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Determination of eutrophication potential of particles in rivers and waterbody sediments

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Ph.D. Thesis

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Annotation

Extraction solutions were assessed to find the most appropriate method for characterisation of particles in the context of release or uptake phosphorus in non-calcareous regions. Advantages and limitations of methods for determination of different phosphorus (P) forms and its important binding components – iron and aluminium (hydr)oxides, were pointed out. Characterisations of these forms, that show highly different behaviour under changing environmental conditions, were used for the assessment of particles saturation with respect to P. Sorption/desorption behaviour of soil particles susceptible to erosion and their content of plant available P was tested. Strong correlation, which is dependent on P saturation ratio, was used to propose a method for the determination of soil erosion impact to supply dissolved P in stream waters of variable dissolved P concentration.

Declaration [in Czech]

Prohlašuji, že svoji disertační práci jsem vypracovala samostatně pouze s použitím pramenů a literatury uvedených v seznamu citované literatury.

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Jan Jiří

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List of papers and manuscripts with author's contribution

The thesis is based on the following manuscripts:

I. 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? Water Res. 47, 547–557. (2013 IF = 5.323)

Jiří Jan designed the experiment setup, prepared samples, carried out laboratory measurements and prepared the manuscript with the help of co-authors

II. Jan, J., Borovec, J., Kopáček, J., Hejzlar, J., 2015. Assessment of phosphorus associated with Fe and Al (hydr)oxides in sediments and soils. J. Soils Sediments 15, 1620–1629. (2014 IF = 2.139)

Jiří Jan designed the experiment setup, collected samples, carried out laboratory experiments and prepared the manuscript with the help of co-authors

III. Borovec, J., Jan, J., (manuscript draft). Simple empirical tool for predicting the behaviour of eroded particle-associated phosphorus in streams.

Jiří Jan participated in the design of the experimental setup, data analyses and writing of the manuscript

Content

Introduction

Eutrophication

Eutrophication has become one of the biggest water quality problems for inland and coastal marine waters around the world today (Schindler, 2006; Smith et al., 2006). Eutrophication is defined as the over enrichment of water with mineral nutrients, which in these cases are considered pollutants. Phosphorus (P) is well recognised as the key element of concern for freshwaters because of its limited natural concentration for primary production. Increased amounts in water, caused by urbanisation and agricultural intensification, directly accelerate the growth of algae, cyanobacteria and plants (net production), which then deteriorates water quality, reduces ecological status and has negative impacts on water use (Carpenter et al., 1998; Dodds et al., 2009; Smith, 2003; Smith and Schindler, 2009; Withers et al., 2014). While N and C can be obtained from the atmosphere, P is transported primarily by surface waters and its concentration is thus more feasible to control. Eutrophication is of special interest in the 2000 EU Water Framework Directive (WFD) which aims to achieve “good status” of freshwaters, rivers, lakes and coastal waters from different perspectives. Based on data from the year 2012, around 36% of total lake surface area or around 44% of total lakes fail water quality targets based on ecological conditions set to reach at least good ecological status (Spears et al., 2013; http://www.eea.europa.eu/). The main driver of ecological deterioration in lakes in urban and rural catchments is P pollution, although it is evidently not the only pressure requiring management in most lakes (Spears et al., 2013). The importance of reducing dissolved P in water by reduction of external load (Jensen et al., 2015; Villena and Romo, 2003), and also by controlling its release from sediment in order to counter algal blooms has been recognised (Egemose et al., 2010; Gibbs et al., 2011; Hupfer et al., 2015; Zamparas and Zacharias 2014). Understanding the mechanisms that lead to increased P bioavailability is necessary for effective lake management.

The importance of sediments and eroded particles (studied in this work) is well declared by recently established international initiatives such as the European Sediment Network (SedNet), the International Sedimentation Initiative (ISI), the International Commission on Continental Erosion (ICCE), the International Association for Sediment Water Science (IASWS) or the World Association of Sedimentation and Erosion Research (WASER) (Owens and Xu, 2011).

P forms

Phosphorus exists in aquatic systems in both particulate and soluble forms (Holtan et al., 1988), of which particulate P constitutes the largest amount (more than 90%) in freshwater ecosystems and is mostly contained in sediments (Wetzel, 2001). Particles in water and sediments include P in: a) organic forms in living organisms as nucleic acids (DNA, RNA), low molecular weight esters of enzymes or vitamins, nucleotide phosphates as adenosine diphosphate (ADP) and triphosphate (ATP), phospholipids or sorbed onto organic matter; and b) inorganic forms either as part of minerals or precipitated phosphate salts, such as hydroxyapatite $CaO(PO_4)_3(OH)$, $FePO_4$, $AlPO_4$, and $Ca_3(PO_4)_2$, but more often as adsorbed anions on the surface or interior of various metal oxides and hydroxides referred to as (hydr)oxides (especially those of Fe, and Al) (Reynolds and Davies, 2001).

Dissolved P forms are composed of orthophosphate ions (PO_4^{3-}), polyphosphates, organic and inorganic colloids and low molecular weight phosphate esters (Wetzel, 2001). Dissolved P is defined as either soluble reactive P (SRP, or sometimes referred to as dissolved reactive P, DRP) and total dissolved P (TDP). Particulate P is defined as the difference between TDP and total P (TP) of the unfiltered sample. The SRP fraction is biologically available but only part of the dissolved organic P (measured as part of the TDP fraction) and P sorbed to particles (included in TP) is considered immediately available (Ekholm, 1994; Sharpley et al., 1992; Uusitalo and Aura, 2005).

Some fractions and forms of P are virtually permanently bound in sediments, while others are potentially mobile, leading to release of P under appropriate conditions (Boström, 1984; Boström et al., 1988, Søndergaard et al., 2003). The environmental behaviour of P is therefore highly dependent on the forms in which it appears within the sediment.

P sources

The rapid increase in human activity in watersheds has greatly accelerated the eutrophication process (Bennett et al., 2001). In addition to natural sources, nutrients enter aquatic ecosystems via anthropogenic originated point sources, such as municipal and industrial wastewater discharge, non-point diffuse sources arising from agricultural intensification of the wider catchment area as runoff from agricultural fields fertilised by mineral and manure application and intermediate sources (Withers and Jarvie, 2008; Zamparas and Zacharias, 2014). These sources differ in composition (concentration, speciation and bioavailability; Ekholm and Krogerus, 2003; Owens and Walling, 2002), time of delivery (episodic and continuous, seasonality; Edwards and Withers, 2008) and are highly site specific due to differences in catchments (Kronvang et al., 2007; Withers and Jarvie, 2008).

Concentration of dissolved P in receiving waters is controlled, not only by point and diffuse sources within the catchment, but by a multitude of biogeochemical reactions (riverine processes) that may occur in the water column during transport (House, 2003; Withers and Jarvie, 2008). Principally, the equilibrium interaction of dissolved P with eroded particles and stream sediments has been recognised as the most important factor controlling concentrations of soluble P in the water column, during both low and high river-flows (House, 2003; Reddy et al., 1999). When the particles settle down to the bottom and become part of the sediment a more complex situation occurs. Numerous chemically and biologically mediated processes come into play which leads to either permanent P deposition in the sediment or to its release into the water column (Hupfer and Lewandowski, 2008).

External load

Water bodies receive P via incoming water from their watersheds, which is called external load. Watersheds differ in anthropogenic pressures and discharge, which influence the relative importance of different P sources. Natural P sources entering rivers in watersheds are most often only important in areas where anthropogenic mediated inputs are low. The main natural sources are weathering of soil parent materials (Holtan et al., 1988), riparian vegetation (Dosskey et al., 2010) and river bank erosion (Walling, 2005). Because the implementation of control over nutrient discharge from point sources has been widely applied, their importance in comparison to diffuse sources has decreased since the nineties of the last century (Behrendt et al., 1999; Kronvang et al., 2005; Macleod and Haygarth, 2003). However, inputs from sewage treatment plants still cannot generally be ignored (Bowes et al., 2005; Jarvie et al., 2006a; Neal et al., 2008). Diffuse sources are much more difficult to identify and control (Edwards and Withers, 2008; Withers and Sharpley, 2008), since P from these sources enters aquatic systems by two main pathways: surface runoff and subsurface flow (Allen et al., 2006; King et al., 2015). Most of the transported P is associated with soil particles eroded from specific areas with rapid hydrological connectivity to the watercourse (Armstrong et al., 2011; Pionke et al., 2000). Erosion is thus not only a serious issue due to the loss of fertile P rich topsoil for agriculture (Boardman et al., 2009), but also due to environmental and water quality impacts (Agudelo et al. 2011; Doody et al., 2012; Hund et al., 2013). Other sources of particles and P in watersheds, called intermediate (Edwards and Withers, 2008), are comprised of bank erosion from within stream channels (Walling, 2005), remobilisation of bottom sediments (Hoffman et al., 2009; House, 2003), effluent discharges from farmyards and septic tanks during storm events and road runoff (Edwards and Withers, 2008; Kayhanian et al., 2007). Particles in a stream may act either as a sink or a source of bioavailable P in water, which highly depends on the dynamic equilibrium between particulate and dissolved P. This process is most often the key driver controlling the P availability in these fluvial systems (Haggard et al., 2007; House et al., 1995; House and Warwick, 1999; Jarvie et al.,. 2005; Reddy et al., 1999). The direction and extent of this P exchange can be characterised by P sorption isotherms as described later (chapter 1.1.5).

Complex management measures which may use qualitative and quantitative decision support tools are required to reduce P supply in the watershed (Edwards and Withers, 2008; Kronvang et al., 2005; Sharpley et al., 2013; Withers et al., 2014).

Internal load

Phosphorus release from sediments, also called internal load, may often be considered the main summer P load to lakes and reservoirs, although this process is often overlooked (Håkanson, 2004; Nikolai and Dzialowski, 2014 Nürnberg, 2009; Søndergaard et al., 2013). There are a lot of difficulties in assessing internal load, especially distinguishing internal from external sources (Hupfer and Lewandowski, 2008). An increased concentration of P in the hypolimnion of a stratified reservoir, which peaks above the sediment, shows the internal P loading; although part of this P accumulated in the hypolimnion may originate from mineralization of sedimenting seston from the epilimnion (Hupfer and Lewandowski, 2008). Budget release from sediments is, however, even more complicated to determine in tributary parts, shallow and polymictic lakes and reservoirs or their parts due to vertical mixing in the whole water column (Burger et al., 2008; Nürnberg, 2009). In many eutrophic lakes the settled particles on the bottom are recycled and the phosphorus released in one year, so this load may be referred as external (Amirbahman et al., 2013; Hupfer and Lewandowski; 2008).

P release from sediments involves a complex set of physical, chemical and biological processes within the sediment and overlying water. The most well-known concept is anoxia mediated reductive dissolution of P complexes with Fe (Einsele, 1936; Mortimer, 1942) as described later (chapter 1.1.1.). Microbial mineralization of organic particles which contain P is another important and often the main cause of P release (Amirbahman et al., 2013; Gächter and Meyer 1993, Gächter and Müller, 2003; Hupfer et al., 1995). Inorganic polyphosphates accumulated in microbial cells may also greatly contribute to the P supply due to die off, especially during anoxia (Hupfer et al., 2004; Reitzel et al., 2006, 2007). Increase in pH, mainly due to photosynthetic activity, results in P desorption from Fe and Al (hydr)oxides surfaces due to ligand exchange reactions in which hydroxyl ions replace phosphate ions (Antelo et al., 2005; Reynolds and Davies, 2001; Zhou et al., 2005).

Water quality of lakes often does not reflect external load reduction. This is due to the large amount of P stored in sediments from too many years of high P loading from the watershed (also known as the P legacy, Jarvie et al., 2013). These highly P saturated sediments start to act as an intense P source and a buffer for keeping the P concentration in the water high (Søndergaard et al., 2003, 2013). The desired improvement of water quality might thus be postponed for a considerable period of years or even decades until the equilibrium between P concentration in sediment and water is reached (Kagalou et al., 2008; Schippers et al., 2006; Søndergaard et al., 2013). External P load reduction is necessary but often restoration measures to disrupt the internal P recycling and loading need to be applied (Hupfer et al., 2015; Huser et al., 2015; Mehner et al., 2008; Spears et al., 2013).

P binding partners

Fe (hydr)oxides

Phosphorus has a strong affinity toward Fe in forms of Fe (hydr)oxides which constitute roughly 1/3 of iron in aquatic environments, sediments and soils. The remaining major fraction of Fe consists of Fe silicates, sulfides and carbonates (Canfield, 1997; Cornell and Schwertmann, 2003; Raiswell and Canfield, 1998). In the continuum from amorphous to highly crystalline (hydr)oxides occurring in aquatic environments as free (hydr)oxides or in association with other particles (Cornell and Schwertmann, 2003), amorphous and poorly crystalline forms have the highest ecological significance.

During the process of redox, P released from sediments is part of the Fe(III) (hydr)oxides that are reduced to their soluble Fe(II) forms, thus P originally associated with these compounds is also released (Smith et al., 2011). The reduction of Fe(III) is induced either chemically by oxidation of H_2S or organic compounds (Dos Santos Afonso and Stumm, 1992; Thamdrup, 2000) but most commonly microbially during organic matter oxidation by bacteria in a process called dissimilatory Fe reduction (Lovley, 1997; Lovley, 2013; Melton et al., 2014; Straub et al., 2001; Thamdrup, 2000). Organic ligands which adsorb to the surfaces of (hydr)oxides (Lovley, 1997; Ratering and Schnell, 2000), humic substances and quinone moieties, which act as electron shuttles between bacteria and oxides (Aeschbacher et al., 2011; Piepenbrock et al., 2014; Rakshit et al., 2009), were shown to enhance these microbial reduction reactions.

The most favourable form for abiotic and microbial reduction, and the major product of reduced Fe re-oxidation, is poorly crystalline ferrihydrite (without a uniform chemical formula) (Bonneville et al., 2004, Fortin and Langley, 2005;), while crystalline oxides and Fe in sheet silicates contribute to Fe reduction in the sediments to a much lesser extent (Komlos et al, 2007; Lovley and Phillips 1986; Thamdrup, 2000,). The dissolution rate depends greatly on the specific surface area of the type of Fe (hydr)oxide structure (Roden and Zachara, 1996; Roden, 2003; Stumm and Sulzberger, 1992; Thamdrup, 2000). Another factor regulating the rate of Fe reduction is the presence of alternative terminal electron acceptors such as nitrates, manganese and sulfates (Perkins and Underwood, 2001; Søndergaard et al., 2003). A higher nitrate concentration may increase the redox potential of the sediment and thus prevent the reduction of Fe/P complexes (Boström et al., 1988; Gachter et al., 1988). In addition high sulfates concentrations may lead to precipitation of insoluble sulphides (FeSx) under low redox conditions and thus inhibit re-oxidation of dissolved Fe(II) and decrease the P binding potential of the sediment (Caraco et al., 1993; Katsev et al., 2006; Penn et al., 2000). The greater reactive surface area of amorphous Fe (hydr)oxides compared to crystalline minerals also means greater sorption capacity for P (Cornell and Schwertmann, 2003; Khare et al., 2005, Li et al., 2012, Lijklema, 1980; McLaughlin et al.1981; Strauss et al., 1997). Correct quantification of Fe (hydr)oxides with high specific surface area appears to be crucial in terms of P sorption and dissolution rates.

Al (hydr)oxides

Aluminium is another important binding partner for P. In an analogy to Fe, silicates are also the most abundant Al form in aquatic environments, although Al (hydr)oxides occurring in small amounts in the environment are much more important for the P cycle. They are naturally found in higher amounts in aquatic environments as precipitates of dissolved Al, originating either from Al minerals in the acidified catchments or from photochemical liberation of organically-bound Al (Kopáček et al., 2000, 2001; Navrátil et al., 2009; Ulrich and Pöthig, 2000). Al as an element is not sensitive to low redox potential in contrast with Fe, however its minerals are highly pH dependent and soluble under pH > 8.5 (Kennedy and Cooke, 1982; Gíslason et al., 2004; Reitzel et al., 2013). These forms are of high importance in sediments as they provide high sorption capacity for P even under anoxic conditions, when P is liberated from reduced Fe complexes or organic matter by microbial activity (Kopáček et al., 2000, 2001, 2005; Lake et al., 2007). The process of P sorption to amorphous Al (hydr)oxides is highly used during restoration measures, to reduce P in the water column or release P from sediments (Cooke et al., 1993; Hupfer et al,. 2015; Huser et al., 2015; Pilgrim et al,. 2007; Rydin et al., 2000). However, in time they crystallise and lose their surface area and thus their potential to sorb P (Berkowitz et al., 2006; De Vicente et al., 2008, Huser et al., 2015).

Analytical approaches

To characterise solid samples in respect to the P cycle different analytical approaches might be applied. We can either simultaneously determine the content of different P forms and sorption active components – Fe and Al (hydr)oxides with specific extraction methods, or determine the P exchange between solid samples and water under defined conditions with sorption/desorption experiments.

Sequential fractionation

Methods called sequential extraction procedures, sequential fractionations or just fractionations as referred to herein have been an important tool in the study of phosphorus forms, availability and dynamics in soils and sediments for almost 60 years. Methods were first used by Chang and Jackson in 1957 for soil P lability; since then many other schemes have been developed and many revisions of them later made. The most used methods are listed according to their main characterisation purpose: i) soil by Chang and Jackson (1957) or Hedley et al. (1982), ii) calcareous sediments by Hieltjes and Lijklema (1980), and Williams et al. (1971, 1980), and iii) non-calcareous sediments by Psenner and Pucsko (1988) and others. Comparisons and reviews of different methods based on the evolution of these methods and their application to the study of P chemistry and dynamics in aquatic and terrestrial ecosystems have been published (Condron and Newman, 2011; Pardo et al., 2003; Pettersson et al., 1988). The scheme of Psenner and Pucsko (1988), which takes into account low redox conditions in the sediment and the importance of Fe in P cycle, was suggested as the most suited method for P assessment in non-calcareous sediments (Condron and Newman, 2011, Lukkari et al., 2007). The original scheme was then modified for the assessment of other systems such as marine sediments (Jensen and Thamdrup, 1993; Jensen et al.; 1998; Ruttenberg, 1992) or freshwater wetlands (Jensen et al., 2005; Paludan and Jensen, 1995; Zak et al., 2008).

Detailed investigation of the dynamics and bioavailability of P requires the correct identification of different P forms and sorption potentials of soil, suspended particles and sediments. The fractionation method operationally defines these various forms of P and other metals, important in the P cycle, into groups of the same behaviour, based mainly on the nature and strength of interactions between P moieties and other mineral and organic components or their sensitivity to different chemical solutions (Condron and Newman, 2011). Individual extraction reagents are chosen and designed to separate groups of P forms, which have predictive value for soil or sediment in relation to processes playing important roles in P “metabolism” (Amirbahman et al., 2013; Hupfer and Lewandowski, 2008; Kopáček et al., 2005). The extraction solutions must be highly selective for particular P forms and used in the proper sequence, called extraction steps (Lukari et al., 2007, Ruttenberg, 1992). Fractionation studies often determine only P forms without any other determination of metals Fe, Al or Ca in the extracts and so loose important information about identification of saturation potential. In other studies these metals are analysed, however, it seems that due to strong extraction solution or long extraction time also crystalline and the inner parts of almost inactive oxides are dissolved (Jensen and Thamdrup 1993; Ruttenberg 1992; Torrent et al., 1987). This then disrupts the correct identification of active partners for P and overestimates the sorption potential of soils and sediments. The Psenner and Pucsko (1988) method sequentially extracts P, Fe, and Al nominally associated with 5 different sediment fractions, which are in order of extraction: easily extractable, reducible, alkali extractable, acid extractable, and recalcitrant.

Oxalate extraction

The acid ammonium oxalate extraction method, originally proposed by Tamm (1922), is often used to determine “noncrystalline Fe and Al (hydr)oxides”. The method is used in modification by Schwertmann (1964), who recommended that extraction should be done in the dark, as the light induces photochemical reduction of crystalline Fe oxides like goethite or hematite, i.e. the minerals with low reactive surface area. The method is usually used for agricultural purposes and in soil science to determine Fe and Al content responsible for P sorption (McKeague and Day, 1966) and especially the degree of soil saturation with P (DPSox; Schoumans, 2000). This soil index is calculated as the P extracted with oxalate divided by the sum of Al and Fe extracted in the same extraction:

DPSox= Pox/(α (Feox+Alox))

Concentrations of Fe and Al are often multiplied by a coefficient α which expresses the proportion of Fe and Al of the solid phase reactive sites dedicated to P sorption (Beauchemin and Simard, 1999; Freese et al., 1995; Van der Zee et al., 1988). The coefficient α varied in studies in the range of 0.4 - 0.7 (Beauchemin and Simard, 1999) but a value of 0.5 is generally considered universal (Schoumans 2000). The saturation degree was often shown to correlate with P concentration in soil runoff and thus is an indicator for P leaching risk from land into ground or stream water (Kleinman and Sharpley, 2002; Zhang et al., 2005). Critical DPSox values (20-30%) were recommended for agricultural fields to prevent ground water P concentration from exceeding 0.1 mg P l^{-1} (Sharpley et al., 1996; Beauchemin and Simard, 1999). Fe and Al extracted by oxalate were also reported to correlate well with maximum sorption capacity of soil (Börling et al., 2001; Zhang et al., 2005). This method is, however, also used for assessment of active Fe and Al (hydr)oxides in sediments where anoxic conditions usually prevail (Bhadha et al., 2014; De Vicente et al., 2010; Jensen and Thamdrup, 1993; Lai and Lam, 2009; Navrátil et al., 2009; Zhou et al., 2005), although it has been demonstrated that the presence of dissolved Fe(II) during oxalate extraction results in the catalytic dissolution of crystalline Fe (hydr)oxides (Phillips et al., 1993; Suter et al., 1988). The extent of this crystalline forms dissolution then depends on the concentration of Fe(II) in the extract, which may originate from FeS or magnetite dissolution (Kostka and Luther, 1994; Poulton and Canfield, 2005; Suter et al., 1988).

Ascorbate extraction

Another extraction method for the characterisation of amorphous Fe (hydr)oxides in sediments was proposed by Kostka and Luther (1994). This method is based on ligand enhanced reductive dissolution under neutral pH (7.5). During this extraction crystalline Fe (hydr)oxides should not be catalysed by the presence of Fe(II), and thus its use is preferred over oxalate extraction (Kostka and Luther, 1994). This method is used for marine and freshwater sediments, for Fe determination and also P associated with these mineral phases (Anschutz et al., 1999, 2007; Hyacinthe et al., 2001, 2006).

Mehlich 3 extraction

As the Mehlich 3 test (Mehlich, 1984) is well suited to a wide range of soils it is used worldwide, throughout Europe, North America and Australia (Bolland et al., 2003; Cox, 2001; Sims et al., 2000, 2002; Zbíral and Němec, 2000), it is a universal extracting agent for estimating macro and micronutrient (P, K, Ca, Mn, Cu, Fe, Mn, Al and Zn) status in soils (Sims, 2009). It combines the effects of low pH with complexing capacity, making it able to extract a wide range of elements from soils. Although this soil test was developed for agronomic purposes, to determine nutrient supply status for crops, the results are often well correlated to the other environmental P tests, for example water extractable P, and to P concentration in the runoff from fields (Hooda et al., 2000; Maguire and Sims, 2002; McDowell and Sharpley, 2001; Pote et al., 1996; Sims et al., 2000, 2002). The Mehlich 3 P concentrations are usually also well correlated with the degree of P saturation determined by oxalate extraction (DPSox, Schoumans, 2000), which is also often used as the critical evaluation of soil saturation and water extractable P (Sims et al,. 2002). Mehlich 3 P concentrations of soils are categorised into 3 groups based on crop yields: i) soils with deficient concentration or below optimum ($\leq$ 50 mg kg^{-1}) , ii) soils with optimum P concentration (51 – 100 mg kg^{-1}), iii) soils with P concentration above optimum (≥ 100 mg kg^{-1}), which means that amounts of nutrients are considered to be inadequate for crop use and these soils should be of significant environmental concern due to the high P loss from these fields (Beegle et al., 1998) .

Quantification of P sorption/desorption

To determine the P exchange behaviour of particles in water of various P concentrations, widely used batch P sorption experiments have been applied (Daly et al., 2015; Jarvie et al., 2005; McGechan and Lewis, 2002; Reddy et al., 1999). In these experiments, a known amount of particles are added to solutions of different concentrations, and the suspensions are equilibrated for a known period (usually 24 to 72 hours) at a constant temperature. The results of the amount of P adsorbed by the solids under different equilibrium concentrations are fitted to either the Freundlich isotherm for determination of equilibrium P concentration at zero net sorption (EPC_0), or to the Langmuir isotherm to determine maximum sorption capacity of the sample (Graetz and Nair, 2009; House and Danison. 2000; Pant and Reddy, 2001). The value of EPC_0 is specific for each individual solid sample and reflects its content of active components for P sorption – mainly Fe and Al (hydr)oxides and already adsorbed P. Whether the particles of specific EPC_0 will release or sorb depends on the dissolved P concentration in the water. When the EPC_0 of the sample is equal to P concentration in stream water no net change of P concentration occurs. However, when the EPC_0 of the particles is higher than SRP in the surrounding water, the particles release P into the water and when EPC_0 is lower than water SRP concentration, the particles will sorb P from the water (House et al., 1995, Jarvie et al., 2005, 2006; Taylor and Kunishi, 1971). Equilibration reactions are influenced by ionic strength and cation species dissolved in the water, equilibration time and range of P concentration, and thus caution regarding these facts must be paid during these experiments (Lucci et al., 2010; Nair 1984). In common with soil aggregates, redox potential and biota activity are important factors influencing P release/sorption by particles. This equilibration method may be most suitable for characterisation of eroded particles transported in stream water compared to soil or bottom sediments (Haggard et al., 2007; House and Denison, 2000; Pant and Reddy, 2001).

Aims

The main goal of the thesis was to find the best and most universal method for assessment of P forms in soils and sediments together with their main binding partners – and to distinguish between highly active Fe and Al (hydr)oxides and their almost non active crystalline analogs. Correct identification of reactive forms to both sorption and dissolution is of crucial importance for the further evaluation of P cycling in streams and waterbodies. As different methods with specific abilities and limitations are used worldwide, their comparison is necessary with the goal of pointing out potential discrepancies in their use. This is enormously important when thinking about the concept of particle continuum in an aquatic environment. It is necessary to establish a universal method for exploring the particle cycle from soil to suspended eroded particles and finally to waterbody sediments as the various methods used in soil science and limnology give results that are hardly comparable.

The sequential extraction procedure (fractionation) of Psenner and Puscko (1988) has high potential for the determination of different P forms in particles, however, the concurrent determination of Fe and Al (hydr)oxides responsible for the P sorption was not sufficiently verified. Earlier results have suggested overestimation of the most active Fe and Al forms, due to the dissolution of the highly crystalline (hydr)oxides during extractions included in the fractionation scheme. The proportion of active Fe and Al (hydr)oxides in the total extracted concentration is important missing information, due to their principal role in P binding ability and dissolution susceptibility. We decided to improve the fractionation method to preclude the misleading results and to propose a fractionation scheme which would be a useful and accurate tool for the determination of important constituents of particles and also a proxy for many processes based on changes of P in different forms.

Eroded particles are the intermediated link between soil in fields and the bottom sediments of waterbodies. We wanted to propose a simple empirical model for P release/uptake by these particles during their transport in the recipient before they become a part of the bottom sediment. With awareness and respect to biological and other processes which take place during transport we decided to suggest a model based only on the equilibration reactions between P concentrations adsorbed onto particles and dissolved P concentration in the surrounding water. The model should use i) data of plant available P concentrations, determined by a soil test obtained during routine monitoring of agricultural fields (e.g. Central Institute for Supervising and Testing in Agriculture, Ministry of Agriculture of the Czech Republic), which are in close relationship with sorption/desorption reactions and ii) dissolved P concentration in stream water monitored by national agencies or other institutions. The model should follow up the widely used erosion models and existing erosion maps, to supply rough, but the best possible, estimates of erosion particles' impact on eutrophication at larger scales.

Material and methodological approach

Sequential fractionation according, to Psenner and Pucsko (1988), was compared to the single step ascorbate method (Kostka and Luther, 1994) and to acid ammonium oxalate extraction (Schoumans, 2000). Comparison of extraction agents` selectivity and efficiency in extracting Fe and Al from the most environmentally common Fe and Al minerals was performed. We prepared in the laboratory or commercially obtained i) Fe minerals that included Fe (hydr)oxides of different crystallinity: ferrihydrite, lepidocrocite, goethite, and hematite; sulphide forms FeS and pyrite and ii) Al minerals which also included a set of Al (hydr)oxides: amorphous Al hydrous oxide, bayerite, gibbsite; and the silicate mineral kaolinite. Minerals were verified using X ray diffraction (performed by the Czech Geological Survey, Prague, Czech Republic), analysed for their specific surface area with the BET method (Brunauer et al., 1938; performed by the Regional Centre of Advanced Technologies and Materials, Olomouc, Czech Republic) and examined for the maximum sorption capacity of P with sorption experiments (McLaughlin et al., 1981). The selectivity of extractions for P was tested on the minerals with pre-adsorbed P and the natural sediment from non-calcareous Římov reservoir (Czech Republic). This was then used for the evaluation of individual steps of fractionation and the other two methods. For compatibility of results gained from all extractions the specific combination of extraction agents were used.

Selective dithionite reagent (BD; 0.1 M $Na_2S_2O_4$+0.1 M $NaHCO_3$, pH 7.2, 25 °C) and the following extraction solution NaOH (1M NaOH, 25°C), used for the determination of Fe and Al (hydr)oxides determination, respectively, were tested for kinetics of dissolution in time, to potentially distinguish the active forms (mostly amorphous) from less active (more crystalline) Fe and Al forms in P sorption. In addition to the laboratory prepared (hydr)oxides, natural samples were used for this experiment. The set of ten samples used, including soils, sediments, and settling seston, widely differed in their origin and proportion of crystalline (hydr)oxides.

A total of 56 soil samples representing the most common soil types and agricultural uses (provided by the Central Institute for Supervising and Testing in Agriculture, Ministry of Agriculture of the Czech Republic) were used for the model focusing on release/uptake of P by eroded particles. Fractionation method was performed to determine the main binding components and their concentration in the particles. The two Universal and worldwide soil P tests were used for the determination of both adsorbed P concentration onto particles (Mehlich 3 extraction Mehlich, 1984) and degree of P saturation (DPSox) (oxalate extraction, Schoumans, 2000). Sorption/desorption characteristics were measured by batch equilibrium experiments. Particles sorption kinetics were then fitted with Freundlich adsorption isotherm equations to determine adsorbed or desorbed P concentration (Pa) under different dissolved P concentrations in the solution (P_e) and with the Langmuir equation to determine maximum P sorption potential. P concentration extracted with the Mehlich 3 test (SRPM3) and calculated DPSox were then correlated to the concentration of sorbed or desorbed P under different solution concentrations (P_e) in the range of 20 to 220 µg L^{-1}.

Results and discussion

Paper I

Significant differences in the ability to dissolve Fe and Al minerals were measured during the comparison of extractions by different individual agents. The second extraction step, the BD reagent, dissolved almost completely the reactive Fe (hydr)oxide ferrihydride, lepidocrocite and also a major portion of crystalline mineral goethite and hematite, over an extraction period of 2 hours. Dissolution of the rest of the goethite and hematite, the inner lattice without phosphorus binding capacity, would probably occur during prolonged extraction time (Jensen and Thamdrup, 1993; Ruttenberg, 1992). However it is not desired due to their low ecological significance. Selectivity of this extraction solution for Fe (hydr)oxides was shown and confirmed. Neither FeS and pyrite, the minerals consisting of the reduced Fe form Fe(II), nor redox stable Al (hydr)oxides were dissolved during their extraction (see also Borovec and Hejzlar, 2001, Lukkari et al., 2007). The extraction efficiency for P sorbed onto Fe minerals and also selectivity for this P phase was demonstrated, as BD reagent did not extract P bound to Al (hydr)oxides. Earlier experiments with the addition of citrate to the dithionite solution (CBD) showed dissolution of part of the FeS (Canfield, 1989) and Al (hydr)oxides with bound P (Garcia-Rodeja et al., 2004; Kaňa and Kopáček, 2006). However crystalline goethite and hematite were, as expected, several orders of magnitude less active in P adsorption than their amorphous analogs due to their lower surface area (McLaughlin et al., 1981). This might result in an elevated molar ratio of determined Fe/P due to extraction of Fe (hydr)oxides of all crystallinity and consequently overestimate the concentration of the active adsorbing Fe phase in real samples of unknown proportion of different minerals.

Following the NaOH extraction step amorphous Al (hydr)oxide, most of the crystalline gibbsite and bayerite were dissolved completely, and the P bound to them effectively extracted. This extraction step was selective for Al in the form of (hydr)oxides because it does not dissolve any Fe from either Fe (hydr)oxides, Fe sulphides or a significant amount of Al from silicate mineral kaolinite. This step was therefore identified as a good tool for determining P bound to Al minerals, however, with analogy to BD agent and Fe minerals, dissolution capability for even highly crystalline minerals such as gibbsite with low P sorption capacity might overestimate accurate determination of the active Al phases.

The HCl extraction step used for determination of P bound to $CaCO_3$ compounds and apatites (Hieltjes and Lijklema, 1980; Psenner and Pucsko, 1988; Ruttenberg, 1992) is of special significance in calcareous or marine environments in comparison to sediments of neutral or acidic water where these forms occur in negligible amount (Borovec and Hejzlar, 2001). This step was however also responsible for the dissolution of a major part (77%) of FeS due to low pH (Cornwell and Morse, 1987) and a part of the Al (hydr)oxides that were not dissolved by the previous steps (BD and NaOH).

The ascorbate reducing agent (Kostka and Luther, 1994), originally proposed for determination of amorphous Fe (hydr)oxides, dissolved only 1/3 of laboratory prepared ferrihydrite and a small portion of other crystalline analogs. This was not consistent with other studies (Hyacinthe and Van Cappelen, 2004; Kostka and Luther, 1994), who reported higher efficiency in dissolving amorphous Fe (hydr)oxides. The reason might be higher crystallinity due to drying and ageing of ferrihydrite used in our study which influenced the dissolution extent. Nevertheless, this extraction solution also dissolved: i) approximately 1/3 of FeS (as previously suggested also by Kostka and Luther 1994; Anschutz et al. 1998, 2007) which is inactive in P sorption, ii) a higher but still minor portion of Al (hydr)oxides, and iii) a major portion of P associated with these redox stable sorption phases compared to the BD step. This extractant is thus shown to be less selective for P and Fe (hydr)oxides determination. Dissolution of FeS and extraction of P bound to both Fe and Al (hydr)oxides with simultaneous extraction of a high portion of Fe and also Al was observed when the specific combination of ascorbate and fractionation method described above, were applied to natural sediment.

Oxalate very effectively dissolved poorly crystalline Fe (hydr)oxides and concurrently ineffectively dissolved crystalline goethite and hematite when measured in single mineral dissolution experiments. During extraction, however, half of the FeS was also dissolved. The presence of a catalytic amount of Fe(II) during oxalate extraction was previously shown to greatly enhance the dissolution of crystalline minerals such as goethite and hematite (Sulzberger et al., 1989; Suter et al., 1988; Poulton and Canfield, 2005), and thus the dissolved portion of crystalline minerals could be much higher if extracted together with FeS. Oxalate almost completely dissolved amorphous Al (hydr)oxides and conversely only a small amount of crystalline analogous bayerite or gibbsite. P was extracted efficiently from both the Fe and Al (hydr)oxides. When a combination of fractionation with oxalate extraction were applied to the sediment from Římov reservoir, we observed an almost equal amount of extracted Fe concentration from (hydr)oxides with the BD and oxalate methods. This result could be caused by natural low concentrations of crystalline (hydr)oxides in the sediment, but more probably by enhanced dissolution of crystalline phases caused by the presence of dissolved Fe(II) originating from detected dissolution of FeS or Fe(II) containing phyllosilicates during oxalate extraction. The capability of oxalate to dissolve these Fe forms is caused by its acidity (pH 3), at which much of Fe(II) is soluble and the chelating effect of the oxalate as was previously suggested (Arshad et al., 1972; Kostka and Luther, 1994). P was almost completely extracted from both Fe and Al (hydr)oxides in its inorganic form, also a major portion of nonreactive P (mostly organic forms) was extracted by this solution.

Paper II

The fractionation scheme of Psenner and Pucsko (1988) with consecutive BD and NaOH steps was shown to be effective in distinguishing between P associated to redox labile Fe (hydr)oxides and Al (hydr)oxides, respectively. Potential dissolution of the stable crystalline (hydr)oxides together with their more active amorphous and poorly crystalline forms, with both extraction agents, remained a major disadvantage of the original scheme. To solve the problem, dissolution kinetics of the previously mentioned minerals were performed using both BD and NaOH extraction solutions. Fe (hydr)oxides were all highly dissolved during 2 hours of extraction time, but during the first 10 minutes the extraction efficiency for individual (hydr)oxides was relative to the surface area of the minerals. The almost complete dissolution poorly crystalline ferrihydrite and also the dissolution efficiency of other minerals suggests the extraction of more available surface (and potentially active) parts of crystalline (hydr)oxides without dissolution of inactive inner parts, which requires longer extraction time. A similar effect was observed during extractions of natural samples of different origin and proportions of crystalline (hydr)oxides. Different extraction rates of various solutions for Fe minerals was also previously shown (Houben, 2003; Postma, 1993; Torrent et al., 1987), this is because of differences in surface area which influences reactivity and the rate of dissolution reactions (Cornell and Schwertmann, 2003; Martynova, 2010; Roden, 2003; Roden and Zachara, 1996; Torrent et al., 1987). On the contrary, the extraction extent was almost independent of extraction time for both inorganic and organic P. Concentration of P was highest for samples extracted for only 10 minutes, a decrease in extracted P concentration, during longer extraction periods, was observed for some samples. This effect of decreased P was probably due to re-adsorption of P to other P sorption active components in the samples, such as Al (hydr)oxides. This may lead to an underestimation of reducible P content if a longer extraction period is used (Hupfer et al., 2009).

The high efficiency of extracting P over a short period of time also confirmed the dissolution of surface parts of (hydr)oxides with great specific area responsible for P sorption (Fontes and Weed, 1996; McLaughlin et al., 1981; Schwertmann, 1988). Very similar behaviour resulted from the dissolution kinetic of Al minerals using NaOH solution. A short extraction of 10 minutes duration was sufficient to completely extract the Al from amorphous Al (hydr)oxides, while only small proportions corresponding to the surface area of crystalline minerals were dissolved. P in both inorganic and organic forms was almost completely extracted during the first 10 minutes, however extraction efficiency for Al highly varied for samples of different origins and proportions of (hydr)oxides of different crystallinity. These findings led us to propose the modification of the fractionation scheme by the incorporation of short extraction steps, BD and NaOH of 10 minutes duration each. These short steps were divided into two 5 minutes extractions with the second 5 minutes extraction serving also as the rinse step (fig. 1). This scheme is more accurate for the determination of most active Fe and Al (hydr)oxides and separate determination of P associated with these phases, that behave differently under various pH and redox conditions. The use of total phosphorus (TP) extracted during short BD and NaOH extraction steps to determine the sorption ratio of Fe/P and the Al/P molar ratio is also discussed. This is because the nonreactive P (NRP) includes a high variety of organic P forms and also inorganic polyphosphates (Reitzel et al., 2006; Turner et al., 2003), that may strongly bind to the specific sorption sites of Fe and Al (hydr)oxides (De Groot and Golterman, 1993; Jensen et al, 2005; Ognalaga et al., 1994; Paludan and Jensen, 1995), and are often to a large extent also bioavailable (Fölmi, 1996; Jensen et al., 2005; Reitzel et al., 2006). Correct identification of sorption molar ratio, Fe/P and Al/P, used for evaluating the efficiency of P inactivation during P restoration measures (De Vicente et al,. 2008; Huser et al., 2015; Rydin and Welch, 1999; Rydin et al., 2000), as well as the stability of P burial in sediments and its potential release during anoxia and microbial mineralization (Kopáček et al., 2005; Norton et al., 2008) is of great significance.

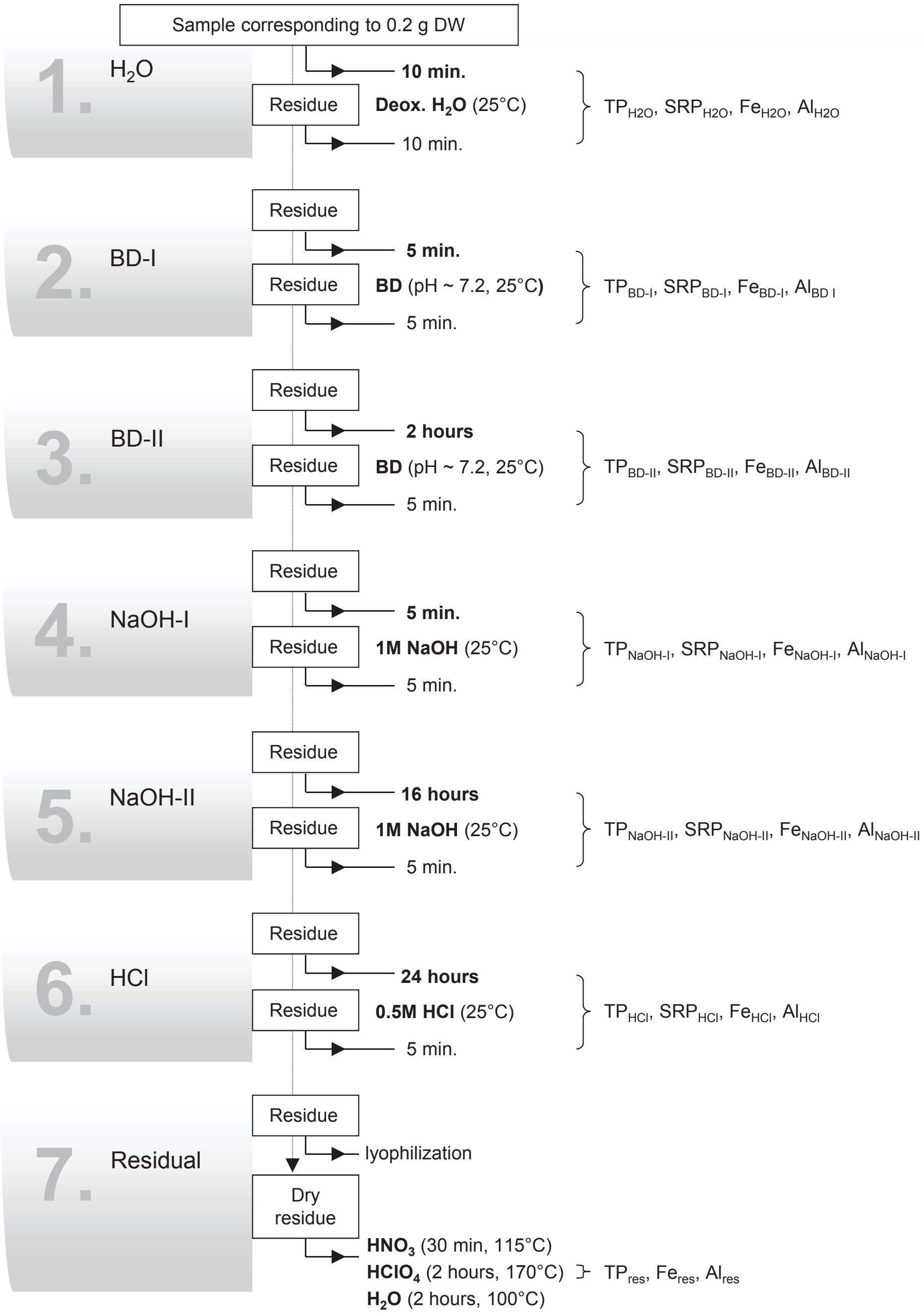

Figure 1. Sequential extraction scheme for determination of different forms of P, Fe and Al as modified from the original method by Psenner and Pucsko (1988).

Paper III

Samples representing a large area of agricultural land from the entire Czech Republic varied over a wide range of total P, Fe, Al, organic carbon (OC) content, and pH, due to differences in soil types, fertilisation, and agronomical practice.

Fe and Al active (hydr)oxides were the main constituents of soil samples responsible for P sorption, determined using the modified fractionation method. Although these Fe and Al forms represented only a minor fraction of the total Fe and Al content (16% and 4% median, respectively), they were responsible for the major portion of strongly adsorbed P after its addition and equilibration with the samples.

Extracted concentrations of TP, Fe and Al with oxalate were well correlated to the concentration extracted with BD-I plus NaOH-I, ($TP_{BD\text{-}I+NaOH\text{-}I}$), BD-I ($Fe_{BD\text{-}I}$) and NaOH ($Al_{NaOH\text{-}I}$), respectively. Although a different extraction extent of oxalate compared to the original BD extraction step was previously shown, the modified BD step (short extraction time, BD-I) extracted a very similar amount of Fe to the oxalate. The reason was probably, that in well oxidised soil samples where Fe reduced forms (FeS) were not highly present, the catalytic effect of Fe(II) enhancing dissolution of crystalline (hydr)oxides forms was excluded.

Mehlich 3 agent extracted an even smaller portion of the total P, Fe and Al compared to above described methods. However, P extracted with Mehlich 3 agent was in close relationship with the molar ratio of TP to Fe and Al in their most reactive (hydr)oxide forms, ($TP_{BD\text{-}I+NaOH\text{-}I}/Fe_{BD\text{-}I} + Al_{NaOH\text{-}I}$). An exponential response of SRP_{M3} to this molar ratio was observed, suggesting a weaker bonding of sorbed P with higher P saturation as might be also declared by sorption isotherms (Hooda et al., 2000). The concentration of SRP_{M3} extracted highly increased when the molar ratio value of 10 (corresponding to SRP_{M3} 50 µg L^{-1}) was exceeded. A very similar relationship was observed for SRP_{M3} and the ratio of TP to Fe and Al extracted with oxalate ($TP_{ox}/Fe_{ox}+Al_{ox}$) (Hooda et al., 2000; Sims et al., 2002), due to the correlation of the above mentioned results from oxalate and fractionation methods. The Mehlich 3 solution acts more like a desorption then a dissolution agent, as P determined with this solution is also well correlated to water extractable P, other mild solutions such as 0.01 M $CaCl_2$ or P concentration in runoff and leaching water from fields (Hooda et al., 2000; Maguire and Sims, 2002; McDowell and Sharpley 2001; Pote et al., 1996; Sims et al., 2000). This soil test extracted an unspecified small quantity of Al (due to F^-component of the solution, Férnandez Marcos et al., 1998) and an especially small amount Fe compared to fractionation and oxalate methods as was previously shown (Férnandez Marcos et al., 1998; Tran et al., 1990; Zhang et al., 2005). The degree of P saturation based on a determination of P, Al and Fe with the Mehlich 3 soil test which was proposed (Maguire and Sims 2002; Sims et al., 2002) may often lead to incorrect conclusions. Unspecified and unbalanced extent of Fe and Al dissolution thus results in concluding that P is mainly bound to Al (hydr)oxides (Khiari et al, 2000), disregarding Fe (hydr)oxides as an important constituent for P association.

Samples varied highly in maximum sorption capacity (P_m) and equilibrium P concentration at zero net sorption (DPC_0) determined by Langmuir and Freundlich isotherms, respectively. Concentrations of adsorbed or desorb P under various simulated equilibrium concentrations (dissolved P concentration in surrounding water) were calculated for every sample according to their regression parameters of Freundlich isotherms. The main result of the study was the finding that the adsorbed P (P_a) or desorbed P ($-P_a$) amount per sample weight was highly linearly correlated with SRP determined with Mehlich 3 (SRP_{M3}) for individual equilibrium concentrations as follows:

Eq. 1.: $P_a = a*SRP_{M3}+b$

The variables a (slope) and b (intercept) of the linear regressions varied for different equilibrium concentrations (P_e). These parameters were thus determined for individual P_e in the range of 20 to 220 µg L^{-1} with an interval of 10 µg L^{-1}. To generalise the pattern we plotted both parameters against P_e concentrations and found a highly significant relationship for both variables with the following equations:

Eq. 2.:

$a = 1.101064E\text{-}06 * P_e^2 - 7.916045E\text{-}04 * P_e - 5.356533E\text{-}01$

Eq. 3.:

$b = -4.852173E\text{-}04 * P_e^2 + 4.145542E\text{-}01 * P_e - 6.643085E{+}00$

By combining the equations above, it is possible to determine the amount of sorbed/desorbed P from erosion particles from/into the recipient water of given SRP concentration (expressed as P_e) only using SRP_{M3} data for individual soil samples. This implies that from a known amount of eroded particles from soils with known SRP_{M3} and known SRP concentration in recipient water, one can reliably calculate the amount of released P and compare it with other P sources or use it in P mass-balance calculations. Vice versa it is also possible to find the concentration threshold value of sample SRP_{M3} under which zero net P release from the sample occurs in water of specific concentration.

An alternative approach was proposed by using the degree of P saturation determined using oxalate extraction (DPS_{ox}) instead of SRP_{M3}. This approach is based on the significant linear relationship of SRP_{M3} with DPS_{ox} as was also earlier observed (Hooda et al., 2000; Sharpley 1995; Sims et al., 2002). The correlation coefficients were not as high as those found for P_{M3}, but this approach may be used when P_{M3} data are not available. Values of EPC_0 were earlier measured to determine the function of stream sediments in the P cycle in streams (Haggard et al., 2007; Jarvie et al., 2005, 2006), however, the sediments do not represent the original eroded soil. Fine eroded particles are the missing link between characteristics of bulk soil (Sharpley et al., 1996; Sims et al., 2002; Withers et al., 2014) and stream sediments (coarser material), as the fine particles are often transported through the stream system, depending on its morphology, velocity rate and particle sizes (Agudelo et al, 2011). These particles represent an important source of dissolved P in stream water due to equilibrium release (Froelich et al., 1988). We are aware that the proposed simple model based on these equilibration reactions is rough and omits water ion composition, stream morphology, particle sizes distribution and microbial reactions during transport from the field and in waterways (Agudelo et al., 2011; Haggard et al., 2007; House and Denison, 2000; Jarvie et al., 2005; Lucci et al., 2010). However, it is the best way to model the impact of eroded particles on eutrophication at a wider scale just using available soil test results and dissolved P concentration data from routine monitoring. This simple model may then supply the necessary information for current erosion models and maps of erosion risk.

Conclusions

To find the most appropriate method for correct determination of P associated with the active soil and sediment particles components, Fe and Al (hydr)oxides, we compared different methods. The original fractionation method proposed by Psenner and Pucsko (1988) using buffered dithionite solution for 2 hours extraction time (step 2) and sodium hydroxide for 16 hours extraction time (step 3), has been shown to be highly selective tools to separately determine concentrations of P forms bound to either Fe or Al (hydr)oxides. The method's disadvantage of overestimation of active (hydr)oxides, mainly responsible for P sorption due to the dissolution of inner inactive parts of the more crystalline forms, was shown. To remove this negative effect, kinetic dissolution experiments using incremented extraction methods were performed with individual defined minerals as well as with natural samples. Variable dissolution rates then enable us to propose the inclusion of the two new short extractions (10 minutes each) into the original method. The verified modifications to the scheme resulted in better determination of most reactive constituents of particles for P sorption and their dissolution – Fe and Al (hydr)oxides.

In contrary, ammonium oxalate reagent (Schoumans 2000) has a disadvantage in concurrently extracting P without distinguishing between P associated partners. This is of crucial significance due to their known highly different sensitivity to changes of redox or pH conditions. The use of oxalate was not recommended even for the determination of active Fe (hydr)oxides in anoxic environments, such as waterbody sediments or wetlands. Dissolution of reduced Fe forms (FeS or Fe(II) containing silicates), usually occurring in these systems, may overestimate the amount of (hydr)oxides and also greatly increase dissolution of crystalline forms, due to the catalytic effect of Fe(II) during extraction. The use of this extraction method is however reasonable in oxic conditions (un-flooded soil or eroded particles in oxic stream water), for the determination of both Fe and Al active (hydr)oxides, and is often used for the determination of the degree of P saturation. The results of oxalate and fractionation are highly correlated but the advantage of fractionation in distinguishing P forms and specific molar ratios and their associated partners still remains. Ascorbate extraction was not recommended for the determination of P, Fe and Al due to insufficient dissolution of active Fe (hydr)oxides, concomitant dissolution of FeS, and a portion of Al (hydr)oxides and unselected extraction of P. The Mehlich 3 extraction method is not designed for the dissolution of the above mentioned Fe and Al forms, the extent of their dissolution is incomparable to other methods. Its desorption effect for P is dependent on the degree of P saturation, also the results correlate to water extractable P, easily desorbable P, and P determined in field runoff as was earlier observed. The positive correlation of Mehlich 3 P to the degree of P saturation governed by the number of free sorption sites of particles and strength of bonding is reflected in sorption characteristics defined by sorption isotherms. The linear correlation of SRP_{M3} to sorbed/desorbed P amount under single specific equilibrium concentration (in the ecologically significant range from 20 to 220 µg L^{-1}), led us to the proposal of a simple empirical model. This simple model based solely on equilibration reactions may be able to predict the behaviour of P exchange between eroded particles transported in water ways and P dissolved in the water. Therefore it could be used to estimate the supply of dissolved P from eroded particles and their importance and extent for eutrophication phenomena, especially in combination with erosion models.

Future prospects

Pore water determination

Fractionation is a method by which we may determine particle composition and identify and separate different forms of P and binding partners based on their potential behaviour under different environmental conditions. Whether the potential is fulfilled depends on many factors and processes ongoing in sediments or soils and their interaction with other environments such as the water column or atmosphere. Such complex systems usually reveal high spatial and time heterogeneity of different scales when physical, chemical or organism mediated reactions run at various rates. These facts imply that the fractionation method is “only” a descriptive tool and samples from different places or sampling times must be analysed and compared to be able to identify processes and changes of P, Fe or Al forms. The sediment pore water surrounding particles is a medium with changing ionic compositions which highly affects ongoing reactions on particles. It is also a transporting shuttle between sediment and water column, because P, Fe and other ions dissolved in this water move according to the concentration gradient (diffusion) from or into the sediment. Exchange of pore water with water above the sediment might also be influenced by other disturbances (Adámek and Maršálek, 2013). Based on the concentration of anions involved in redox reactions (NO_3, SO_4) or NH_4 concentration originating from microbial degradation of organic matter, we may determine the potential for Fe-P associations, reductive dissolution or P concentration originating from organic matter mineralization in different soil, sediment layers or during seasons (Alewell et al., 2008; Bołalek and Frankowski, 2003; Gíslason et al., 2004; Weston et al., 2006). High ion concentration ratios under specific conditions may also result in precipitations of different minerals according to the precipitation equilibrium (Heiberg et al., 2010; House et al., 2003). Dissolved organic acids in pore water may also compete with P for sorption sites on (hydr)oxides and thus decrease their P sorption capacity (Geelhoed et al., 1998; Antelo et al., 2007). To measure gradients and thus actual release rates of P from sediments (Belzile et al., 1996) and also the ionic composition of pore water, a gentle sampling technique with high resolution must be applied. The use of gel probes using DET mechanism (diffusive equilibration in thin-films, Davison et al. 1994; Ding et al., 2010; Dočekalová et al. 2002; Zhang and Davison, 1999) should satisfy this requirement; however, validation of these techniques is still not complete due to their application for limited purposes. A combination of particle composition (measured by fractionation) and pore water actual ionic composition (sampled with DET), is thus another step towards determining accurate behaviour of sediments under different situations. Using these methods together with correct interpretation of results, should contribute to the determination of dynamic P release rates from sediment and the complicated assessment of internal P load in water bodies.

Organic matter characterisation

The second challenge is assessment of organic matter quality in sediments. Organic matter mainly serves as an electron donor during its degradation via multiple reactions involving organisms and oxidants, which utilise terminal electron acceptors including Fe(III). Degradation efficiencies are not constant and are highly variable in space and time. Among factors such as particle deposition rate, temperature, benthic community and electron acceptor availability, the composition of organic matter based on different origin and its various bulk degradability are dominant factors driving sediment reaction rates (for review see Arndt et al., 2013). Organic matter may also contribute to the stability of Fe and Al in the sediments by complexation (Lalonde et al., 2012), while other organic compounds may act as alternative electron acceptors during anaerobic respiration (Keller and Takagi 2013; Lau et al., 2015). Characterisation of organic compounds in sediment is thus important in P and other elements’ cycles and needs more attention. Coupling of organic matter quality determination with fractionation results and pore water composition is another highly demanded and challenging step for future research.

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Research articles

Paper I

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? Water Res. 47, 547–557.

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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?

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ABSTRACT

Correct identification of P forms together with their main Fe and Al binding partners in non-calcareous sediments is of crucial importance for evaluation of P cycling in water bodies. In this paper, we assess extraction methods frequently used for this purpose, i.e., a sequential five-step fractionation (water, bicarbonate buffered dithionite solution (BD), NaOH, HCl, nitric-perchloric acid), ascorbate extraction (pH ~7.5), and oxalate extraction (pH ~3), directly on a range of laboratory prepared Fe and Al minerals enriched with adsorbed P. Extraction selectivity and efficiency for particular P, Fe and Al forms were also verified by specific combinations of these extraction methods applied on freshwater sediment samples. In the sequential fractionation, BD was highly effective in dissolving both amorphous and crystalline Fe (hydr)oxides and the associated P, while neither FeS nor Al (hydr) oxides were dissolved. The following NaOH extraction effectively dissolved both amorphous and crystalline Al (hydr)oxides. The high solubilizing power of BD and NaOH to dissolve crystalline Fe and Al oxides that have only a small P-sorption ability prevents the use of resulting Fe/P and Al/P ratios as simple predictors of total P sorption capacity of sediments and soils. Ascorbate non-selectively extracted small proportions of FeS and amorphous Fe and Al (hydr)oxides, but significant amounts of adsorbed P, which hinders its use for the characterization of P forms in non-calcareous sediments. Similar nonselective characteristics were found for oxalate extractions. As oxalate extracts most of the adsorbed phosphate, it is not possible to use it unambiguously to determine specific Fe/P and Al/P ratios of active complexes. However, this method is convenient (and more selective than NaOH step in the sequential fractionation) for the determination of amorphous Al (hydr)oxides.

1. Introduction

Phosphorus (P) is an essential nutrient for organisms, often limiting algal and cyanobacterial growth in freshwaters, thereby determining water quality and use. Particulate P forms originating in the watershed or a water body as former rocks, soil or organic seston particles can settle down and become more or less an active part of the P cycle in sediments. Phosphorus can then be released, temporarily retained or permanently locked up, depending on the composition of the

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Paper II

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SEDIMENTS, SEC 1 • SEDIMENT QUALITY AND IMPACT ASSESSMENT • RESEARCH ARTICLE

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

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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 [H_2O, 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 (Ppart). Ppart 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

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Paper III

Borovec, J., Jan, J., (manuscript draft). Simple empirical tool for predicting the behaviour of eroded particle-associated phosphorus in streams.

Simple empirical tool for predicting the behaviour of eroded particle-associated phosphorus in streams.

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Highlights

- An approach for accurate identification of sorption properties of eroded particles was developed.
- A close relationship between P saturation, plant available P and sorption/desorption behaviour of eroded particles was found.
- Empirical model for P desorption based on Mehlich 3 P and/or P saturation was developed.
- Model can easily fit the erosion, plant available P, and recipient P concentration data.

Abstract

This study focuses on the missing link between the bulk soil and the stream sediments – eroded particles and quantification of their impact on the available instream P concentration.

The cycling of phosphorus (P) in watersheds is often described with the aid of complex models. These models do not, however, due to their high data demand, offer sufficient support to decision makers and water managers.. On the other hand, there are also the results from erosion models available, usually covering entire watersheds, as well as the widely monitored concentrations of plant-available P. We used 56 soil samples from the permanent monitoring areas of the Ministry of Agriculture of the Czech Republic, which covered the most common combinations of soil type and land and agricultural use, for the determination of the relationship between the molar ratio of sorption-active Fe and Al (hydr)oxides to P and plant available P, determined by the commonly used Mehlich 3 extractions (P_{M3}). Concentration of adsorbed/desorbed P (P_a) by soil particles in water of specific SRP concentrations (described by the Freundlich isotherms) were found to be strongly related to P_{M3} ($P_a=a*P_{M3}+b$) and/or degree of P saturation measured by oxalate extraction (DPS_{ox}; $P_a=c*DPS_{ox}+d$).

Described relationships varied in slope and intercept parameters for discrete equilibrium P concentration in the water (P_e). However, strong ($R^2 > 0.99$) nonlinear correlation was found between the individual parameters and P_e in the environmentally important range from 20 to 220 µg L^{-1} SRP. Combination of described equations in this study is used for design of simple model, which can quantitatively predict P exchange on the eroded soil particles in the recipient water of known or targeted P concentration. The presented model, together with the frequently measured plant available P concentration, can easily follow the results of the widely used erosion models and thus enable to quantify direct important impact of soil erosion to instream bioavailable P concentration/supply.

Key words

soil erosion, diffuse P sources, eutrophication potential, P fractionation, watershed management, ecological potential

Introduction

Eutrophication, caused by the increased phosphorus loading from point and nonpoint sources, has been one of the biggest water quality problems of inland waters for more than 40 years now (Schindler, 2006; Smith et al., 2006). This phenomenon is of special interest to the implementation of the 2000 EU Water Framework Directive (WFD; Directive 2000/60/EC). Hundreds of River Basin Management Plans are currently being developed and adopted as part of the WFD to secure at least good ecological quality of all natural water bodies (Kronvang et al., 2012). In many developed countries with both intensive agricultural production and well treated household wastewaters, P losses from diffuse sources (mainly erosion and drainage leaks) are currently the dominant components of P budgets at the river basin or catchment scale (Kronvang et al., 2007; Maguire et al., 2009; Sharpley et al., 2013).

In comparison to other sources, such as poorly treated household wastewaters, the total amount of P carried by eroded particles can easily be two orders of magnitude higher.

However, only a small part of the erosion particle-associated P is readily bioavailable and responsible for the increased trophy levels (Ekholm, 1994). The ability of particles to release or retain P depends on their composition - the relative ratio of binding partners like iron (Fe), aluminium (Al) or calcium (Ca), and the P content as well as its forms (Hupfer and Lewandowski, 2008; Nair, 2014; Zhang et al., 2005). The concentration ratio of P to its binding partners is influenced by geology, morphology, land use, and agricultural practice (tillage, watering /dewatering, crop management and fertilizer application) (Daly et al., 2015; Jarvie et al., 2008; McDowell et al., 2004; Sharpley et al., 2003, 2007,).

Similar particle composition in terms of binding partner/P ratios can be found at different altitudes. Regional target “good ecological status” with regards to P concentrations usually follows the limnological altitude gradient, where lowland rives will always be P-rich in comparison with highland rivers. For example, Czech highland rivers should reach a target 30 µg L^{-1} P (20 µg L^{-1} PO_4-P) threshold, while lowland rivers are allowed to carry up to 70 µg L^{-1} P (50 µg L^{-1} PO_4-P).

One of the typical indirect approaches to estimating erosion-based dissolved P at a larger scale consists of (i) computing soil loss, (ii) calculating “enrichment ratio” and (iii) applying “literature based” dissolved P/total P ratio. Basic equation of P enrichment ratio derived by Sharpley (1980) is most commonly used for estimating amount of total transported P. Dissolved P concentration in surface runoff has to be further defined independently, but its accurate estimation strongly depends on the precipitation intensity, soil P concentration or presence and quality of vegetation cover (Hahn et al., 2012; Sharpley, 1995; Shigaki et al., 2007). In a relatively short time frame (weeks) eroded soil particles can maintain their P properties which they had on the field, but later, due to a number of other processes, their P behaviour can change (Baldwin et al., 2002; House et al., 1995; Withers and Jarvie, 2008).When a more detailed information is needed, the equilibrium phosphorus concentration (EPC_0) can be calculated. It provides the information on whether soil particles will release or sorb when placed in contact with fresh water of particular PO_4-P concentration (Froelich, 1988; Haggard et al., 2007; House et al. 1995; Jarvie et al., 2005; Taylor and Kunishi, 1971). The EPC_0 is based on the kinetics of interactions between sediment particles and PO_4-P in the water, and is usually described by a sorption isotherm. If the EPC_0 is greater than the PO_4-P concentration, the particle will release PO_4-P, if the EPC_0 is lower, the sediment will remove PO_4-P from water. This parameter works well for suspended particles or oxic sediments but may give incorrect results when the system is greatly disturbed from its natural state (e. g. anoxic sediment is oxygenated during the measurements or its pH is changed)(House and Denison, 1998, 2000).

While P sorption isotherms might be very useful for environmental characterization and eutrophication risk potential determination, the procedure is time-consuming and complicated for routine use. The determination of extractable soil P by standard P soil test is less laborious. Very often these one step extracts are used in agriculture for the estimation of plant available P concentration. Different approaches with varying extractants, soil sampling and testing frequencies, as well as density of sampling points in the watershed can be found throughout the world (Brazier et al., 2005; Herlihy and McCarthy, 2006; Jarvie et al., 2006; Neyroud and Lischer 2003). Both oxalate and Mehlich 3 extraction are universal P tests widely used in Europe, North America, and Australia (Bolland et al., 2003; Sharpley et al., 2003; Cox, 2001; Zbíral and Němec, 2000). In many cases, water extractable soil P was suggested to estimate the P amount which can be released into the recipient water. Vadas et al. (2005) showed the comparability among different single step P extractions and the filterable P leaching from experimental fields during rainfall simulations.

As the P amount released from a particle does not only depend on the particle properties, but also on the surrounding environment, i.e. the recipient water, another concept for P uptake/release estimates should be employed. Moreover, when considering the erosion under higher rain/flow situations, the particle life time in the surface water is usually longer than during the short erosion episode on the field (Agudelo et al., 2011). Taking into account the agronomic and surface water screening data availability and the river basin managers needs to establish the knowledge of major P sources to cost-effectively combat the eutrophication problem in surface waters in accordance to WFD (Haygarth et al., 2009), it seems to be better to use a relationship which combines particle P sorption/desorption properties and the P concentration in the recipient, with respect to the target P concentration. While erosion modelling results and erosion maps calculated worldwide by USLE/RUSLE equations (Hickey, 2000; Renard et al., 1994; Schönbrodt et al, 2010) or with detailed models such as the WATEM/SEDEM (Van Oost et al., 2000; Van Rompaey et al., 2001; Verstraeten et al., 2002) are widely available, the model of eroded particles P behaviour in the recipient water is missing.

The aim of this paper is to describe the relationship between soil particle P sorption properties and particle composition using the most common approaches and extrapolate it into a simple empirical model, which enables the prediction of the eroded soil behaviour in both the current stream P concentrations and the “good ecological status” P targets.

Materials and methods

The national database of long term monitoring of physical, chemical, and biological qualities of soils in the network of permanent monitoring areas of the Ministry of Agriculture of the Czech Republic consist of 190 plots. Soil samples from these plots cover the most common combination of soil type and land and agricultural use. The soils are periodically sampled in a consistent way. A total of 56 soil samples from the database representing the most common soil types with a wide range of plant available P concentrations (Mechlich 3 P, see above) were provided by the Central Institute for Supervising and Testing in Agriculture, Ministry of Agriculture of the Czech Republic.

Samples from the database were archived air dried a sieved through 2mm sieve, hence eroded particles were not represented. Particles <63 µm in diameter (i.e. silt- and clay-sized material) are the most common fraction of sediment suspended load which is also important due to high surface area and thus biogeochemical fluxes of nutrients (Owens et al., 2005; Walling et al., 2000, 2001). Particle soil fraction <63 µm is considered to be fraction of soil potentially eroded (Foster et al., 1996; Machesky et al., 2010) and to contribute to suspended sediment load of the rivers. The particle size distribution during an erosion episode varies substantially, but the clay and silt size particles were supposed to be responsible for most of the soil chemical properties. To separate the particle fraction of <63 µm, samples were rewetted, freeze dried, and sieved through a 63-µm nylon sieve prior to all analyses.

Soil pH was measured in water at a soil:solution (w:v) ratio of 1:5. Total concentrations of P, Fe, and Al (TP, TFe, TAl, respectively) in all samples were measured colorimetrically after nitric-perchloric acid digestion (Kopáček et al., 2001). Soluble reactive phosphorus (SRP) concentrations were determined according to Murphy and Riley (1962), using a flow injection analyzer (Lachat QuikChem 8500; Lachat Instruments, Loveland, CO, USA).

Mehlich 3 extractions

Soils samples were extracted by Mehlich 3 soil test (Mehlich, 1984) at a 1:10 soil:solution ratio of 2 g of soil shaken with 20 ml Mehlich3 reagent (0.2 M CH_3COOH, 0.25 M NH_4NO_3, 0.015 M NH_4, 0.13 M HNO_3, 0.001 M EDTA) for 5 minutes on a horizontal shaker.

After extraction, samples were centrifuged, filtered, and solutions were analyzed for SRP, and total dissolved P, Fe and Al (SRP_{M3}, TDP_{M3}, Fe_{M3} and Al_{M3}, respectively).

Oxalate extractions

Acid ammonium oxalate extraction (oxalate extraction) was performed according to Schoumans et al. (2000). Extraction solution was prepared by dissolving 16.2 g of ammonium oxalate monohydrate [$(COONH_4)_2.H_2O$] and 10.8 g of oxalic acid dihydrate [$(COOH)_2.2H_2O$] in 1 L of distilled water. The pH of this solution was 3.0±0.1. Samples were extracted at a 1:20 soil:solution ratio of 1 g soil shaken with 20 ml oxalate reagent in the dark for 2 hours on a shaker. After extraction, samples were centrifuged, filtered, and solutions were analyzed for SRP, and total dissolved P, Fe and Al (SRP_{ox}, TDP_{ox}, Fe_{ox} and Al_{ox}, respectively).

P forms and binding partner composition

Samples were extracted by sequential fractionation according to Psenner and Pucsko (1988) with modification by Jan et al. (2015). The modification is important to distinguish between reactive Fe and Al compounds with large surface areas responsible for sorption/desorption, and the older, crystalline minerals. The soil samples with zero and 4 mg L^{-1} of added P, which remained in test tubes after P sorption experiment (see below) were extracted in 6 sequential steps as follows: 1) deoxygenated H_2O (10 min), 2) BD-I (0.1M dithionite buffered by 0.1M sodium bicarbonate, 5 min), 3) BD-II (as previous, but 2h), 4) NaOH-I (1M NaOH, 5 min), 5) NaOH-II (as previous but 16h), 6) HCl (24h min). After each step, the sample was centrifuged at ~3000×g, and the pellet was immediately exposed to fresh extraction solution for an additional 5-min extraction (except for the H_2O fraction; 10 min), centrifuged again, and both extracts were filtered and combined for analyses of SRP, TP, Fe, and Al. The TP, SRP, Fe, and Al extracted by individual extraction steps are abbreviated in the text, with each step specified by a subscript (eg. $SRP_{H2O,}$ SRP_{BD-I}, SRP_{BD-II}, SRP_{NaOH-I}, $SRP_{NaOH-II}$, SRP_{HCl}).

Sorption isotherms and EPC_0

0.25 g of soil samples were equilibrated in 25 ml of tap water containing different amounts of P (0.0, 0.5, 1.0, 2.0, 4.0, 8.0, 16.0 mg P L^{-1}). Fifty ml centrifuge tubes with the suspensions were shaken on a horizontal shaker for 72 hours, then centrifuged at ~3000×g and supernatant filtered through glass-fiber filters (0.4-µm pore size; MN GF-5, Macherey-Nagel, Düren, Germany). Longer equilibration time of 72 hours was chosen to reach both the fast initial surface sorption as well as the “slow” sorption typical for Fe and Al (hydr)oxides (Barrow and Shaw, 1975; Froelich, 1988; Strauss et al., 1997). The amount of P adsorbed was determined by the difference between the initial P concentration and final equilibrium P concentrations in the filtrate. Data obtained, expressed as P adsorbed per unit weight (P_a) of soils and equilibrium solution concentrations (P_e) were fitted to both the Freundlich and the Langmuir adsorption isotherm equations.

Phosphorus adsorption isotherms were determined with the linearized form of Langmuir equation to determine maximum P sorption as follows:

$$\frac{Pe}{PA} = \frac{1}{b * Pm} + \frac{1Pe}{Pm}$$

Where $P_A = P_a + P_o$, the total amount of P retained, µg g^{-1}, comprised of P_a – P retained by soil during experiment, µg g^{-1} and P_o – already sorbed P µg g^{-1}, P_e = final equilibrium P concentration in filtrate, mg L^{-1}, P_m = maximum P sorption, µg g^{-1}, b = constant related to the bonding energy, L $µg^{-1}$ P.

P_o was calculated by the method of least square fit based on the linear relationship between P_a and P_e at low equilibrium P concentration as follows:

$P_o = b'*P_e-P_a$

Where b' = the linear adsorption coefficient.

Sorption data were fitted to the Freundlich equation in the linear form for EPC_0 determination as follows:

$\mathrm{Log}P_A = \log a + b*\log P_e$

P_A and P_e has the same meaning as described earlier, a = adsorption constant, expressed as µg g^{-1} P, b = constant expressed as L g^{-1}. A plot of $\log P_A$ against $\log P_e$ gives a straight line with log a as an intercept (indicative of the number of sorption sites) and b as a slope (indicative of the bonding energy). It implies that the energy of sorption decreases exponentially with increasing saturation of the surface.

Soil P saturation

P available to be released into solution in relation to the remaining binding capacity of soils is generally defined as follows (Kleinman and Sharpley, 2002; Sharpley, 1995):

$$DPS = \frac{Sorbed\ P}{P\ sorption\ capacity}$$

Degree of P saturation based on oxalate extraction (DPS_{ox}) was calculated as follows:

$$DPSox = \frac{Pox}{\alpha\ (Feox + Alox)}$$

where P_{ox}, Fe_{ox} and Al_{ox} are concentrations of P, Fe, Al extracted by oxalate and α represents the proportion of Fe_{ox} and Al_{ox} dedicated to P sorption (Beauchemin and Simard, 1999; Van der Zee et al., 1988). The coefficient α represents the fraction of solid phase reactive sites variable between in studies (Beauchemin and Simard, 1999), but the value of 0.5 used in this study is generally considered as universal (Schoumans, 2000).

Results

Chemical characteristics of soil samples

Samples representing a relatively large area of agricultural land over the entire Czech Republic varied over a wide range of total content of P, Fe, Al, organic carbon (OC) and pH due to differences in soil type, fertilization, and agronomical practice (Table 1). The pH value of the soils was neutral to slightly acidic (median 6.5) and only six samples had higher pH than 7.5 with maximum value of 8.1. Total content of P was 1.1 mg g^{-1} (median) and only one sample exceeded 2 mg g^{-1}. Total P content was only weakly correlated to Fe (R^2 = 0.36) and Al (0.27). Soils greatly varied in organic matter content as the range of OC proportion was large (6-68%).

Table 1: Ranges, medians, and standard deviations (SD) of the measured chemical parameters of the l 56 selected soil samples (fraction < 63 µm).

Parameter (unit)	Range	Median	SD
pH	5.1-8.1	6.5	0.6
Total concentrations (µg g^{-1})			
P (TP)	510-2218	1100	368
Fe (Fe)	9776-55716	25597	11165
Al (Al)	19707-76559	37849	13705
Total C content (%)			
TOC	6-68	26	14
Mechlich 3 (µg g^{-1})			
P (P_{M3})	20-316	100	72
Fe (Fe_{M3})	31-470	290	89
Al (Al_{M3})	269-1200	749	194
Oxalate (µg g^{-1})			
P (P_{ox})	144-1558	551	263
Fe (Fe_{ox})	817-9892	3672	1892
Al (Al_{ox})	872-3054	1670	510
Oxalate saturation index (DPS_{ox}; %)	8-51	19	9
Fractionation - TP (µg g^{-1})			
H2O (TP_{H2O})	4-45	16	9
BD-I ($TP_{BD\text{-}I}$)	67-598	198	111
BD-II ($TP_{BD\text{-}II}$)	22-180	87	39
NaOH-I ($TP_{OH\text{-}I}$)	125-804	361	194
NaOH-II ($TP_{OH\text{-}II}$)	8-177	82	38
HCl (TP_{HCl})	30-566	102	113
Fractionation - SRP (µg g^{-1})			
H2O (SRP_{H2O})	4-41	13	9
BD-I ($SRP_{BD\text{-}I}$)	43-484	162	92
BD-II ($SRP_{BD\text{-}II}$)	20-178	82	32
NaOH-I ($SRP_{OH\text{-}I}$)	35-449	145	110
NaOH-II ($SRP_{OH\text{-}II}$)	7-106	41	21
HCl (SRP_{HCl})	9-614	107	123
Fractionation - Fe (µg g^{-1})			
BD-I ($Fe_{BD\text{-}I}$)	1849-11128	4306	1946
BD-II ($Fe_{BD\text{-}II}$)	2690-13413	5981	2415
Fractionation - Al (µg g^{-1})			
NaOH-I ($Al_{OH\text{-}I}$)	750-3026	1673	554
NaOH-II ($Al_{OH\text{-}II}$)	858-4793	2221	890
Sorption characteristics			
Sorption maxima (P_m; µg g^{-1})	130-755	403	134
EPC_0 (µg L^{-1})	33-1617	225	373
P_o (µg g^{-1})	15-177	63	39
Sorption saturation index (P_o/P_m; %)	4-50	16	10

Comparability between the <2mm and <63µm soil fractions

As the wet sieving homogenisation of soil samples is very common, but does not fully represent the fraction of erodible particles, a comparison of chemical analyses of soil samples variants (<2mm and <63µm) was done. Fig. 1a shows the week relationship between TP concentrations in both soil sample variants (similar was found for Fe and Al). As the fine particles are responsible for most of the chemical soil properties, and strong correlation was found for P_{M3} concentrations between both soil variants (Fig. 1b), we proceeded to work further only with the fine particle variant.

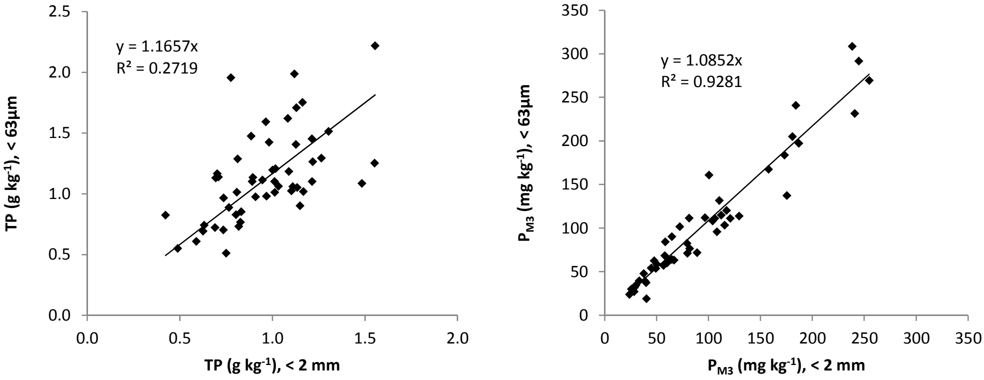

Fig. 1. Relationship of total P (TP) (a) and Mehlich 3 extracted P (P_{M3}) (b) from soil samples sieved through 2mm and 63µm mesh.

Single step extractions

Mehlich 3 extracted only a small part of total P, Fe and Al (median 9.1, 1.1 and 2.0 % respectively, Table 1). Neither $P_{M3,}$ Fe_{M3} or Al_{M3} were well correlated to their total contents as the coefficients of determinations of linear relationships were low (R^2=0.34; 0.17 and 0.13, respectively, P<0.05).

As oxalate solution is stronger extractant in comparison to the Mehlich 3 solution, higher concentrations of P, Fe and Al (median 50, 14.3 and 4.4 % respectively, Table 1) were extracted. Similarly to Mehlich 3 extraction, there was again no correlation between P_{ox}, Fe_{ox} and Al_{ox} and their total concentrations.

Sequential fractionation

Neither Mehlich 3 nor oxalate extractions specifically extract the sorption/desorption available P together with its natural binding partners (Jan et al., 2013). The improved fractionation scheme is able to distinguish between poorly crystalline Fe and Al minerals with very high sorption ability and the remaining matrices (Jan et al., 2015). Comparison of fractionation data with no P added and after P addition enables us to see what processes took part during the 72 h long sorption isotherm equilibration.

Fractionation data revealed various proportions of different P forms (Table 1). The sum of total extracted P in the six steps was 77 % compared to TP. The rest of the P was in refractory forms. On average 65% of TP was in inorganic forms determined as SRP (Fig. 2).

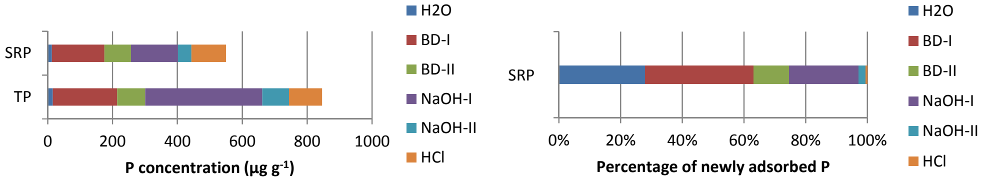

Fig. 2. Phosphorus distribution among individual extraction steps (left part), average of 56 soil samples with no P addition. Relative distribution of added P among individual extraction steps (right part), average of 56 samples with P added during the P sorption experiment.

The main SRP fractions were $SRP_{BD\text{-}I}$ and $SRP_{NaOH\text{-}I}$, (17 and 21 % of total SRP, respectively), which comprised of P bound to Fe and Al hydroxides. These most active Fe and Al forms in soils constituted only 16 % and 4 % of their total content, respectively. The relationship of $Fe_{BD\text{-}I}$ to total content of Fe, and of $Al_{OH\text{-}I}$ to total Al was not strong (R^2=0.19 and 0.22, $P<0.05$, respectively).

Soil samples with no adsorbed (vial without P addition) and adsorbed P (soil P increase of about 1 mg g^{-1} P) showed important changes after the sorption equilibration period (Fig. 2). In comparison with 2 % of SRP_{H2O} extracted in the variant with no P addition, 28 % of SRP was extracted as readily desorbable P in the H_2O step of the variant with sorbed P, which constituted a major increase in adsorbed P. Major portion of P was adsorbed onto Fe (hydr)oxides extracted in the BD-I fraction (35 %), followed by P adsorbed onto Al (hydr)oxides extracted in the NaOH-I step (23 %). Increase in SRP_{HCl} was negligible; we therefore assume that neither adsorption onto $CaCO_3$ and similar minerals or precipitation of hydroxyapatites occurred. Fractionation data clearly showed that Fe and Al (hydr)oxides were major sorption components of soil samples.

Relationship between single step and sequential extractions

In order to compare P_{M3} and P sorption properties, P_{M3} and P_{ox} concentrations and the sequential fractionation results were analysed. A strong relationship between P_{M3} and the molar ratio of sorption-active Fe and Al (hydr)oxides to P was evident (Fig. 3). The P_{M3} starts to rapidly increase when the molar ratio is less than 10, which suggests higher P saturation and weaker P bonding. The molar ratio of 10 roughly corresponds to P_{M3} of 50 µg g^{-1}.

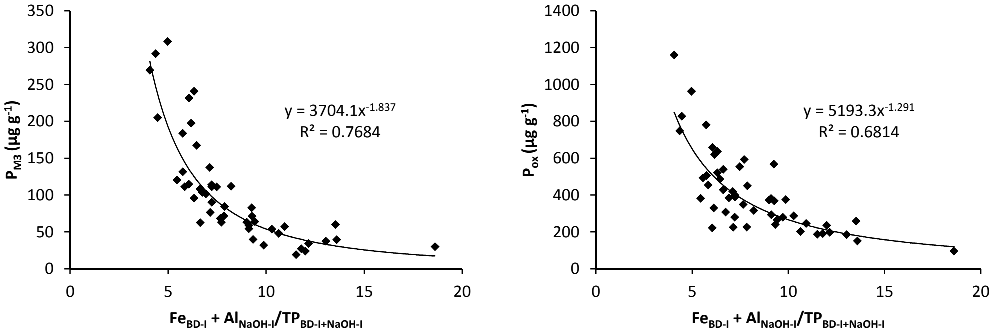

Fig. 3. Relationship between the molar ratio of sorption active Fe and Al (hydr)oxides to P and P concentrations extracted by Mehlich 3 (P_{M3}) and oxalate (P_{ox}) extractants.

A weaker relationship was found for the relationship between the P_{ox} concentration and the molar ratio, based on fractionation results (Fig. 3). Looking in detail at the separate relations of P, Fe and Al (Fig. 4), the largest uncertainty can be seen within the Al compounds, where the oxalate dissolves different minerals (or their parts) than NaOH. On the other hand the slope of the regression curve for P shows that oxalate extracts the same amount of P as BD-I and NaOH-I combined (Fig. 4).

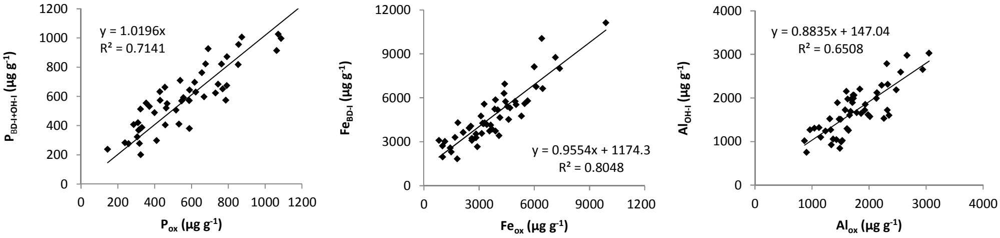

Fig. 4. Relationships between P, Fe and Al concentrations extracted by oxalate and their equivalents analysed by sequential extraction.

Sorption characteristics

To describe soil sorption properties, both Langmuir and Freundlich sorption isotherms were calculated for all samples. Maximum P sorption capacities calculated by the Langmuir isotherm were determined to be in the range of 130 to 755 µg g^{-1} P (Table 1). Equilibrium P concentration at zero net sorption (EPC_0), calculated from the Freundlich isotherm, greatly varied from 33 to 1617 µg L^{-1}, with median of 225 µg L^{-1}. The soil samples had high potential to release P into the recipient water with natural P background concentrations. Not a single sample would adsorb P in stream water SRP concentration under 30 µg L^{-1}. The concentrations of P already adsorbed onto particles ranged from 15-177 µg g^{-1}, with a median of 66 µg g^{-1}, which constituted from 4 to 50 % of P saturation, expressed as the sorption saturation index based on sorption characteristics and to 8 – 51 % based on DPS_{ox}.

Mehlich 3 phosphorus relationship to sorption characteristics

As the sorption isotherms are too laborious and hardly suited for routine laboratory practise we examined the changes in the adsorbed P concentration (P_a) under various simulated equilibrium concentrations (P_e). For each soil sample, the adsorbed P (P_a) or desorbed P ($-P_a$) concentrations were calculated using the Freundlich isotherm with regression parameters based on the sorption characteristics. The range of P_e concentrations from 20 to 220 µg L^{-1} with the interval of 10 µg L^{-1} P was used according to Czech Methodology for Ecological State Evaluation for PO_4-P. Highly significant linear relationship between P_a and P_{M3} was found for individual P_e concentrations in the range 20-220 µg L^{-1} (R^2 = 0.93-0.83, P<0.001). Examples of the relationships of different equilibrium P concentrations (P_e = 30, 60 and 100 µg L^{-1}) are shown in Fig. 5.

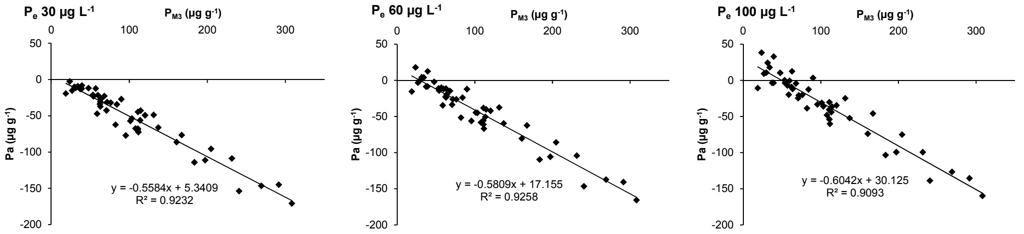

Fig. 5. Relationship between the Mehlich P concentration (P_{M3}) and the amount of adsorbed P (P_a) or desorbed P ($-P_a$) calculated for three selected P equilibrium (P_e) concentrations.

The linear equation $P_a=a*P_{M3}+b$ differed in both the slope (*a*) and intercept (*b*) for each P_e value. To generalize the pattern, we plotted both *a* and *b* regression parameters against P_e concentrations (Fig. 6) and found highly significant relationship with R^2 > 0.99* for both variables with the following equations Eq. 1 and Eq. 2.

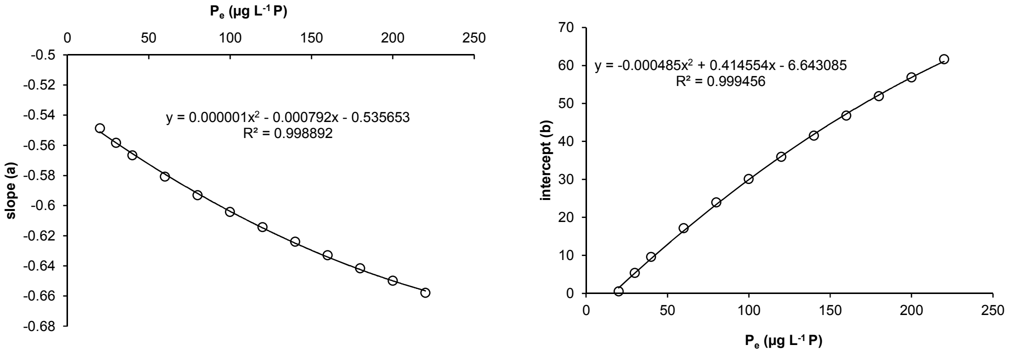

Fig. 6. Model for slope (a) and intercept (b) regression parameters calculated from recipient actual or target equilibrium P concentration (P_e). Valid for calculations based on Mehlich 3 P.

Table 2. Calculated slope (a) and intercept (b) for selected P_e concentrations in range from 20 to 190 µg L^{-1}.

Pe (µg L^{-1})	20	30	50	70	90	110	130	150	170	190
slope (a)	-0.5510	-0.5584	-0.5725	-0.5857	-0.5980	-0.6094	-0.6199	-0.6296	-0.6384	-0.6463
intercept (b)	1.4539	5.3568	12.8716	19.9981	26.7365	33.0867	39.0488	44.6227	49.8083	54.6059

Eq. 1. $a = 1.101064E{-}06 * P_e^2 - 7.916045E{-}04 * P_e - 5.356533E{-}01$

Eq. 2. $b = -4.852173E{-}04 * P_e^2 + 4.145542E{-}01 * P_e - 6.643085E{+}00$

By combining the equations above, it is possible to determine the amount of P sorbed/desorbed from erosion particles from/into the recipient water of given PO_4-P concentration (expressed as P_e). This means that, from the known amount of eroded particles of soils with known P_{M3} and known SRP recipient concentration, one can reliably calculate the amount of released P and compare it with other P sources or use it in P mass-balance calculations. Example: *Soil with the P_{M3} concentration 100 µg g^{-1} (P_{M3} median of our sample set) will release 46, 26 or 4 mg P from 1 kg of material into a stream with SRP concentration 30, 100 and 200 µg L^{-1}, respectively.*

It is also possible to find the P_{M3} concentration threshold for the soils which enter the recipient with actual or targeted SRP concentration. Example: *Erosion particles with no net P release into stream water with SRP concentration 30, 100 and 200 µg L^{-1} must have P_{M3} concentration 17, 56 or 94 µg g^{-1}, respectively.*

Alternative approach using oxalate extraction results

Soil P saturation estimates based on the oxalate extraction results (DPS_{ox}) are widely used in many countries for the evaluation of soil P availability. The relationship between the binding partners (Fe, Al), the P molar ratio from sequential extraction, and oxalate P was not very strong (Fig. 3, right part) and favoured the use of P_{M3} instead. However the direct correlation between DPS_{ox} and P_a (Fig. 7) shows that the relationship can be used in a similar way as with the P_{M3}. The correlation coefficients were not as high as those found for P_{M3}, but this approach may be used when P_{M3} data are not available.

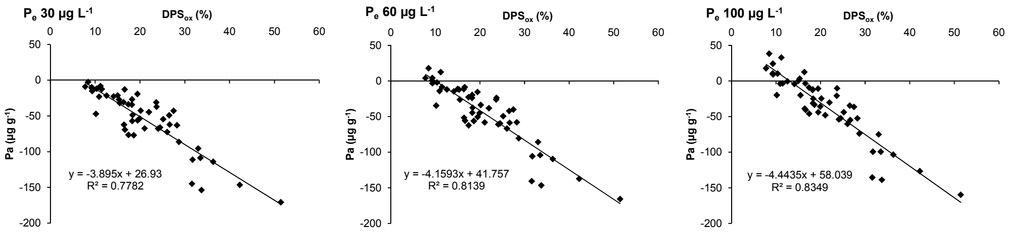

Fig. 7 Relationship between soil P saturation based on the oxalate extraction (DPS_{ox}) and the amount of adsorbed P (P_a) or desorbed P ($-P_a$) calculated for three selected P equilibrium (P_e) concentrations.

Again, the linear equation P_a=c*DPS_{ox}+d differed in both the slope (*a*) and intercept (*b*) for each P_e value and the pattern was generalized by plotting both *a* and *b* regression parameters against P_e concentrations (Fig. 8). Highly significant relationship with $R^2 > 0.99$* for both variables was described by equations Eq. 3. and Eq. 4.

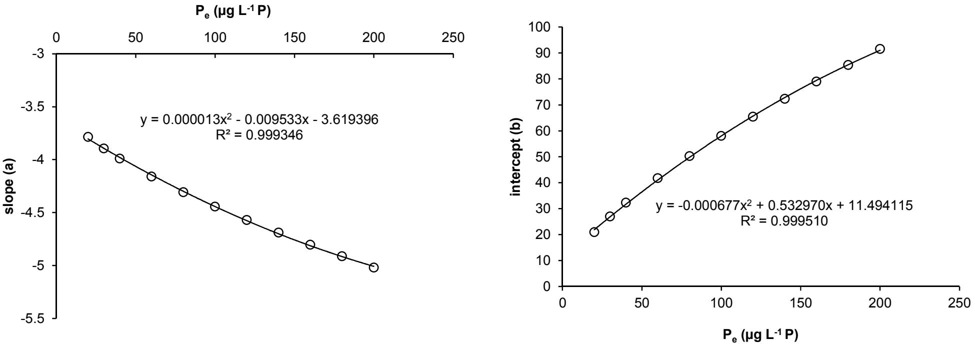

Fig. 8. Model for slope (a) and intercept (b) regression parameters calculated from recipient actual or target equilibrium P concentrations (P_e). Valid for calculations based on soil P saturation derived from the oxalate extraction.

Eq. 3. $c = 1.295798E\text{-}05*DPS_{ox}^2 - 9.533492E\text{-}03*DPS_{ox} - 3.619396E+00$

Eq. 4. $d = -6.7738535E\text{-}04*DPS_{ox}^2 + 5.3296956E\text{-}01*DPS_{ox} + 1.1494115E+01$

Discussion

Soils used in this study were non-calcareous and covered large range of TP, Fe and Al concentrations (up to 2, 56 and 76 mg g^{-1}, respectively), while, according to sequential fractionation results, Fe and Al were the main P-binding partners. As it was showed elsewhere, the prevailing soil composition governs the P binding processes and hence not all methods used for estimating soil P availability or P saturation are universally suitable for all soils. Moreover, some laborious methods are not suitable for routine agricultural screening. Bauchemin and Simard (1999) reviewed the P saturation concept for Canadian soils and found the P saturation index based on P, Fe and Al contents extracted by ammonium oxalate to be the most relevant the agricultural P dosing management in non-calcareous soils.. As an alternative, the ratio of Mehlich 3 extractable P to Al was proposed, as it relies on the use of a routine laboratory test, but with the exception of samples where Al_{ox} concentrations are >6 mg g^{-1}. Recently Daly et al. (2015) studied the P sorption properties on calcareous and non-calcareous soils and confirmed large differences in the relationships between soil P availability test results (Morgan P, Mehlich 3) and soil P sorption properties. Soil samples examined in this paper showed P saturation values within the range published by Daly et al. (2015), De Smet et al. (1996), Sharpley et al. (1996), Zhang et al. (2005)and others.

Many authors reported a relationship between soil P sorption properties and the extractable Al and Fe in non-calcareous soils. The strong association between P sorption maxima and amounts of extractable Al in preference to Fe have been shown (Burkitt et al., 2002; Daly et al., 2001; Maguire et al., 2001; Pautler and Sims, 2000). Higher importance of Al may relate to the very good selectivity of oxalate extraction to Al (hydr)oxides, i.e. minerals with a very large sorption active surface. For Fe minerals, dissolution of sorption active Fe (hydr)oxides and sorption inactive minerals was shown (Jan et al., 2013). Furthermore, Mehlich 3 extraction does not dissolve Fe minerals, but it is able to substitute P adsorbed on to Fe minerals (measured on synthetic (hydr)oxides with sorbed P, not shown).

As our data show, the Mehlich 3 solution extracts a large part of Al_{ox} (due to the presence of F which dissolves Al; Fernández Marcos et al., 1998), but very low amount of Fe_{ox} compounds. Both Al_{ox} and Fe_{ox}, however, have been shown to be the proxy for the most sorption active Fe and Al compounds in oxic conditions (Jan et al., 2013). The low extraction efficiencies of the Mehlich 3 solution, especially with respect to Fe and in comparison to oxalate, have been demonstrated previously (Fernández Marcos et al., 1998; Sims et al., 2002; Tran et al., 1990). It is, nevertheless, often used to estimate the P saturation of soils (Khiari et al., 2000). Because Fe is not taken into account by this approach, Al is erroneously considered to be the main constituent in P sorption. According to our data Fe (hydro)oxides ($Fe_{BD\text{-}I}$) are very important for the P sorption.

Due to these uncertainties many relationships are described as "black boxes", without deeper documentation of processes. As the P sorption/desorption processes strongly depend on the mineral surfaces available for P sorption (Jan et al., 2015; Li et al., 2012; Lijklema, 1980; McLaughlin et al., 1981), we used a modified sequential fractionation scheme which targets poorly crystalline Fe and Al minerals with large sorption ability (Jan et al., 2015) to reveal the chemical composition consequences of the single step extractions and P saturation of sorption minerals. In contrast to other soils, we have found very strong relationship between the P_{M3} concentration and Fe +Al/P ratio in BD I and OH I steps (Fig. 3). The P_{M3} concentration seems to be almost constant, fluctuating around 50 µg g^{-1} P when Fe +Al/P molar ratio is > 10, but lower ratios are accompanied by higher P_{M3} concentrations. As the Mehlich 3 solution is a weaker extractant in comparison to dithionate and hydroxide step from sequential extraction, this can be explained by weaker P binding onto Fe and Al minerals due to available P excess, as all the preferential strongly bonding sites on mineral surfaces have already been occupied (Hiemstra and Van Riemsdijk, 1996, 1999). The strong P-mineral bonds may be the reason why P_{M3} concentrations < 45 µg g^{-1} were suggested to be below the optimum concentration of P available for crop yield (Beegle et al., 1998; Sims, 2000a).

It is well known that the majority of TP within overland flow from cultivated fields is in particulate forms, however not all the content of TP is bioavailable (Sharpley et al., 1996). One approach to address this P source is to identify critical places in watersheds with high potential for P export, quantify the P export, and assesses the ability of management practices to minimize the export (Coale et al., 2002). This approach usually requires detailed spatial information about the soil erosion losses and relevant soil chemistry.

During the last decade, our understanding of sources and transport pathways of pollutant P transfer has improved markedly (Pärn et al., 2012; Sims et al., 2000b; Withers et al., 2014). However, this improved understanding is not necessarily reflected in the widely used computer models (Sharpley et al., 2002), despite their critical role in identifying areas in watersheds with a high potential for P export. It is partly due to low comparability of the experiment setups when, for example, measuring sorption/desorption soil properties. Lucci et al. (2010) documented difference of an order of magnitude in P sorption maxima and EPC_0 determination when using stream water or 0.01 M $CaCl_2$ solution as the base water for P sorption experiments. Stronger solution led to lower EPC_0 and overestimation of sorption maxima. The other reason for the slow model improvement may be the low possibility of generalization of the experimental information, as it usually fits only one modelled or described situation.

Because of that, we have tried to develop a simple tool, which enables us to describe the soil particle P behaviour under various surrounding P conditions according the specific particle properties derived from widely used analyses.

Most of the dynamic watershed models, like AGNPS (Young et al., 1989), EPIC (Williams and Singh, 1995) or SWAT (Arnold et al., 2010) are not, due to their structure, able to reflect the spatial heterogeneity of soil particles which can be found even over areas as small as one field. Instead of that, average values of soil P tests have to be used for entire spatial model subunits. This may not be a problem when solving heavy eutrophication issues within a large watershed, but the employment of such models is not useful when trying to make finer comparisons between dissolved P sources.

Another approach, simpler and without the possibility to simulate consequent processes, can be the use of empirical statistical models targeting basic, but important information for decision makers. The information about the P sorption maxima, P saturation or P availability is not very helpful when answering questions such as how much does erosion contribute to eutrophication or how are the soil particles influencing P concentrations in a particular stream.

The empirical equations suggested in this paper can easily fit the results from detailed erosion models. Rough estimates of P adsorption/desorption can be made by combining the suggested equations with erosion modelling results and erosion maps calculated worldwide by the USLE/RUSLE equations (Schönbrodt et al, 2010 and many others). Much detailed and precise information can be obtained when the suggested equations are combined with models such as the WaTEM/SEDEM (Van Oost et al., 2000; Van Rompaey et al., 2001, Verstraeten et al., 2002), which are able to simulate areas of erosion particle origin and deposition. This spatial information can be connected with soil P test spatial data (in case of Czech Republic with Mehlich 3 P), which allows the calculation of the P adsorption/desorption particle short term P behaviour in the stream water. As the suggested approach is based on the reversible sorption/desorption processes, it should be robust enough for particle composition changes which can take place during an erosion episode. The P which is temporarily sorbed or desorbed by particles during erosion is supposed to be a subset of Mehlich 3 P under normal conditions. This is of course not true for P leaking from plant material, which can be found on the field during an erosion episode.

There are many reports in literature linking the soil P availability, measured by various analytical approaches, and P concentrations found in the runoff from fields. The soil, however, is neither homogeneous nor static. Factors such as microbial processes, especially in the organic topsoil, the varying extent of soil aggregation, soil sorption complexes, preferential runoff, or soil horizons – all of these have a profound influence on P concentration measured in runoff from fields, which therefore cannot be meaningfully linked to our approach.

Another group of studies focuses on sediments which are already in the waterways. These however differ substantially from the original soil as they have undergone changes due to microbial action or fluctuations in redox potential and pH. Because different particle types constitute sediments in different parts of the waterways, based on river and stream morphology, flow velocity, and particle size, it is difficult to link sediment-based data back to the soil.

Fine eroded soil particles were determined as the missing link between the characterization of bulk soil and stream sediments, as the fine particles are usually transported through stream systems and may represent important source of dissolved P in stream water due to equilibrium concentration (Agudelo et al., 2011). What we have aimed at in this study is to provide a model that would bridge the gap between the above mentioned two types of studies – by focusing on the influence of erosion particles which have been suspended for prolonged time periods and which have the greatest potential to influence the concentration of bioavailable P. Although this approach also has its limitations, we believe it is a significant improvement on the methods currently used.

Conclusions

The molar ratio of sorption-active Fe and Al (hydr)oxides to P was found to be strongly positively correlated with both the P_{M3} and the P_{ox} concentrations. Using the P sorption described by the Freundlich isotherm, a strong linear relationship between both P_{M3} concentration and DPS_{ox} saturation, and the P concentration which can be sorbed to/desorbed from the soil particles has been described for selected equilibrium P concentrations. The results were generalized (for the specific water SRP concentrations ranging from 20 to220 µg L^{-1}) into an empirical statistical model, which can predict the behaviour of eroded soil particles in the recipient water with known or targeted P concentration. The presented model, together with the commonly obtained plant available P concentration, can easily follow the results of widely used erosion models and provide the missing link between the bulk soil and the stream sediments.

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