REVIEW ARTICLE

Sequential extraction procedures for the determination of phosphorus forms in sediment

Changyou Wang · Yong Zhang · Hongli Li · R. John Morrison

Abstract This article summarizes the main extraction methods for sedimentary phosphorus (P) determination. With sequential chemical extractions, P is supposed to be selectively removed from different compounds in the sediments. Extraction schemes using strong acids and alkaline solutions have been tested on different sediments and found not to extract well-defined fractions. In addition, several systematic errors in these schemes have been detected. Thus, these schemes have been modified and simplified accordingly. The Standards Measurements and Testing Program of the European Commission (SMT) method is a popular modification of these extraction schemes, as it is simple to handle, allows laboratories to achieve reproducible results and could provide a useful tool for routine use by water managers. The SEDEX (sequential extraction method) method, another popular modification, is widely applied in biogeochemical research as it can separate authigenic carbonate fluorapatite from fluorapatite. Other chemical extractions using chelating compounds have attempted to extract P bound with iron and calcium in sediments without disturbing clay-bound or organic P, the purpose being to determine the algal-available non-apatite, apatite and organic fractions of sediment P. All extraction procedures still yield operationally defined fractions and cannot be used for identification of discrete P compounds. Future modifications of the extraction scheme should aim to achieve better extraction efficiency and selectivity, simple handling techniques and methods that can prevent the extracted P from being re-adsorbed onto Fe(OOH) and $CaCO_3$.

Keywords Phosphorus · Extraction · Sediment · Forms

C. Wang (✉) · H. Li
School of Marine Sciences, Nanjing University of Information Science and Technology, Nanjing 210044, China
e-mail: chy.w@hotmail.com

Y. Zhang
Key Laboratory of Coastal Zone Environmental Processes, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China

R. J. Morrison
School of Earth and Environmental Sciences, University of Wollongong, Wollongong, NSW 2522, Australia

Introduction

As a key component of fertilizer, phosphorus is crucial for the world's food supplies and is intimately involved in both terrestrial and marine biogeochemical cycles (Blake et al. 2005; Jaisi and Blake 2010). P is a potentially limiting nutrient that sustains primary productivity and has been recognized as a key factor responsible for eutrophication in lake, estuarine and some other waters (Schindler et al. 1973). The excessive supply of P (mainly of anthropogenic origin) in water systems induces a degradation of their quality through the proliferation of algae, thus hindering various water uses. P in water has two origins, i.e., external and internal. P from external origins comes from diffuse sources (natural, agricultural) or point sources (industrial and domestic effluents). This nutrient is also released from the sediment, which acts as an internal source. Sediment can contribute phosphate to the overlying waters at levels comparable to the external source (Yuan et al. 2010). However, most sediment P is in the particulate form, dissolved P comprising only a few percent of total P (TP) (Ruban et al. 1999a, b).

The recorded P mineral particulates include apatite ($Ca_{10}(F, OH)(PO_4)_6$), brushite ($CaHPO_4 \cdot 2H_2O$), octocalciumphosphate

($Ca_3(HPO_4)_3 \cdot 3H_2O$), anapaite ($Ca_3Fe(PO_4)_3 \cdot 4H_2O$), strengite ($FePO_4 \cdot 2H_2O$), vivianite ($Fe(PO_4)_2 \cdot 8H_2O$), lipscombite ($Fe_3(PO_4)_2 \cdot Fe(HO)_2$), phosphoferrite (($Mn, Fe)_3(PO_4)_2 \cdot 3H_2O$), ludlamite (($Fe$, Mn, $Mg)_3(PO_4)_2 \cdot 4H_2O$), variscite ($AlPO_4 \cdot 2H_2O$) and wavellite ($Al_3 (PO_4)_2(OH, F)_3 \cdot 5H_2O$) (Pettersson et al. 1988). The P organic particulates, a complex fraction the exact nature of which is not precisely known, mainly consist of biogenic material. However, significant diagenetic reorganization of P occurs during burial, owing to changes in pH and redox potential. Not all the forms of particulate P are likely to be released and become bioavailable and therefore likely to increase eutrophication. The ability of sediment to store or release P has repercussions on the trophic state of waters, hence on their productivity. The study of the behavior of P in the sediment is therefore a key factor that helps our understanding of the P cycle in rivers, lakes and other marine waters.

To understand the burial and diagenesis of P in sediments, it is necessary to identify, separate and quantify the various solid-phase reservoirs of sedimentary P, which is difficult because of the low concentration and the fine-grained nature of most sediments. These two factors preclude the use of most standard methods for direct identification of mineral phases, such as X-ray diffraction. Independent chemical analyses of phosphatic phases, such as isotopic or trace element signatures, clearly cannot be applied when discrete phases are not separable (Ruttenberg 1992). The ^{31}P nuclear magnetic resonance (^{31}P NMR) can be used to assess the general composition of P in a variety of matrixes on both solid samples (solid state ^{31}P-NMR) and on samples in solution (high-resolution ^{31}P-NMR). Though it is possible to learn something about solid-phase P in sediment using solid-state ^{31}P-NMR, this is seldom used because of the inherently low sensitivity of NMR and low natural abundance of P in sediment. High-resolution NMR is the better method because it allows pre-concentration of the sample before analysis, but high-resolution ^{31}P-NMR also requires extraction of P from the original solid matrix (Ahlgren et al. 2006, 2007). As a result, it is necessary to use fractionation of inorganic P to identify the amount in each discrete chemical form.

The various forms in which P occurs in sediments have received considerable attention in recent decades, and many extraction schemes have been developed. The methods for the chemical extraction of different forms of sediment P originated from soil science. Sequential extractions were designed to quantify step-by-step discrete chemical or mineralogical compounds. Extraction methods not only provide information on the potential mobility of P species, they also allow the assessment of the origin of the sediment P. The best example of these early extraction schemes is the one presented by Chang and Jackson in 1957. The Chang and Jackson (1957) procedure was

further developed by Williams et al. (1967, 1971, 1976), Hieltjes and Lijklema (1980), Psenner and Pucsko (1988), Ruttenberg (1992), Golterman (1982, 1995, 1996) and Golterman et al. (1998). These authors pointed out the shortcomings of the former procedure and suggested their own modifications. However, to date, no standardized method is available for the determination of different forms of P in sediments. These P forms determined using sequential extraction procedures are operationally defined and are related to specific reagents and procedures, such as authigenic carbonate fluorapatite (CFAP) separated from detrital apatite by acetate buffer, i.e., results are interpreted to be related to a specific phase of sediment (although, sensu stricto, it is related solely to a chemical procedure). It has been recognized that the different P fractions are of different significance in terms of ecological meaning. Bioassays are the main method to give some insight into the availability of P in sediment. Williams et al. (1980) showed a linear correlation between algal growth with the sediments as the sole source of P and the non-apatite inorganic P fraction extracted by NaOH. Dorich et al. (1985) found that P extracted by NaOH correlated strongly with bioavailable P, but overestimated the bioavailable P by a constant amount, presumably because of the hydrolysis of non-available organic P (OP). This knowledge has also been updated gradually with the use of new technology and methods: for example, the belief that P extracted by NaOH reflects the P most available to algae (Williams et al. 1980) was questioned by Golterman (1996), who stated that ethylenediaminetetraacetic acid (EDTA) as a P extractant (instead of NaOH) gave more information on the quantity of P available for algae.

This article summarizes the main extraction methods for sedimentary P determination, including the methods of Williams (Williams et al. 1967, 1971, 1976), Hieltjes-Lijklema (Hieltjes and Lijklema 1980), Golterman (Golterman 1982, 1995, 1996), sequential extraction (SEDEX) (Ruttenberg 1992), standards measurements and testing (SMT) (Ruban et al. 1999a, b, 2001), Penn (Penn et al. 1995; Penn and Auer 1997) and Jensen (Jensen and Thamdrup 1993; Jensen et al. 1998), discusses the ecological significance of the fractional composition, comments on the inherent problems and applicability of chemical fractionation, and makes a practical recommendation.

Development of sequential extraction procedures of P forms in sediments

Sequential extraction methods take advantage of the fact that different solid phases show dissimilar reactivity toward different solutions. Sediment is extracted with a

series of extractants, each chosen to selectively dissolve a single phase or group of phases of similar chemical characteristics. The sequence is designed so that the most reactive phases are removed first, and the severity of the extractants increases with each step. Sequential extraction schemes were first developed for soils and then extended to sediments. Characterization of the different forms of inorganic phosphorus in soil by sequential extraction with acid and alkaline reagents was initiated by Dean in 1938 (Dean 1938) and later modified by Chang and Jackson in 1957. Most procedures used in sediments are modifications or improvements of the sequence, based on extraction using acidic and alkaline reagents, originally suggested by Chang and Jackson (1957; Tiyapongpattana et al. 2004). There are no radical differences in extractants between the soil and sediment extraction scheme except for the specific method for sediment to distinguish authigenic apatite from detrital apatite and pretreatment approaches to treat soils and sediments prior to extraction (Williams et al. 1971; Hieltjes and Lijklema 1980; Ruttenberg 1992; Condron and Newman 2011). Most operationally defined schemes available address inorganic forms of phosphate. The main inorganic forms of P are the fraction adsorbed by exchange sites and referred to as loosely bound, labile or exchangeable P, the fraction associated with Al, Fe and Mn oxyhydroxides, and the fraction in Ca-bound compounds generally referred to as apatite P or Ca-bound (Ruban et al. 1999b). Organic P is a complex fraction, the exact nature of which is not precisely known, and is normally taken into account as a whole. The steps involved in each method are summarized in Table 1.

Williams method

The Chang and Jackson (1957) procedure using acid and alkaline reagents was modified and applied to the sediment by Williams et al. (1967, 1971, 1976). The shortcomings of the original procedure were pointed out, including the extraction of iron-bound P plus aluminum-bound P with ammonium fluoride, as well as the re-adsorption of phosphate due to formation of calcium difluoride, especially in calcium-rich sediments. They therefore suggested several modifications (Williams et al. 1967, 1971, 1976), as indicated in Table 1.

Williams et al. (1976, 1980) used an extraction method with tri-sodium citrate, sodium dithionite and sodium bicarbonate (CDB) followed by NaOH. A subsequent extraction with HCl is supposed to extract Ca–P. The shortcomings of these two versions have already been outlined, including re-adsorption of phosphate onto carbonate, which could occur in the NaOH extraction, especially in calcareous sediments (Hieltjes and Lijklema 1980). It was also shown that a substantial amount of calcium-bound P was solubilized by the CDB reagent of Williams (1971, 1976), for which the strongly chelating citrate ion was responsible. The CDB extraction was omitted by Burrus et al. (1990), but the name of the modified procedure was not changed and usually listed as a later version of the Williams scheme (Golterman 1996; Ruban et al. 1999b; Hoyle 2004). The reason for this change was the belief that P extracted by NaOH reflects the P available to algae. The idea of identifying discrete P compounds was gradually abandoned, and sediment P content was finally separated into non-apatite P, apatite P and OP. The non-apatite P was considered as bioavailable, non-available apatite P and partly available OP. OP was considered to be completely extracted by hydrochloric acid and sodium hydroxide, the latter in two consecutive steps. Total P and molybdate reactive P were measured in the pooled extracts and OP calculated from the difference (Williams et al. 1976). The extraction scheme of Williams as modified by Burrus et al. (1990) is not completely sequential, involving two independent procedures.

The Hieltjes-Lijklema method

The need for chemical characterization was stressed in the Hieltjes and Lijklema (1980) method in order to improve comprehension of the P exchange processes between sediment and water and the effects of environmental conditions such as pH, redox potential and ionic strength on these processes (Hieltjes and Lijklema 1980).

The Hieltjes-Lijklema (1980) method uses NaOH to solubilize Fe and HCl to dissolve Ca, and the NaOH extraction is preceded by NH_4Cl extraction. In this method, residual P is given by the difference between the TP content and the sum of reactive (inorganic) fractions and mainly consists of OP. Although the same reagents are used in the Williams (Burrus et al. 1990) and Hieltjes-Lijklema (1980) methods, their concentrations differ; they are higher in the Williams method (Burrus et al. 1990). The Williams (Burrus et al. 1990) method yields OP, which is not the case with the Hieltjes-Lijklema (1980) method (OP can be calculated as the difference between TP and IP). The Hieltjes-Lijklema (1980) method yields soluble labile P, whereas this phase is not determined in the Williams (Burrus et al. 1990) scheme. Also, the Hieltjes-Lijklema (1980) method is a sequential extraction scheme, whereas in the Williams (Burrus et al. 1990) protocol the steps are independent, not sequential.

That only one sediment sample is needed is considered an advantage of the Hieltjes and Lijklema (1980) method compared to the Williams (Burrus et al. 1990) method. However, the concentration of the NaOH and the influence of the extraction time were not taken into account in this method. Repeating the treatment with NaOH, Golterman

Table 1 Extraction schemes for determining the fractional composition of sediment phosphorus

Procedure	Extraction	Proposed fraction	Advantages	Shortcomings
Chang and Jackson (1957)	a. NH$_4$Cl 1 M	Labile P	Separating and quantifying the P reservoirs most available	Extraction of Fe–P by NH$_4$F resorption by CaF$_2$ precipitation of phosphate with iron
	b. NH$_4$F 0.5 M pH 8.2	Al-bound P		
	c. NaOH 0.1 M	Fe-bound P		
	d. HCl 0.5 M	Ca-bound P		
	e. CDB	Reductant-soluble P		
	f. NaOH	Refractory P		
Williams et al. (1976)	a. CDB 0.22/0.1 M	Non-apatite P	Simple, practical	Resorption by carbonates in calcareous sediments; Ca–P and org-P released by CDB
	b. NaOH 1 M	Apatite P		
	c. HCl 0.5 M	Organic P		
Williams (Burrus et al. 1990)	a. NaOH 1 M	Non-apatite P	Simple, practical	Partial resorption of P extracted by NaOH on CaCO$_3$
	b. HCl 1 + 3.5 M	Apatite P		
	c. HCl 3.5 M + calcination	Total P		
	d. HCl 1 M + calcination	Organic P		
Hieltjes and Lijklema (1980)	a. NH$_4$Cl 1 M pH 7	Labile P	Simple, practical	Dissolution of small amounts of Fe–P and Al–P by NH$_4$Cl; hydrolysis of organic P; no relation with bioavailability
	b. NaOH 0.1 M	Fe- and Al-bound P		
	c. HCl 0.5 M	Ca-bound P		
Golterman (1996)	a. H$_2$O	Labile P bioavailable	Giving more information on the quantity of P available for algae	Not practical; EDTA interferes with P determination; complicated solution preparation; in some sediments, extraction must be repeated
	b. Ca-EDTA 0.05 M + dithionite	Iron-P bioavailable Ca–P non-available		
	c. Na$_2$-EDTA 0.1 M	Acid-soluble OP bioavailable		
	e. H$_2$SO$_4$ 0.25 M	Reductant OP non-available		
	f. NaOH 2 M			
SEDEX (Ruttenberg 1992)	a. MgCl$_2$ 1 M	Loosely sorbed P	Separating authigenic CFAP from detrital FAP	Very long; not practical; partial OP released by CD
	b. CDB 0.3/1 M	Ferric Fe-bound P		
	c. Acetate buffer 1 M	CFAP + biogenic apatite + CaCO$_3$–P		
	e. HCl 1 M	Detrital apatite		
	f. Calcination + HCl 1 M	Organic P		
SMT (Ruban et al. 2001)	a. NaOH 1 M (extract + 3.5 M HCl)	NaOH-P HCl-P	Simple, practical	Partial resorption of P extracted by NaOH on CaCO$_3$
	b. 1 M HCl	IP		
	c. HCl 1 M	OP		
	d. HCl 1 M + calcination	Conc. HCl-P		
	e. HCl 3.5 M + calcination			

Table 1 continued

Procedure	Extraction	Proposed fraction	Advantages	Shortcomings
Penn et al. (1995)	a. NH_4Cl 1 M (3×)	Loosely bound P loosely sorbed and $CaCO_3$-associated P	Owing to loosely sorbed and $CaCO_3$-associated P, Fe- and Al-bound Ps are combined and termed loosely bound P, dissolution of small amounts of Fe–P and Al–P by NH_4Cl was avoided	Hydrolysis of organic P; no relation with bioavailability
	b. NaOH 0.1 M (split)	Fe and Al bound P		
	c. NaOH 0.1 M (split)	Extractable biogenic P		
	d. HCl 0.5 M	Calcium mineral P		
	e. Persulfate digestion	Refractory organic P		
Psenner et al. (1988)	a. NH_4Cl 1 M	Soluble P	Separating and quantifying the P reservoirs most available	Resorption by carbonates in calcareous sediments; hydrolysis of organic P
	b. DB 0.11 M 40 °C	Reductant-soluble P, Fe- and Al-bound P		
	c. NaOH 1 M	Refractory OP		
	d. NaOH 1 M	Ca-bound P		
	e. HCl 0.5 M			
Jensen et al. (1998)	a. $MgCl_2$ 1 M	Loosely adsorbed IP and leachable OP	Separating authigenic CFAP from detrital FAP	Very long; not practical; resorption by carbonates in calcareous sediments
	b. DB 0.11 M	Iron-bound IP		
	c. NaOH 0.1 M	Adsorbed IP + leachable OP		
	d. Acetate buffer 1 M	Authigenic apatite + $CaCO_3$–P + leachable OP		
	e. HCl 0.5 M	Detrital apatite		
	f. Ignition + HCl 1 M boilling	Refractory OP		

(1996) found that a second extraction may extract another ~30 % of this P pool, while increasing the NaOH concentration again extracted more orthophosphate. It is obvious that what is extracted with the NaOH is certainly not only Fe-bound P (Golterman 1996). The other shortcomings of this method include that dissolution of small amounts of Fe–P and Al–P by NH_4Cl is possible in the Hieltjes-Lijklema (1980) scheme. Furthermore, though the back precipitation onto $CaCO_3$ in the NaOH extraction was taken into account, the improvement in removing the calcium carbonate by ammonium chloride extraction was inefficient, especially in highly calcareous sediments. This procedure does not extract specific compounds and therefore gives no information on the quantity of P available for algae if $CaCO_3$ and/or org-P is present in reasonable amounts (Golterman 1996).

Golterman method

Golterman (1982, 1995, 1996) has argued that strong acids and alkaline solutions should be avoided in P extraction schemes since they are too aggressive and do not deliver well-defined fractions. By using a chelating compound, Fe- and Al-bound P would be extracted without disturbing clay-bound or OP.

Several modifications were suggested by Golterman (1982, 1995, 1996). At first, repeated extractions with 0.01 M sodium nitrilotriacetate (NaNTA) solution were suggested, but later sequential dissolution of Fe- and Ca-bound P with 0.05 M calcium nitrilotriacetate (CaNTA) and 0.05 M NaNTA, respectively, was proposed (Golterman 1982). Nitrilotriacetic acid or its salts (NTA) are replaced subsequently by EDTA. The EDTA fractionation of sediment-bound inorganic phosphate was improved and made more effective. The Fe-bound phosphate in a recent version was extracted with Ca-EDTA plus dithionite, followed by an extraction of Ca-bound phosphate by Na_2-EDTA at pH = 4.5 (Golterman 1996). The method using EDTA as P extractant instead of NaOH is different from the Williams (Williams et al. 1967, 1971, 1976; Burrus et al. 1990) and Hieltjes-Lijklema (1980) methods, and the Fe-bound phosphate extracted with Ca-

EDTA gives more information on the quantity of P available for algae than the P extracted by NaOH. NaOH is too aggressive and does not deliver well-defined fractions (Golterman 1996), as the pH during the extraction is very different from the pH of the sediment, causing changes in the original P composition. Fabre et al. (1996) have shown that P extracted by NaOH is not equal to the P available for algae. Dorich et al. (1985) demonstrated a strong correlation between algal available P and P extracted by NaOH, but also that the NaOH extraction largely overestimated the available P. It seems that this overestimation is caused by the hydrolysis of non-available OP.

The Golterman (1996) method is not without pitfalls. EDTA solutions have the disadvantage of interfering with the orthophosphate and Fe determinations. However, Golterman insisted that for the orthophosphate determination 2 ml 0.1 M of EDTA could be used without interference (Golterman 1996). Another disadvantage of the NTA/EDTA extractions is that they must be repeated, as one single extraction can never give complete recovery.

SEDEX

The Ruttenberg (1992) method, i.e., SEDEX (Ruttenberg 1992) scheme, initially developed for marine sediments, is a five-step procedure capable of separating authigenic CFAP from detrital apatite of igneous or metamorphic origin (FAP); it is widely applied in biogeochemical research.

The SEDEX (Ruttenberg 1992) method uses $MgCl_2$ to extract loosely sorbed or exchangeable P, CDB to solubilize ferric Fe-bound P, acetate buffer to dissolve authigenic carbonate fluoroapatite and biogenic apatite and $CaCO_3$ associated P, HCl to dissolve detrital apatite and a second HCl extraction after calcination to measure OP. The SEDEX method is the first devised to chemically separate two of the main categories of authigenic phosphate phases called upon most often as sedimentary sinks for diagenetically mobilized P: ferric oxyhydroxide-associated P (Fe–P) and authigenic CFAP. It also offers a means for separating authigenic CFAP from FAP, which is the main advantage of the SEDEX method. The importance of this distinction is that CFAP represents an oceanic sink for reactive P, whereas detrital apatite does not. Coupled with pore-water and other solid-phase data, the SEDEX method is capable of revealing otherwise inaccessible information on the chemical nature of sedimentary P. However, although Ruttenberg (1992) also described the problem of analytical artifacts resulting from redistribution of P onto residual solid surfaces during extraction also being resolved by washing the sediment residue with $MgCl_2$ between extraction steps, no data were found to support this claim. The five-step SEDEX (Ruttenberg 1992) was

streamlined to a four-step procedure by Anderson and Delaney (2000). The major modifications were the combination of extraction of adsorbed and oxyhydroxide-associated pools into a single step and the use of a lower dithionite concentration, resulting in a decreased analytical background and number of working days required. In addition, automated spectrophotometric flow injection analysis was used to determine P concentrations rather than traditional spectrophotometric techniques.

The underestimates of OP values due to SEDEX pre-extraction of OP in the prior steps were discussed by Ruttenberg (1992). Pre-extracted OP will not affect the accuracy of the measured quantities of P in steps before calcination if it remains unhydrolyzed. At least a portion of OP extracted by HCl remains unhydrolyzed (Ruttenberg 1990). Golterman (1996) showed that the SEDEX (Ruttenberg 1992) extraction gave results not different from those with Ca-EDTA or Ca-NTA, but extracted less $CaCO_3$–P. This difference cannot be explained with certainty, but it seems likely that the CDB extracted some $CaCO_3$-associated P. The CDB reagent was found to be not sufficiently effective in separating Fe–P from $CaCO_3$–P, especially for calcareous sediments, presumably because citrate is a strong complexing agent for both Fe and Ca (Hieltjes and Lijklema 1980). Furthermore, citrate has also been found to interfere with spectrophotometric determination of phosphate. For these reasons, Zhang et al. (2004) made an important modification of the SEDEX (Ruttenberg 1992) scheme by omitting citrate from the CDB step when they studied sedimentary phosphorus in Florida Bay. The fact that iron (oxy)hydroxides are not completely extracted makes a re-adsorption onto iron (oxy)hydroxides likely. In fact, some forms of apatite behave differently (Barbanti et al. 1994). The SEDEX (Ruttenberg 1992) method must be tested to see whether repetition of an extraction (especially that with acetate buffer) would yield some extra P (Golterman 1996).

SMT

Although the various forms of P in sediments have received considerable attention in recent decades and many extraction schemes have been developed, there is no standardized method for P extraction. However, the comparability of data is only possible on the basis of standardized procedures that require collaborative testing and agreement by group(s) of researchers. In order to improve this situation, the European Commission launched a collaborative project to design a harmonized sequential extraction scheme with the Standards, Measurements and Testing Program.

This scheme, the so-called SMT extraction scheme, was a modified version of the Williams (Burrus et al. 1990)

protocol, which involved three independent procedures, yielding NaOH-P, HCl-P, IP, OP and TP. The SMT protocol was further tested on three sediments (calcareous, siliceous, organic rich), and the results reported were considered satisfactory (Ruban et al. 2001). The SMT (Ruban et al. 1999a) and the Golterman (1996) schemes were compared for a sediment of the Bort-Les-Orgues Reservoir, France. The SMT method appeared to be more satisfactory than the Golterman method (1996), as the Golterman (1996) method was mainly designed for calcareous sediments and the Bort-Les-Orgues sediments are siliceous (Ruban et al. 1999a).

The SMT (Ruban et al. 1999a, b, 2001) method is simple to handle, allows laboratories to achieve reproducible results and could be a useful tool for routine use by water managers, especially at a time when quality assurance and data comparability are of paramount importance in laboratory analysis. Moreover, the method could help in calculating the releasable P stock in lake sediment and hence provide information on lake recovery delay (Ruban et al. 2001). However, it should be noted that the SMT (Ruban et al. 1999a, b, 2001) protocol was not better with regard to the evaluation of different OP fractions, information on bioavailable fractions and distinction between different apatite forms. It would appear to be most useful as a tool for management.

Other modifications of extraction procedures

Penn's modification of the Hieltjes and Lijklema (1980) method

Penn et al. (1995) and Penn and Auer (1997) proposed a sequential chemical extraction method to quantify P fractions, which was applied to the sediment in Onondaga Lake, a calcareous, eutrophic lake in Syracuse, NY, USA.

This method was a modification of the original procedure of Hieltjes and Lijklema (1980), which called for two consecutive extractions with NH_4Cl followed by single extractions with NaOH and HCl. In the Penn et al. (1995) scheme, a third NH_4Cl extraction was added for highly calcareous sediments, and NaOH extracts were split for reactive P (NaOH-RP) and non-reactive P (NaOH-NRP) determinations (NaOH-NRP is determined as the difference between TP and NaOH-RP). NaOH-NRP includes easily hydrolyzable OP and polyphosphates (Hupfer et al. 1995) and is thought to be an indicator of biologically available P.

This technique does not appropriately differentiate the Fe– and Al–P and $CaCO_3$–P fractions on oxidized samples because of adsorption of solubilized P to iron (oxy) hydroxides during the NH_4Cl extraction. Here the two fractions are combined and termed loosely bound P. This analytical artifact does not influence estimates of labile P that are based on the sum of Fe and Al–P, $CaCO_3$–P and extractable biogenic-P. The shortcoming in the Hieltjes and Lijklema (1980) scheme of dissolution of small amounts of Fe–P and Al–P by NH_4Cl was avoided. However, the concentration of the NaOH and the influence of the extraction time were not taken into account in this method either.

Psenner's modification of the Chang and Jackson (1957) method

The fractionation of the P scheme recommended by Psenner et al. (1988) agrees with the original ideas of Chang and Jackson (1957) about finding chemical or mineralogical definitions of the P forms in sediments, although the authors were aware of the difficulties and restrictions involved. In the later versions of the Psenner et al. (1988) scheme, a 1-M NH_4Cl extraction was used instead of water for extraction of loosely adsorbed P in the first step (Psenner and Pucsko 1988). Kerr et al. (2010) proposed a modification of the Psenner et al. (1988) scheme and applied this to subtropical river sediment in Australia. A subsample of extract was digested with 1 M NaOH using the persulfate digestion before analysis, leading to the determination of non-reactive NaOH-extractable P (NaOH-NRP), which is thought to represent labile organic and bacterial P.

This extraction scheme was originally developed for siliceous sediments, and re-adsorption of P by carbonates was unavoidable in calcareous sediments (Psenner and Pucsko 1988; Jensen and Thamdrup 1993).

Jensen's modification of the Psenner et al. (1988) method

A sequential six-step extraction scheme for P pools was developed by Jensen and co-workers (Jensen and Thamdrup 1993; Jensen et al. 1998) for use in marine sediments that permitted an operational discrimination between seven different P pools (see Table 1).

The extraction scheme was a modification of the scheme proposed for freshwater sediment by Psenner et al. (1988). NH_4Cl in the Psenner (1988) scheme was found to extract more Ca and soluble reactive P. This indicates dissolution of $CaCO_3$–P. The major modifications were the use of 1 M $MgCl_2$ instead of 1 M NH_4Cl for extraction of loosely adsorbed P in the first step and the inclusion of an additional acetate buffer extraction after extraction with NaOH and before the HCl extraction. Both modifications were adapted from Ruttenberg (1992). Moreover, a NaCl wash was added after each extraction step in order to minimize the re-adsorption of phosphate. With this modified extraction procedure, the loosely adsorbed IP, along with

some OP, was intended to be extracted in the first step. The dithionite reduces oxidized Fe and Mn species and dissolves both the metals and the associated IP (Fe–P). The BD reagent was found to be very specific for Fe–P, and BD-extractable P was by far the most exchangeable P pool even deep in the sediment where the pool size was small (Jensen and Thamdrup 1993). The NaOH extraction was intended to extract a large proportion of OP and remove IP adsorbed onto surfaces other than those of reducible metal oxyhydroxides (e.g., clay minerals, gibbsite). IP associated with humic acids is also extracted in this step. The acetate buffer dissolves the biogenic carbonates and associated CFA. Detrital apatite will dissolve in 0.5 M HCl. Combustion followed by hot HCl extraction dissolves and hydrolizes the residual OP compounds (Jensen et al. 1998).

This modified extraction scheme was also originally developed for siliceous sediments, so P re-adsorption by carbonates was unavoidable in calcareous sediments (Psenner and Pucsko 1988; Jensen and Thamdrup 1993).

Ecological interpretation of operationally defined P fractions

Generally, bioavailable or mobile P in the sediment can be defined as the sum of immediately available P and potential P that can be transformed into an available form by naturally occurring physical, chemical and biological processes (Wang et al. 2009). The exchangeable or loosely sorbed phosphate is available for algal growth according to bioassays. The iron-bound phosphate is potentially bioavailable, depending primarily on sediment redox intensity (Katsaounos et al. 2007). The OP could become bioavailable by microbial remineralization.

Since P was identified as the primary limiting factor for algal growth in many natural waters several decades ago (Ruban et al. 1999a), a considerable number of researchers have focused their work on sedimentary P speciation and on water-sediment interactions (Lukkari et al. 2007). One of the main aims of these studies was to assess the bioavailability of sedimentary P within the range of natural physical and chemical characteristics in water. In other words, it is important to know whether certain forms of P can be released from the sediment, under certain conditions, into the water column for subsequent algal development. Among the various P-containing minerals, calcium salts (mainly apatites, generally coprecipitated with calcium carbonate) are probably the most inert in slightly alkaline, poorly complexing, normal aquatic conditions. Dissolution of these minerals implies a sharp pH decrease. Iron-bound phosphate is both pH and redox dependent since ferric hydroxide precipitates are involved in its formation. Under anoxic conditions, generated by

intense organic matter mineralization, Fe(III) is reduced into Fe(II), which dissolves in the water phase along with associated phosphate. Bioavailability of OP requires bacterial mineralization into phosphate (Anderson et al. 2010).

By measuring uptake of sediment P by algae in culture and extraction by NaOH and nitrilotriacetic acid solutions and by H resin, Williams et al. (1980) tested several extraction schemes on eroding bluff materials and lake and fluvial sediments from the Lake Ontario drainage basin, aiming to determine which of the fractions of sediment P was most available to algae and to relate these fractions to the amounts of P removed by various chemical extractants proposed for measuring "available P." They found that P uptake by the algae was related to the amount of non-apatite inorganic P in the sediments. Apatite P was not consumed. The non-apatite inorganic P fraction was highly correlated with the amounts of inorganic P extracted by three techniques for estimating "available P," and cell uptake equaled NaOH-extractable inorganic P in several instances. Organic P in the sediments was not utilized by the algae (Williams et al. 1980).

Since the 1980s, interest in OP has been renewed with the use of ^{31}P NMR spectroscopy. The chemical forms of OP were identified, such as orthophosphate monoesters, diesters and phosphonates. Microbial P lipids and orthophosphate monoesters decompose rapidly in sediments. Some forms of OP, such as teichoic acid P, are barely decomposed. The degradation of OP compounds in the sediment is substantial and may be an important source of bioavailable P to the water column (Ahlgren et al. 2006, 2007). Owing to the lengthy nature of algal assays, an alternative technique using iron oxide-impregnated filter paper strips (Pi-strip) was developed in the 1980s. In this, iron oxyhydroxide precipitate on paper strips reacts with phosphate ions in solution forming water-insoluble iron phosphates on the paper; these are subsequently removed in dilute acidic solution. The strips therefore act as P sinks, approximating P removal from water by algae (Sharpley 1993a, b). Sharpley (1993a, b) compared the bioavailable P content determined by the Pi-strip method to the growth of P-starved algae and found that the two methods were strongly correlated and that, in turn, P determined by NaOH extraction produced a 1:1 relationship with Pi-strip P.

However, it has been proposed that not only is the NaOH extractant concentration important, but that the duration of the extraction also influences the quantity extracted. It has also been shown that when NaOH-P largely overestimated the P available for algae, the NaOH extract was certainly not removing Fe-bound P only (Dorich et al. 1985; Fabre et al. 1996). It seems very probable that this overestimation is caused by the hydrolysis of non-available OP. If, as in the Williams method

(Burrus et al. 1990), NaOH is used as P extractant, the method is not different from the Hieltjes-Lijklema method (1980), which is essentially the old Chang and Jackson (1957) method with a preliminary washing with NH$_4$Cl at pH 7, the function of which is rather uncertain. The presence in all sediments of different forms of OP that are partly hydrolysed by NaOH and HCl should be taken into account by geochemists, as these compounds behave biologically differently from the iron- and calcium-bound phosphates.

By comparing the BD extractable P pool with both the pool of iron in the BD fraction and the pool of oxidized, amorphous or poorly crystalline iron oxyhydroxides, highly significant correlations ($p < 0.001$) were observed; Jensen and Thamdrup (1993) concluded that the BD reagent was very specific for iron-bound P. Further evidence for this came from two experiments: (1) enhanced BD treatment did not result in additional phosphate extraction; (2) no phosphate was recovered in the BD fraction by sequential extraction of P pools in pure cultures of diatoms and cyanobacteria. Further, an isotopic exchange experiment with ^{32}P revealed that BD-extractable P was by far the most exchangeable P-pool even deep in the sediment where the pool size was small (Jensen and Thamdrup 1993).

Golterman (1996) stated that using EDTA as a P extractant instead of NaOH, which was different from the Williams (Burrus et al. 1990) and Hieltjes-Lijklema (1980) methods, gave more information on the quantity of P available for algae and that, for those authors who did not obtain good extraction with Ca-NTA/EDTA, this was due to the use of a Ca-NTA/EDTA extractant for a very short time only and without a reducing agent. Ruban et al. (2001) also believed inorganic P extracted by Ca-EDTA gave more information on bioavailable fractions.

The main problems with sequential extraction methods for sediment P and a practical recommendation

Extractant

Strong acids and alkaline solutions should be avoided in P extraction schemes since they are too aggressive and do not deliver well-defined fractions. By using a chelating compound such as EDTA, iron- and aluminum-bound P would be extracted without disturbing clay-bound or OP; however, EDTA solutions have the disadvantage of interfering with the orthophosphate and Fe determinations. There is an urgent need to identify a "new" extractant with better efficiency and selectivity. In fact, soil scientists, oceanographers and limnologists have been working on this for over 30 years. More attention should also be paid to pH as it strongly influences P speciation in sediment. The extractants should be different for the different sediments

(calcareous, siliceous, organic rich) and be standardized to achieve better comparability of the results of different investigators, but not the extraction conditions such as duration of the extraction and the concentrations of the extractants, as these depend strongly on the nature of the sediments, the concentrations of the different P fractions and the solid:solution ratio.

Redistribution

The second problem is the analytical artifacts resulting from redistribution of P onto residual solid surfaces during extraction. Ruttenberg (1992) stated that the secondary adsorption onto residual solid surfaces during extraction could be successfully reversed by washing the sediment residue twice with MgCl$_2$ between extraction steps. This method is time consuming, and the many steps are a source of cumulative error in spite of the detailed protocol. Any new methods should be simple to carry out and able to prevent re-adsorption of extracted P onto Fe(OOH) and CaCO$_3$ completely.

Pretreatment of the sediment

It is obvious that in many laboratories, the environmental conditions under which samples for P analysis are stored are different from those in the natural sediments, especially the content of water and oxygen. The quantity of OP and Fe–P would change with changes in pH and redox potential. P produced by organic matter decomposition would be redistributed by adsorption onto iron oxyhydroxide in the oxic atmosphere. Golterman (1996) stated that fresh sediments should be used, as freezing or drying change the fractionation results. The disadvantage for a methodological study is that not all sediments are intercomparable in water and dissolved oxygen. Monbet et al. (2007) tried to improve the pretreatment. They made sediment cores sectioned in a homemade glove box filled with argon. Each slice was immediately centrifuged under argon. After the removal of pore water, the sediment samples were freeze-dried. All sediment slicing and pore-water extractions were performed directly on site immediately after core collection in order to minimize disturbance of the core. By this procedure, the impact of oxygen on sediment P could be diminished; however, the fractionation results could still be changed in the freeze-drying step.

Recommendation

There is still not a widely acceptable and standardized method for the determination of P speciation because of its variety and changeability in sediments. With the many types of naturally occurring P classified via only a few

extraction steps, chemical fractionation methods cannot be more than an approximate approach. However, determination of the chemical character of sediment P still allows a general estimate of the portion of sediment P that, under certain environmental conditions, can become available for primary production in aquatic environments. At the same time, sequential extraction provides useful information on the proportions and forms of P that do not participate in the nutrient cycle but are buried with deposited material.

As to the different sediments, a suitable extraction scheme should be selected in order to acquire useful information. The Williams (Williams et al. 1976; Burrus et al. 1990) method was originally developed by modifying the Chang and Jackson (1957) soil P extraction scheme and applied to lake sediments. This method gives better results for siliceous sediments, and the non-apatite P extracted by NaOH can be considered as bioavailable, though it often leads to overestimates (Williams et al. 1976; Burrus et al. 1990). This method is not suitable for use in calcareous sediments because of re-adsorption by carbonates (Hieltjes and Lijklema 1980; Golterman 1996; Pettersson et al. 1988).

As the NaOH extraction is preceded by a NH_4Cl extraction, the Hieltjes and Lijklema (1980) method could be applied not only to siliceous sediments, but also to calcareous lake sediments (Hieltjes and Lijklema 1980). However, the extracted P was not related to bioavailability if any substantial amount of $CaCO_3$ and/or org-P was present (Golterman 1996). Moreover, the capacity of $CaCO_3$ removal by the NH_4Cl extraction was limited, especially in highly calcareous sediments. This method can be a good choice in siliceous sediments or calcium-poor sediments when information on the chemical characterization of the extracted P and the P exchange processes between sediment and water is needed (Hieltjes and Lijklema 1980).

When the data quality of bioavailable P and OP are of paramount importance, the Golterman (1996) method is the best option for calcareous sediments (Ruban et al. 1999a), in which Fe-bound phosphate extracted with Ca-EDTA gives more information on the quantity of P available for algae, and having no pre-solubilization of OP resulted in underestimates of OP values (Golterman 1996).

The SEDEX (Ruttenberg 1992) method was originally developed for use with marine sediments and is now also used for sequential extraction of P from freshwater sediments (Ruban et al. 1999b; Simon et al. 2009). This method is the best option for biogeochemical research as it is capable of separating CFAP from FAP, which is an important distinction as authigenic CFAP represents an oceanic sink for reactive P and detrital FAP does not.

The SMT (Ruban et al. 2001) method is simple to operate, suitable for laboratories to achieve reproducible

results and therefore a popular extraction scheme in water management. It gives no information, however, on bioavailable fractions, especially for highly calcareous lake sediments, because of re-adsorption of P extracted by NaOH on $CaCO_3$, and also no distinction between different apatite forms. This method could be the best option for siliceous sediments when a useful tool for routine use by water managers is needed.

The modifications to extraction procedures have improved the original procedures. For example, the Penn et al. (1995) scheme, a modification of the Hieltjes and Lijklema (1980) method, can be used in highly calcareous sediments by adding a third NH_4Cl extraction before extractions with NaOH and HCl. Jensen's modification (Jensen and Thamdrup 1993), mainly by an additional acetate buffer extraction after extraction with NaOH and before the HCl extraction in the Psenner method (Psenner and Pucsko 1988), can be used for biogeochemical research as it can separate CFAP from FAP, but would be most suitable for siliceous sediments as re-adsorption by carbonates is unavoidable in calcareous sediments. Endeavors to modify sequential extraction procedures for determination of P are ongoing because this is necessary for sedimentary P research, and we look forward to the development of even better techniques.

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