$) and 84 ± 5 % of $TP_{BD-I+II}$ from all samples. Similarly, the SRP_{NaOH-I} and TP_{NaOH-I} represented 84 ± 10 and 88 ± 7 % of their total amounts extracted by both NaOH steps in all samples regardless of their composition.

Amounts of Fe and Al extracted by individual steps of the sequential fractionation reflected differences in sample composition (Figs. 4 and 5) and were consistent with the

dissolution kinetics (Figs. 2 and 3). Fe_{BD-I} represented almost 90 % of the Fe extracted by both the BD-I and BD-II ($Fe_{BD-I+II}$) steps from particles of mostly autochthonous origin (Seston and S-auto), but only 61 and 41 % from the more crystalline samples S-allo1 and Soil1, respectively. The NaOH-I step extracted up to 97 % of $Al_{NaOH-I+II}$ from the sediments of acidified lakes (S-auto2 and S-auto3), but only 44 % from soil sample Soil2.

The unequal extractability of P versus Fe and Al by the BD-I, BD-II, NaOH-I, and NaOH-II steps affected the Fe/P and Al/P molar ratios obtained for the short (I) and the whole (I+II) extraction steps. Samples with a higher proportion of autochthonous particles (Seston, S-auto1) had similar Fe_{BD-I}/P_{BD-I} and $Fe_{BD-I+II}/P_{BD-I+II}$ ratios (Electronic Supplementary Material (7)) because most of the P and Fe were extracted during the first extraction step. Analogously, samples S-auto2 and S-auto3 had similar Al_{NaOH-I}/P_{NaOH-I} and $Al_{NaOH-I+II}/P_{NaOH-I+II}$ ratios (Electronic Supplementary Material (8)) due to the high amorphous proportion in the total Al (hydr)oxides in these samples. In contrast, differences between the Fe/P and Al/P ratios obtained by the first and both extraction steps were higher in samples with a higher proportion of allochthonous particles, especially soils. The Fe_{BD-I}/SRP_{BD-I} was 11 vs. 20 for $Fe_{BD-I+II}/SRP_{BD-I+II}$ and Al_{NaOH-I}/SRP_{NaOH-I} was 12–14 vs. 23–25 for $Al_{NaOH-I+II}/SRP_{NaOH-I+II}$ for soil samples (Electronic Supplementary Material (7) and (8)).

The respective Fe/SRP for BD-I and Al/SRP for NaOH-I ratios varied in wider ranges (11–21 and 12–38) than the Fe/TP and Al/TP ratios (10–14 and 7–15) for individual samples in these 10-min fractions (Electronic Supplementary Material (7) and (8)) because most of the NRP (mainly formed by organic P forms) was extracted in the first step and formed an important part of TP. This liberation of organic P closely accompanied the simultaneous extraction of DOC in the BD-I and NaOH-I steps (Figs. 4 and 5).

4 Discussion

In our modification of the fractionation method by Psenner and Pucsko (1988), we used different lengths of extraction steps to distinguish between highly soluble and less soluble Fe and Al (hydr)oxides, assuming that the more soluble forms play a major role in P sorption and release.

4.1 Dissolution kinetics of Fe and Al (hydr)oxides

The BD extractions of synthetic minerals confirmed different extraction rates for Fe (hydr)oxides of different crystallinity (Fig. 1). Similar results have also been observed for other solvents (Torrent et al. 1987; Postma 1993; Houben 2003). Almost all Fe (hydr)oxides (including highly crystalline

Fig. 4 Soluble reactive phosphorus (*SRP*), total phosphorus (*TP*), non-reactive phosphorus (*NRP*), dissolved organic carbon (*DOC*), and Fe concentrations in BD-I and subsequent BD-II fractions in natural samples of sediments and soils

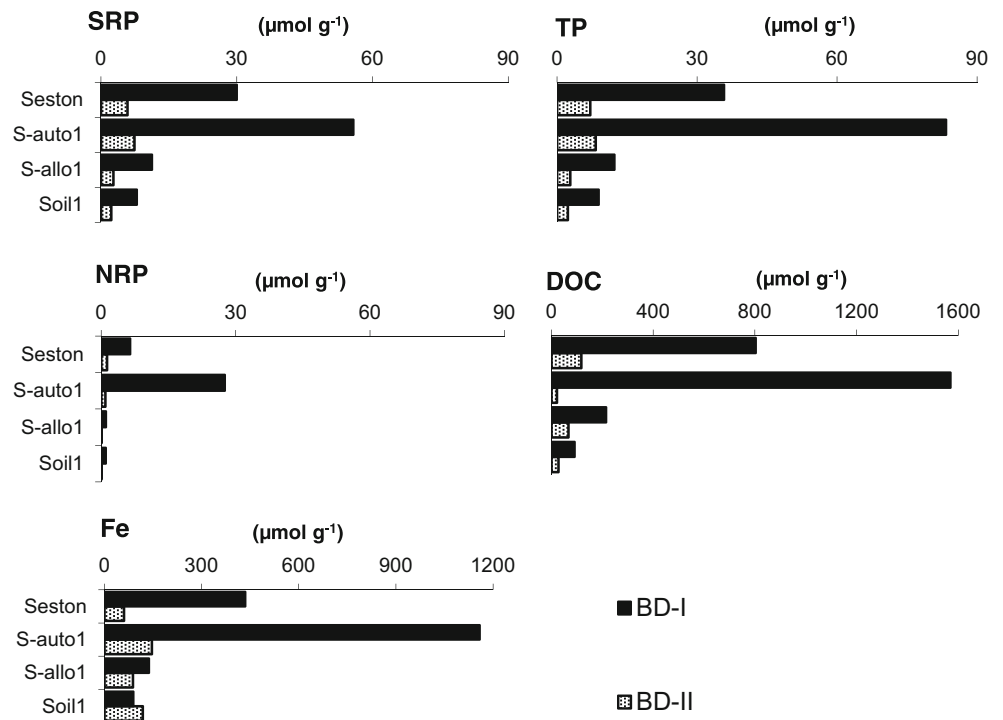
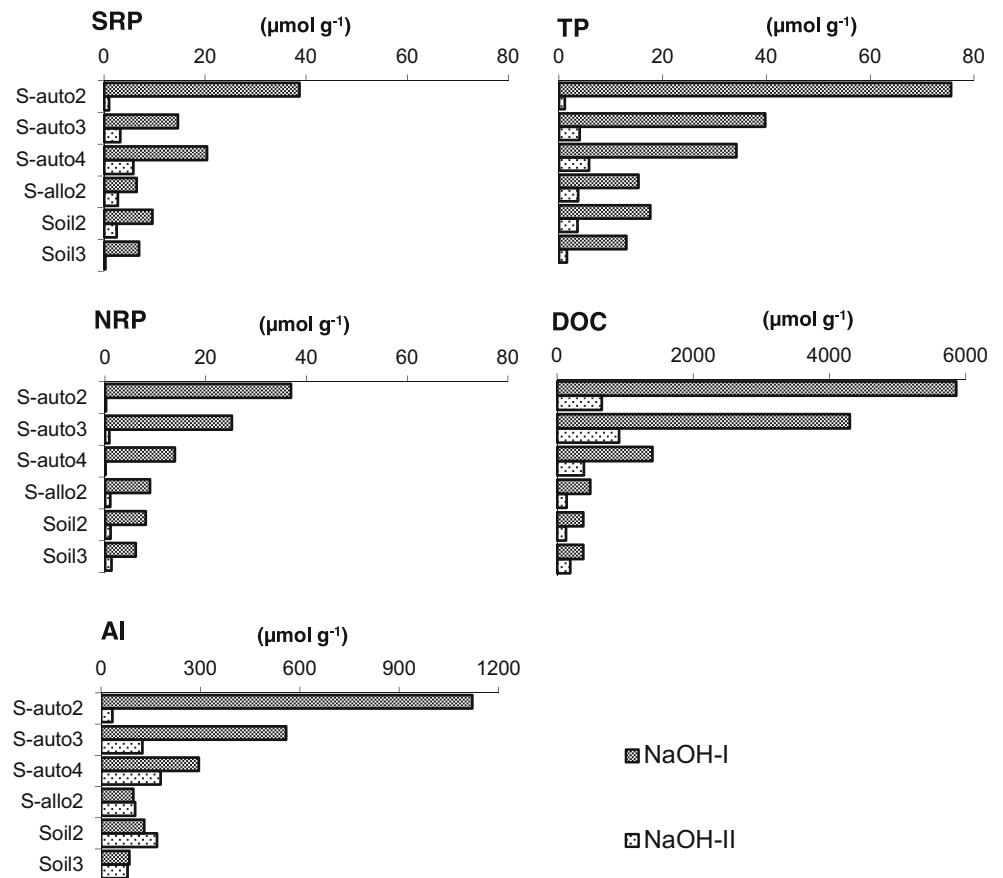


Fig. 5 Soluble reactive phosphorus (*SRP*), total phosphorus (*TP*), non-reactive phosphorus (*NRP*), dissolved organic carbon (*DOC*), and Al concentrations in NaOH-I and subsequent NaOH-II fractions in natural samples of sediments and soils



forms) were dissolved during the 5-h extraction (Fig. 1). Thus, the long extraction step can be successfully used for determining total Fe in the form of (hydr)oxides (Jensen and Thamdrup 1993; Jan et al. 2013). In contrast, the 10-min extractions provided estimates of the less crystalline Fe (hydr)oxides or the surface fraction of the more crystalline (hydr)oxides, which could increase the usefulness of the Psenner and Pucsko (1988) fractionation method. The preferential dissolution of the surface fraction of crystalline minerals is indicated by the similar values of surface-specific extraction efficiencies obtained for individual minerals during the 10-min extraction compared to the 2-h extraction (Table 1). The remaining crystalline minerals were not dissolved during the 10-min extraction and a longer time was needed for their complete dissolution. Surface area affects the reactivity of minerals more than the type of particular (hydr)oxide species (Cornell and Schwertmann 2003) and determines the rapidity of their reduction and dissolution (Torrent et al. 1987; Roden and Zachara 1996; Roden 2003; Houben 2003; Martynova 2010) as well as their ability to bind P (McLaughlin et al. 1981; Schwertmann 1988; Fontes and Weed 1996).

The extractions of natural samples showed that most of the Fe and Al was extracted from samples with a high proportion of autochthonous particles during the BD-I (Seston, S-auto1) and NaOH-I (S-auto2, S-auto3) steps (Figs. 2 and 3). The sediment S-auto4 from a dystrophic reservoir with forested catchment represented a transition between sediments originated by predominantly autochthonous (S-auto2 and S-auto3) and allochthonous (S-allo2, Soil2, and Soil3) origin. This sediment is formed by a mixture of largely crystalline Al forms, originating from erosions, and amorphous Al formed by in-lake photochemical liberation of organically bound Al (Kopáček et al. 2009). Consequently, Al dissolution from S-auto4 was slower than from the S-auto2 and S-auto3 samples, but faster than from Soil2 and Soil3 (Fig. 3).

4.2 Efficiency of extraction steps to liberate P forms from Fe and Al (hydr)oxides

Almost all SRP and TP was liberated from the natural samples during the BD-I and NaOH-I extractions (Figs. 2 and 3). Even though the longer extraction liberated additional Fe and Al from samples containing more crystalline (hydr)oxides, the extracted amount of P did not increase. A similar phenomenon was also observed by Jensen and Thamdrup (1993) for marine sediments, but their experiment lasted from 1 to 4 h and did not include shorter extraction steps. The kinetics of SRP liberation from samples highlighted another advantage of the BD-I step and support our modification. The BD-I extraction liberated more SRP than longer extractions. The observed decrease in SRP concentrations during prolonged extraction of samples S-allo1 and Soil1 (Fig. 2) was probably caused by a partial re-adsorption of P liberated from Fe (hydr)oxides to

other active components of the samples, probably Al (hydr)oxides. This phenomenon could cause an underestimation of the actual saturation level of Fe minerals with P. The P re-adsorptions during both the BD and NaOH extractions and formation of new P phases have already been observed, e.g., by Hupfer et al. (2009), who also suggested to shorten the extraction time to avoid this effect. Another advantage of shortening the NaOH extraction might be a reduction of organic compound hydrolysis during long extraction (Turner et al. 2003; Zak et al. 2008).

NRP includes a high variety of organic P forms (Reitzel et al. 2006; Turner et al. 2003) and forms Fe-NRP and Al-NRP complexes (e.g., De Groot and Golterman 1993; Ognalaga et al. 1994; Paludan and Jensen 1995; Qiu and McComb 2000; Jensen et al. 2005). These NRP compounds are still difficult to exactly define, and their determination is frequently omitted from fractionation schemes. NRP may importantly contribute to the total sediment P, as was demonstrated for samples Seston and S-auto1 by the BD-I extraction, and for all tested samples by the NaOH-I extraction (Figs. 4 and 5). Organic P forms can be released under anoxic conditions from sediments to the water (Föllmi 1996). Part of the NRP and Fe extracted in the BD fraction may also originate from the simultaneous dissolution of humic substances (Jensen et al. 2005). NRP in the BD and NaOH extracts from natural samples thus represents a quantitatively (but probably also environmentally) important part of TP, which undoubtedly deserves more attention in future fractionation studies.

4.3 Implications for P fractionation studies

The important contribution of NRP to TP in the BD and NaOH extracts, observed for the majority of natural samples (Figs. 4 and 5), should be kept in mind when using the Fe/P and Al/P ratios in environmental applications of fractionation results. For example, the Fe_{BD-I}/SRP_{BD-I} ratio of 21 indicates low P saturation of Fe (hydr)oxides in sample S-auto1, while its Fe_{BD-I}/TP_{BD-I} ratio of 14 suggests a relatively greater Fe saturation with P in this sample. NRP compounds may be to a large extent bioavailable (Reitzel et al. 2006) and may represent an important P source for lake water as well as soil solutions. Both Al/SRP and Al/TP ratios should be taken into account when evaluating the P sorption capacity of sediments (or a potential P release under anoxic conditions or elevated pH) in environmental studies. Consequently, we recommend including both SRP and TP determinations in all P fractionation studies.

Our results show that most SRP and TP associated with Fe and Al (hydr)oxides are liberated during the short BD-I and NaOH-I extractions (Figs. 2 and 3), i.e., during dissolution of the most P-active Fe and Al (hydr)oxides. These results also have implications for using P/Al/Fe ratios in environmental studies. SRP/Al ratios are often used for evaluating the

efficiency of P inactivation by Al after addition of Al salts to the water column during lake restorations (e.g., Rydin and Welch 1999; Rydin et al. 2000), as well as the stability of P burial in sediments and its possible release during anoxia (Kopáček et al. 2005; Norton et al. 2008). Similar evaluations also would benefit from estimates of the proportions of less and more crystalline Al (hydr)oxides in sediments. Fresh colloidal Al (hydr)oxides are formed in the water column (1) after artificial Al addition during lake restoration, (2) in acidified areas with elevated terrestrial export of ionic Al, and (3) naturally by photochemical liberation of organically bound Al (e.g., Rydin et al. 2000; Kopáček et al. 2009). Implementation of both NaOH-I and NaOH-II steps into the fractionation scheme could help distinguish fresh and active Al forms, mostly of autochthonous origin, from more crystalline and less active Al compounds entering sediments from the erosion of soils in the watershed. The currently used 16-h NaOH extraction step probably provides inaccurate results for samples with a high content of crystalline Al due to their low P sorption ability, but still a high solubility of crystalline Al (hydr)oxides during such a long period.

Similarly, the commonly used long BD extraction is able to dissolve even poorly active or inactive parts of crystalline Fe (hydr)oxides such as goethite and hematite. The short (BD-I) extraction is thus more appropriate for the determination of Fe, which can be potentially reduced in anoxic sediments, and estimates of P saturation.

5 Conclusions

We propose a simple modification of the widely used P fractionation method, which involves the division of dithionite (BD) and NaOH extractions into short (10-min) and long (original length) steps. The incorporation of the short extraction steps is based on the dissolution kinetics of Fe and Al (hydr)oxides measured for a set of artificially prepared Fe and Al minerals and natural samples of soils, sediments, and settling seston with different proportions of active Fe and Al (hydr)oxides. The dissolution kinetics confirmed different dissolution rates for (hydr)oxides of different crystallinity. The short extraction periods are a good tool for estimating the amount of less crystalline (hydr)oxides with greater specific surface area and higher importance for P cycling. The 10-min extraction steps are also sufficient for the extraction of most of the mineral and organic P. An additional advantage of the short extraction is the prevention of P re-adsorption to other active components in the sample, which may occur during the original long extractions. We believe that our modification provides a more complex and accurate determination of P forms, and better estimates of their active binding partners in soils and sediments than the original method.

Acknowledgments This study was supported by the Grant Agency of the Czech Republic (project no. 206/09/1764 and P504/13-17398S) with additional support by the Grant Agency of the University of South Bohemia (GAJU142/2010/P). We thank Dr. D. Sirová for proofreading.

References

- Berkowitz J, Anderson MA, Amrhein C (2006) Influence of aging on phosphorus sorption to alum floc in lake water. *Wat Res* 40:911–916
- Brunauer S, Emmett PH, Teller E (1938) Adsorption of gases in multimolecular layers. *J Am Chem Soc* 60:309–319
- Cornell RM, Schwertmann U (2003) The iron oxides: structure, properties, reactions, occurrences and uses, 2nd edn. Wiley-VCH
- De Groot CJ, Golterman HL (1993) On the presence of organic phosphate in some Camargue sediments: evidence for the importance of phytate. *Hydrobiologia* 252:117–126
- De Vicente I, Huang P, Andersen FO, Jensen HS (2008) Phosphate adsorption by fresh and aged aluminum hydroxide. Consequences for lake restoration. *Environ Sci Technol* 42:6650–6655
- Detenbeck NE, Brezonik PL (1991) Phosphorus sorption by sediments from a soft-water seepage lake. 2. Effects of pH and sediment composition. *Environ Sci Technol* 25:403–409
- Föllmi KB (1996) The phosphorus cycle, phosphogenesis and marine phosphate-rich deposits. *Earth Sci Rev* 40:55–124
- Fontes MPF, Weed SB (1996) Phosphate adsorption by clays from Brazilian oxisols: relationships with specific surface area and mineralogy. *Geoderma* 72:37–51
- Hansen J, Reitzel K, Jensen HS, Andersen FØ (2003) Effects of aluminum, iron, oxygen and nitrate additions on phosphorus release from the sediment of a Danish softwater lake. *Hydrobiologia* 492:139–149
- Houben G (2003) Iron oxide incrustations in wells. Part 2: chemical dissolution and modeling. *Appl Geochem* 8:941–954
- Hupfer M, Zak D, Roßberg R, Herzog C, Pöthig R (2009) Evaluation of a well-established sequential phosphorus fractionation technique for use in calcite-rich lake sediments: identification and prevention of artifacts due to apatite formation. *Limnol Ocean Methods* 7:399–410
- Jan J, Borovec J, Kopáček J, Hejzlar J (2013) What do results of common sequential fractionation and single-step extractions tell us about P binding with Fe and Al compounds in non-calcareous sediments? *Wat Res* 47:547–557
- Jensen HS, Thamdrup B (1993) Iron-bound phosphorus in marine sediments as measured by bicarbonate-dithionite extraction. *Hydrobiologia* 253:47–59
- Jensen HS, Caraco N, Hansen J, Christensen KK (2005) Humic-bound phosphorus in soil and sediment. In: Golterman HL, Serrano L (eds) Phosphate in sediments: proceedings of the 4th international symposium Carmona (Spain), 9–12 September 2003. Backhuys Publishers, Leiden, pp 99–107
- Kaňa J, Kopáček J, Camarero L, Garcia-Pausas J (2001) Phosphate sorption characteristics of European alpine soils. *Soil Sci Soc Am J* 75: 862–870
- Kennedy RH, Cooke GD (1982) Control of lake phosphorus aluminium sulfate: Dose determination and application techniques. *Wat Res Bull* 18:389–395
- Kingston FJ, Posner AM, Quirk JP (1972) Anion adsorption by goethite and gibbsite. I. The role of the proton in determining adsorption envelopes. *J Soil Sci* 23:177–192
- Kopáček J, Borovec J, Hejzlar J, Porcal P (2001a) Spectrophotometric determination of iron, aluminum, and phosphorus in soil and sediment extracts after their nitric and perchloric acid digestion. *Commun Soil Sci Plant Anal* 32:1431–1443

- Kopáček J, Ulrich KU, Hejzlar J, Borovec J, Stuchlik E (2001b) Natural inactivation of phosphorus by aluminum in atmospherically acidified water bodies. *Water Res* 35:3783–3790
- Kopáček J, Borovec J, Hejzlar J, Ulrich KU, Norton SA, Amirbahman A (2005) Aluminum control of phosphorus sorption by lake sediments. *Environ Sci Technol* 39:8784–8789
- Kopáček J, Marešová M, Hejzlar J, Norton SA (2007) Natural inactivation of phosphorus by aluminum in preindustrial lake sediments. *Limnol Ocean* 52:1147–1155
- Kopáček J, Hejzlar J, Kaňa J, Norton SA, Porcal P, Turek J (2009) Trends in aluminium export from a mountainous area to surface waters, from deglaciation to the recent: effects of vegetation and soil development, atmospheric acidification, and nitrogen-saturation. *J Inorg Biochem* 103:1439–1448
- Lake T, Jin X, Wang S, Pang Y, Chang F (2006) Phosphorus fractions and the effect of pH on the phosphorus release of the sediments from different trophic areas. *Environ Pollut* 139:288–295
- Lijklema L (1980) Interaction of orthophosphate with iron(III) and aluminum hydroxides. *Environ Sci Technol* 14:537–541
- Lukkari K, Hartikainen H, Leivuori M (2007) Fractionation of sediment phosphorus revisited: I. Fractionation steps and their biogeochemical basis. *Limnol Ocean Methods* 5:433–444
- Martynova MV (2010) Iron compound occurrence forms in freshwater deposits: analytical review. *Wat Resour* 37:488–496
- McLaughlin JR, Ryden JC, Syers JK (1981) Sorption of inorganic phosphate by iron and aluminum containing components. *J Soil Sci* 32:365–377
- Mortimer CH (1941) The exchange of dissolved substances between mud and water in lakes. *J Ecol* 29:280–329
- Mortimer CH (1971) Chemical exchanges between sediments and water in the Great Lakes: speculations on probable regulatory mechanisms. *Limnol Ocean* 16(2):387–404
- Murphy J, Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. *Analyt Chim Acta* 27:31–36
- Norton SA, Coolidge K, Amirbahman A, Bouchard R, Kopáček J, Reinhardt R (2008) Speciation of Al, Fe, and P in recent sediment from three lakes in Maine, USA. *Sci Tot Environ* 404:276–283
- Ognalaga M, Frossard E, Thomas F (1994) Glucose-1-phosphate and myo-inositol hexaphosphate adsorption mechanisms on goethite. *Soil Sci Soc Am J* 58:332–337
- Paludan C, Jensen HS (1995) Sequential extraction of phosphorus in freshwater wetland and lake sediment: significance of humic acids. *Wetlands* 15:365–373
- Pierzynski GM (ed) (2000) Methods of phosphorus analysis for soils, sediments, residuals, and waters. Southern Cooperative Series Bulletin No. 396. URL, North Carolina State University
- Postma D (1993) The reactivity of iron oxides in sediments: a kinetic approach. *Geochim Cosmochim Acta* 57:5027–5034
- Psenner R, Pucsko R (1988) Phosphorus fractionation: advantages and limits of the method for the study of sediment P origins and interactions. *Arch Hydrobiol Beih Ergebn Limnol* 30:43–59
- Qiu S, McComb A (2000) Properties of sediment phosphorus in seven wetlands of the Swan Coastal Plain, south-western Australia. *Wetlands* 20(2):267–279
- Reitzel K, Ahlgren J, Gogoll A, Jensen HS, Rydin E (2006) Characterization of phosphorus in sequential extracts from lake sediments using ^{31}P nuclear magnetic resonance spectroscopy. *Can J Fish Aquat Sci* 63:1686–1699
- Reitzel K, Jensen HS, Egemose S (2013) pH dependent dissolution of sediment aluminum in six Danish lakes treated with aluminum. *Wat Res* 47:1409–1420
- Roden EE (2003) Fe(III) oxide reactivity toward biological versus chemical reduction. *Environ Sci Technol* 37:1319–1324
- Roden EE, Zachara JM (1996) Microbial reduction of crystalline iron(III) oxides: influence of oxide surface area and potential for cell growth. *Environ Sci Technol* 30:1618–1628
- Rydin E, Welch E (1999) Dosing Al to Wisconsin lake sediments based on possible formation of aluminum bound phosphate. *Lake Reserv Manag* 15:324–331
- Rydin E, Huser B, Welch E (2000) Amount of phosphorus inactivated by Al treatments in Washington lakes. *Limnol Ocean* 45:226–230
- Schwertmann U (1988) Some properties of soil and synthetic iron oxides. In: Stucki JW, Goodman BA, Schwertmann U (eds) Iron in soils and clay minerals SE—9. Springer, Netherlands, pp 203–250
- Torrent J, Schwertmann U, Barron V (1987) The reductive dissolution of synthetic goethite and hematite in dithionite. *Clay Min* 22:329–337
- Turner BL, Mahieu N, Condrón LM (2003) Phosphorus-31 nuclear magnetic resonance spectral assignments of phosphorus compounds in soil NaOH-EDTA extracts. *Soil Sci Soc Am J* 67:497–510
- Wetzel RG (2001) *Limnology, lake and river ecosystems*, 3rd edn. Academic Press
- Zak D, Gelbrecht J, Wagner C, Steinberg CEW (2008) Evaluation of phosphorus mobilization potential in rewetted fens by an improved sequential chemical extraction procedure. *Eur J Soil Sci* 59:1191–1201