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Relationships between phosphorus fractionation and major components in sediments using the SMT harmonised extraction procedure

Abstract Leaching procedures are one of the most widely used approaches to determine phosphorus fractionation in soils and sediments. Within the framework of the Standards, Measurements and Testing programme (SMT), an extraction protocol, based on the Williams procedure, was harmonised in order to improve reproducibility among laboratories. The so called SMT protocol was then used for the certification of a reference material (BCR 684) in five phosphorus fractions: non-apatite, apatite, inorganic, organic and total phosphorus. In the present paper, the SMT protocol has been applied to sediments of different composition (organic, calcareous and Fe-rich sediments). The P, Al, Ca, Fe and Mn contents extracted in each fraction were determined. The relations among these elements and the organic matter content in the samples were studied. The results obtained support the SMT protocol as a valuable tool for the study of phosphorus fractionation in sediments.

Keywords Phosphorus · Sediments · SMT fractionation procedure · Eutrophication

Introduction

As a key nutrient, phosphorus plays a relevant role in the trophic state of aquatic systems, since dissolved orthophosphate is readily available to algae and macrophytes[1]. Considerable attention has been paid to study the release of this element from sediments[2, 3, 4] and several authors have pointed out that successful restoration policies for eutrophic systems should take this contribution into account[5, 6, 7]. Phosphorus mobility is related to its interaction with the different sediment matrix components, so the knowledge of the different forms in which phosphorus is present in sediments is necessary. Phosphorus is found in sediments in both organic and inorganic forms. The main inorganic forms are labile phosphorus (exchangeable forms weakly bound to the sediment matrix); phosphorus associated to Al, Fe and Mn oxides and hydroxides; phosphorus associated to Ca minerals, and residual inorganic phosphorus (included in very resistant minerals and in the crystal lattices of some silicates). The reduction of Fe(III) to the more soluble Fe(II) and the subsequent release of phosphorus associated to iron oxyhydrates is one of the most relevant processes for phosphorus mobilisation[8, 9], even in calcareous sediments[10]. Several authors have also demonstrated the role of oxides and hydroxides of Al in the processes of the release and uptake of phosphorus from sediments. Individual contributions of Fe and Al are difficult to distinguish[11]. Phosphorus sorption by Al is pH-sensitive, whereas under reducing conditions Al maintains its adsorptive capacity[12]. This fact, and the higher affinity for P sorption which Al shows over Fe has led to the proposal of transforming Fe-P to Al-P by means of alum treatment as a method for P immobilisation[13, 14]. As for iron, sorption of P onto oxides and hydroxides of Mn is controlled by redox processes[15]. However, Mn is usually found in sediments in minor amounts, its role in the phosphorus cycle being less relevant than that of Al and Fe. Ca-bound P can be orthophosphate adsorbed onto $CaCO_3$ (labile forms of P), or different forms of apatite (calcium phosphate)[16]. These forms of apatite are considered to be unavailable[1, 17], although they are pH sensitive. So, calcium can be relevant for the removal of phosphorus from the water column and can contribute to the permanent burial of P in sediments[15]. Although the organic phosphorus is usually considered in a single fraction, its origin and nature have been studied by several authors[18, 19, 20]. The organic pool of phosphorus in sediments includes humic and fulvic complexes, phosphate esters, sugar phosphates, phytate and other compounds. Organic matter can act on phosphate sorption in two ways, either by sorbing phosphate or by blocking sorption sites[19, 21]. The four elements mentioned above (Al, Ca, Fe and Mn) can form

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complexes with the organic matter of the sediment [14, 20], Mn being the one that shows the strongest affinity [9].

To study the bioavailability/mobility of sediment phosphorus several methods can be used, such as algae bioassays, chemical fractionation, exchange with anion resin, electrodialysis and isotopic exchange [1]. Among these, chemical fractionation, involving extraction procedures, has been widely used [22, 23, 24, 25]. However, the main problem of such procedures is that they lead to operationally defined fractions, i.e., that depend on the experimental conditions and the reagents used for the separation [26]. With the aim of improving reproducibility and allowing comparison of results among laboratories, an extraction protocol based on the procedure proposed by Williams [23] was harmonised within the framework of the Standards, Measurements and Testing Programme of the Commission of the European Communities [27]. Moreover, the SMT protocol has recently been used for the certification of the extractable phosphorus content of a reference material (CRM BCR 684) [28]. The protocol was originally designed to obtain five phosphorus fractions: Total Phosphorus (TP), Inorganic Phosphorus (IP), Organic Phosphorus (OP), Apatite Phosphorus (AP, calcium associated forms) and Non-Apatite Inorganic Phosphorus (NAIP, the forms associated with oxides and hydroxides of Al, Fe and Mn).

The aim of the work described here was to test the suitability of the SMT protocol to study phosphorus fractionation in sediments. The protocol was applied to determine phosphorus partitioning in fourteen sediment samples of different composition (organic, calcareous and iron rich sediments), and the Al, Ca, Fe and Mn contents extracted in each fraction were also measured. The relationships among the extractable fractions of these elements as well as the organic matter content were studied.

Experimental

Reagents

Standard stock solutions were prepared from anhydrous K_2HPO_4 (Suprapur, Merck). The reagents used to prepare the extracting solutions and those used for the spectrophotometric determination of phosphate were Suprapur (Merck) quality or pro-analysis quality. All solutions were prepared using double-deionised water (USF Purelab Plus 18.3 $M\Omega\, cm^{-1}$ resistivity).

Apparatus

A single-beam Helios Gamma Spectrometer (Unicam) was used for spectrophotometric measurements of phosphate. Measurements were performed at 882.0 nm.

Aluminium, calcium, iron and manganese determination was carried out by means of a Thermo Jarrell Ash Model 25 ICP-AES spectrometer, consisting of a radiofrequency source working at a power of 1150 W and a frequency of 27.12 MHz, a cross-flow nebulizer a 2 mm internal diameter plasma torch and a polychromator of 2400 lines mm^{-1}.

X-ray fluorescence (XRF) measurements to determine major components were carried out using a Phillips PW-1400 X-ray spectrophotometer with Rh and Au excitation tubes.

A NA 2100 Protein Thermo Quest SA elemental analyser equipped with a flash combustion furnace, a Porapak chromatographic column, and a thermal conductivity detector was used for C. Samples were weighed with a Mettler micro-balance using tin capsules. Determination of organic carbon was carried out after acidic attack of the samples [29].

Procedures

SMT protocol

The protocol consisted in three extraction procedures that were applied to 0.2 g aliquots of sediment samples:

1. an extraction (16 h) using 20 mL of 1 mol L^{-1} NaOH was performed and after centrifugation and separation of the supernatant liquid, the residue was extracted again with 20 mL of 1 mol L^{-1} HCl (16 h). AP was determined in the extract. 4 mL of 3.5 mol L^{-1} HCl was added to one aliquot of 10 mL of the 1 mol L^{-1} NaOH extract and let stand for 16 h to precipitate organic matter. NAIP was determined in the supernatant liquid,
2. an extraction (16 h) with 20 mL of 1 mol L^{-1} HCl was performed to determine IP. The residue of this extraction was placed in a porcelain crucible and calcined in a furnace for 3 h at 450 °C. Then, the residue was extracted again (16 h) with 20 mL of 1 mol L^{-1} HCl. After centrifugation, OP was determined in the extract, and,
3. after sample calcination during 3 h at 450 °C, a single extraction (16 h) with 20 mL of 3.5 mol L^{-1} HCl was carried out, and TP determined in the extract.

Figure 1 shows a flow chart of the SMT protocol. Detailed experimental conditions were described in a previous work [28].

Determination procedures

Spectrophotometric determination of phosphate in all the extracts was carried out using the molybdenum blue method proposed by Murphy and Riley [30], as modified by Watanabe and Olsen [31]. External calibration was used as calibration method, since previous validation studies demonstrated that matrix matching was not necessary [32].
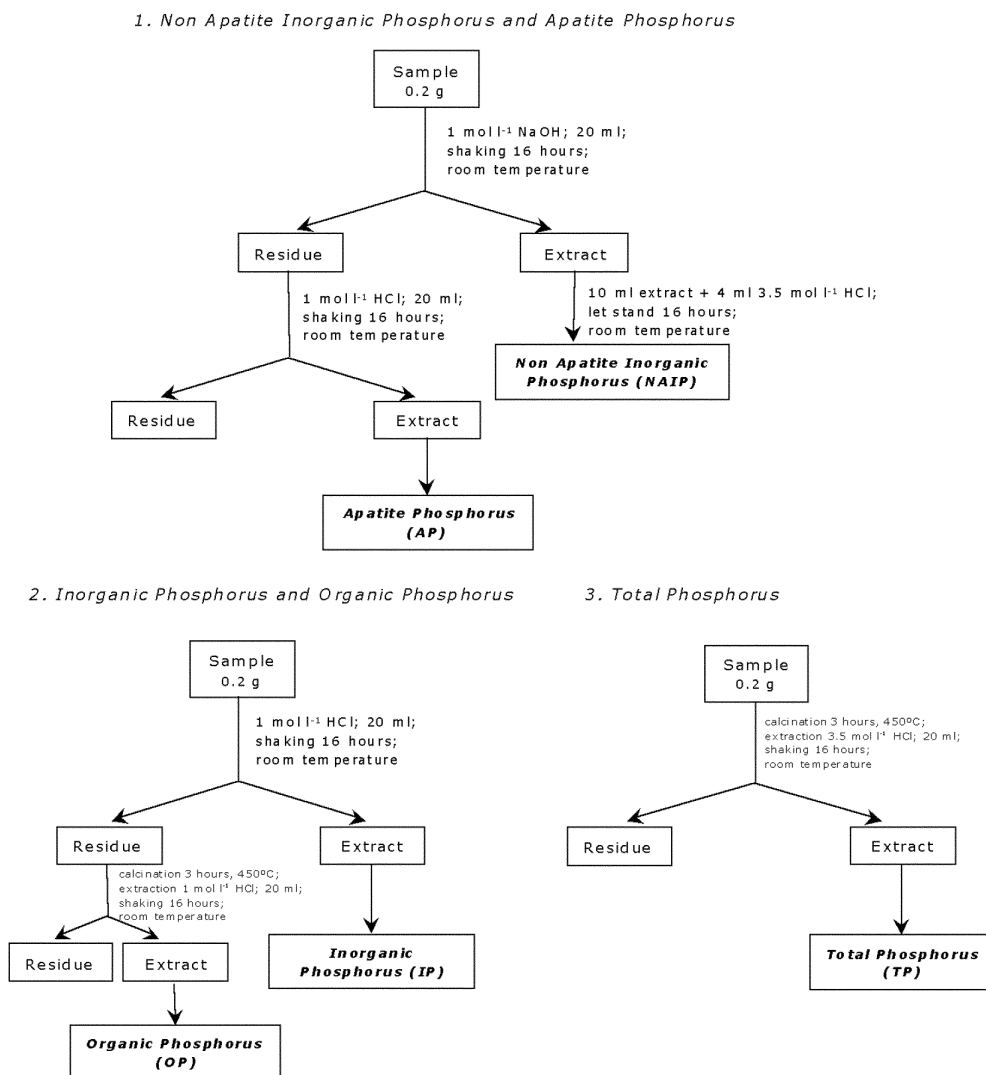
Aluminium, calcium, iron and manganese were determined in the extracts by ICP–AES. The emission lines used for these elements were 308.215 nm for Al, 317.933 nm for Ca, 259.940 nm for Fe and 257.610 nm for Mn. The calibration method used was the external calibration curve with matrix matching when necessary, according to results obtained in validation studies [32].

Samples

Samples from S2 to S34 were supplied by the Environment Institute of the Joint Research Centre (Ispra, Italy). They are all lake sediments, except S20 which is a reservoir sediment, and were air-dried and sieved to 90 μm. Samples from B3/12/86 to T5/12/85 are river sediments collected in the Besós River basin (Barcelona, Spain), air-dried at room temperature, disaggregated and sieved to 63 μm. BCR 684 is a river sediment, certified reference material, whose extractable phosphorus contents applying the SMT protocol are certified [28].

Quality control of the analytical data

Eight batches of extractions were carried out to analyse all the samples. Certified Reference Material BCR 684 was used for quality control of the analytical data. One sample of the CRM was analysed along with each batch of extractions. In Table 1, the mean value of the eight results obtained for BCR 684 reference material is compared to the certified values.

Fig. 1 Flow chart of the SMT protocol

1. Non Apatite Inorganic Phosphorus and Apatite Phosphorus

Sample 0.2 g

1 mol l⁻¹ NaOH; 20 ml; shaking 16 hours; room temperature

Residue

Extract

1 mol l⁻¹ HCl; 20 ml; shaking 16 hours; room temperature

10 ml extract + 4 ml 3.5 mol l⁻¹ HCl; let stand 16 hours; room temperature

Non Apatite Inorganic Phosphorus (NAIP)

Residue

Extract

Apatite Phosphorus (AP)

2. Inorganic Phosphorus and Organic Phosphorus

Sample 0.2 g

1 mol l⁻¹ HCl; 20 ml; shaking 16 hours; room temperature

Residue

Extract

calcination 3 hours, 450°C; extraction 1 mol l⁻¹ HCl; 20 ml; shaking 16 hours; room temperature

Residue

Extract

Inorganic Phosphorus (IP)

Organic Phosphorus (OP)

3. Total Phosphorus

Sample 0.2 g

calcination 3 hours, 450°C; extraction 3.5 mol l⁻¹ HCl; 20 ml; shaking 16 hours; room temperature

Residue

Extract

Total Phosphorus (TP)

Table 1 Results, expressed as mg kg⁻¹, for the control sediment CRM BCR 684 (mean±standard deviation of eight independent determinations)

	Obtained value	Certified value
TP	1355±16	1337±13
OP	205± 7	209± 9
IP	1107±20	1113±24
AP	505±17	536±28
NAIP	580±18	550±21

Results and discussion

The Si, Ca, Al, Mn, Fe, total carbon and organic carbon and phosphorus contents of the studied samples are summarised in Table 2. The application of Principal Component Analysis to this data set allowed the classification of the sediment samples in three groups according to their compositional characteristics: organic rich, calcareous and sediments with high iron content and medium to low calcium and organic matter contents. This classification is also shown in Table 2. The SMT protocol was applied to the sediment samples and at least three replicates were carried out. The Ca, Al, Mn, Fe and P contents were determined in all the extracts as described in the experimental section. Table 3 shows the results (given as mean±standard deviation of three replicates) for the different fractions. Correlation analysis was also applied to the data in order to explore the relationships among the variables studied. The corresponding correlation coefficients (r) were obtained.

Total phosphorus fraction, TP

For phosphorus, the element for which the protocol was designed, the sum of phosphorus contents in the OP- and the IP-fractions is in general lower than the phosphorus extracted in the TP-fraction. However, previous studies demonstrated that the phosphorus extracted as TP agrees with the phosphorus content determined after total digestion of the sample [27]. The extracted contents of Ca, Fe,

Table 2 Sample characterisation. Total contents of Si, Ca, Al, Mn Fe and P determined by XRF. C determined by EA/TCD. All the results are expressed as a percentage of dry sample weight

	SiO$_2$	CaO	Al$_2$O3	MnO	Fe$_2$O3	C tot	C org	P$_2$O5
Group I: Organic rich sediments								
S2	24.3	3.34	6.98	0.76	4.47	23.8	21.9	0.99
S10A	42.6	2.21	9.35	0.14	3.79	19.1	17.5	0.53
B6/12/86	26.7	11.9	11.0	0.13	4.42	18.5	15.1	3.35
T5/12/85	31.3	14.2	9.39	0.17	9.66	15.4	11.4	1.16
Group II: Calcareous sediments								
S22	24.6	30.0	6.04	0.06	2.47	8.99	2.36	0.13
S24	28.3	27.9	6.18	0.10	2.32	9.95	4.23	0.22
S34	30.5	22.4	8.60	0.10	3.44	7.38	2.33	0.17
B3/12/86	15.3	36.7	4.06	0.08	2.03	11.6	5.96	0.66
B3/10/88	27.4	25.7	8.68	0.09	3.27	9.94	4.28	1.19
Group III: Sediments with high iron content and medium to low calcium and organic matter contents								
S16	48.8	5.73	13.9	0.16	7.27	9.72	5.67	0.88
S20	58.7	0.85	15.0	0.05	5.76	5.11	5.11	0.24
S23	39.3	14.0	12.6	0.10	6.14	4.59	1.44	0.19
S27	45.3	10.6	12.9	0.10	5.58	4.94	1.73	0.29
BCR 684	46.1	7.00	13.4	0.12	6.43	4.10	2.41	0.37

Mn and P in the TP-fraction are highly correlated with the total contents determined by XRF (correlation coefficients, r, of 0.998, 0.900, 0.996 and 0.995 respectively). The fact that the acid-soluble compounds obtained after sample calcination are closely related to the total contents in the samples points out that the studied elements are related to carbonates, metal hydroxides or organic matter in the original sample. On the contrary, aluminium extracted in the TP-fraction is poorly correlated with the total content determined by XRF (r=0.485), whereas the correlation between the Si and Al contents by XRF is high (r=0.901). So, this element is mainly present in the samples as aluminosilicates, which remain after the thermal treatment. The extracted contents of Ca in the TP-fraction are also correlated with the inorganic carbon content (r=0.909) indicating that this element mainly occurs in the samples as calcium carbonate.

Organic phosphorus fraction, OP

Phosphorus extracted in the OP-fraction is highly correlated to the organic carbon content in the sediment samples (r=0.927), whereas no relationships were obtained between Ca, Al, Fe, and Mn contents extracted in this fraction and the organic matter content. In the studied samples phosphorus is mainly associated to inorganic compounds as can be concluded from data reported in Table 3. However, no relationship can be established between the IP/(IP+OP) ratio and the organic matter content in the sediment samples. Therefore, the distribution of phosphorus between the organic and inorganic fractions appeared not to be related with the organic matter content in an obvious way. This is probably due to the complex nature of the organic matter itself (humic and fulvic substances, etc) and to the intricate relationships among the different sedi-

ment components (coating formation, particle cementation, competition for adsorption sites, etc.).

Inorganic phosphorus fraction, IP

Phosphorus is mainly associated to inorganic forms (>60%) in the studied samples, including those with high organic carbon contents. This is also supported by the strong correlation observed between the phosphorus extracted in the IP-fraction and the XRF contents (r=0.995). Moreover, the sum of the AP- and the NAIP- fractions is in good agreement (±5.0%) with the phosphorus extracted in the IP-fraction for most of the samples. Thus, as the data reported in Table 3 show, 1.0 mol L^{-1} HCl releases almost all extractable Ca (>90%) in the IP-fraction as it is stressed by the strong correlation observed between calcium extracted in the IP-fraction and the XRF contents (r=0.997). High correlation is also obtained for IP-fraction Mn contents (r=0.993), but poorest correlation (r=0.730) and no correlation (r=0.099) is obtained for Fe and Al respectively, confirming that both elements are present in the sediment in chemical forms not easily soluble in 1.0 mol L^{-1} HCl. On the other hand, strong relationships were also observed among the aluminium with phosphorus extracted in this step (r=0.938), and with the phosphorus total content determined by XRF (r=0.927), showing the role of aluminium oxyhydrates in phosphorus retention in the studied samples.

Non-apatite phosphorus fraction, NAIP

Phosphorus extracted in the NAIP fraction is strongly correlated with XRF phosphorus total content (r=0.971), with phosphorus extracted in the TP fraction (r=0.987) and in

Table 3 Extractable amounts (mean±standard deviation) of Ca, Al, Fe, Mn and P in the TP, OP and IP fractions of the SMT protocol (Al, Ca and Fe are expressed as g kg^{-1}, Mn and P are expressed in mg kg^{-1})

		Ca	Al	Fe	Mn	P
Total fraction (TP)						
Group I	S2	17.8±0.43	5.74±0.44	21.7±0.68	5805±150	4242±33
	S10A	10.2±0.15	8.85±0.33	19.2±0.58	1024±19	2266±21
	B6/12/86	79.7±0.07	25.5±0.19	21.8±0.04	719±1	13639±745
	T5/12/85	93.5±0.62	13.6±0.29	51.2±1.63	980±7	4166±43
Group II	S22	203.8±1.61	6.53±0.36	9.69±0.33	379±5	537±5
	S24	175.0±1.47	5.16±0.11	6.43±0.10	618±4	766±2
	S34	152.2±0.78	7.41±0.33	12.6±0.16	593±2	622±7
	B3/12/86	239.0±1.04	8.47±0.14	10.9±0.13	533±2	1915±51
	B3/10/88	167.6±0.37	13.3±0.42	15.4±0.28	488±4	3974±45
Group III	S16	33.8±0.28	12.6±0.47	25.1±0.58	734±9	3833±18
	S20	4.89±0.04	12.3±0.11	22.7±0.37	323±3	938±1
	S23	87.8±0.74	13.4±0.43	17.1±0.28	524±2	662±7
	S27	56.7±0.49	8.96±0.56	18.0±0.69	274±6	849±18
	BCR 684	44.4±0.31	16.3±0.76	26.9±0.59	745±9	1337±13
Organic fraction (OP)						
Group I	S2	0.27±0.05	2.55±0.14	4.42±0.16	93±11	906±10
	S10A	0.17±0.03	3.81±0.31	5.36±0.68	55±4	611±11
	B6/12/86	0.14±0.01	5.22±0.17	5.71±0.10	53±1	778±3
	T5/12/85	0.17±0.07	3.03±0.08	7.72±2.42	96±20	332±8
Group II	S22	0.51±0.08	2.79±0.28	2.94±0.20	28±2	95±9
	S24	0.34±0.03	2.54±0.12	2.05±0.07	20±0.5	159±4
	S34	0.27±0.06	3.37±0.11	3.28±0.16	31±1	121±7
	B3/12/86	0.15±0.02	1.38±0.04	1.27±0.09	21±2	127±7
	B3/10/88	0.36±0.001	3.65±0.26	3.77±0.28	42±3	266±21
Group III	S16	0.22±0.01	4.72±0.55	7.10±0.58	106±10	440±21
	S20	0.07±0.001	6.21±0.06	6.98±0.23	58±2	306±6
	S23	0.42±0.04	6.18±0.08	6.46±0.24	51±3	140±2
	S27	0.15±0.002	3.23±0.40	4.71±0.50	38±5	82±3
	BCR 684	0.33±0.02	6.22±0.001	7.97±0.51	53±3	203±3
Inorganic fraction (IP)						
Group I	S2	17.7±0.54	3.59±0.15	18.5±0.61	5751±230	2786±30
	S10A	9.78±0.06	6.14±0.35	14.0±0.76	953±9	1393±19
	B6/12/86	80.1±0.34	15.0±0.09	14.0±0.05	667±5	12107±246
	T5/12/85	92.4±1.20	7.34±0.12	45.9±2.31	895±18	3752±91
Group II	S22	208.9±1.41	4.29±0.12	7.94±0.20	400±2	380±11
	S24	179.7±0.55	3.13±0.04	5.30±0.05	647±1	532±5
	S34	136.7±0.70	4.20±0.07	7.53±0.10	512±2	449±1
	B3/12/86	239.9±1.09	5.56±0.01	8.56±0.02	512±3	1483±33
	B3/10/88	171.3±10.4	7.28±0.45	8.99±0.58	457±29	3383±215
Group III	S16	37.0±0.38	6.79±0.16	11.5±0.33	642±11	3180±39
	S20	5.04±0.04	2.57±0.04	8.28±0.07	260±1	486±6
	S23	88.6±0.44	5.02±0.03	11.2±0.01	529±1	485±3
	S27	52.6±0.24	5.30±0.09	10.0±0.14	218±2	737±9
	BCR 684	44.7±0.39	4.63±0.09	15.8±0.16	711±4	1118±11
Apatite fraction (AP)						
Group I	S2	11.4±0.38	3.10±0.08	14.3±0.22	3970±136	509±15
	S10A	6.45±0.29	3.80±0.20	11.9±1.53	719±25	319±20
	B6/12/86	72.0±1.25	2.41±0.02	12.8±0.17	583±10	4929±192
	T5/12/85	81.5±1.80	3.20±0.12	37.5±1.22	803±25	1980±47
Group II	S22	191.7.±15.1	3.46±0.27	7.72±0.52	371±28	293±8
	S24	180.3±1.82	2.82±0.10	5.62±0.02	637±1	352±7
	S34	126.1±1.51	3.12±0.05	7.19±0.12	478±8	332±6
	B3/12/86	203.8±12.9	2.79±0.15	7.71±0.51	426±2	1126±38
	B3/10/88	148.9±2.87	3.03±0.08	8.07±0.15	396±9	2147±44

Table 3 (continued)

		Ca	Al	Fe	Mn	P
Group III	S16	28.2±4.85	3.81±0.64	9.85±1.63	508±84	1733±17
	S20	3.21±0.06	1.81±0.02	7.70±0.03	229±1	263±6
	S23	78.1±0.78	4.14±0.04	10.3±0.11	477±4	347±6
	S27	47.2±0.98	4.37±0.20	9.52±0.36	200±6	575±7
	BCR 684	39.6±0.89	3.75±0.08	14.0±0.13	626±13	498±20
Non apatite inorganic fraction (NAIP)						
Group I	S2	3.73±0.14	0.75±0.04	3.11±0.10	1020±36	2231±23
	S10A	1.48±0.05	1.90±0.06	0.90±0.05	82±4	1029±18
	B6/12/86	0.65±0.03	12.2±0.17	0.71±0.03	29±2	6949±269
	T5/12/85	1.12±.06	3.79±0.03	0.39±0.02	n.d.	1657±11
Group II	S22	1.52±0.17	0.76±0.02	0.11±0.02	4±0.3	93±5
	S24	1.81±0.11	0.61±0.002	0.13±0.004	19±4	136±0.6
	S34	0.75±0.04	1.06±0.03	0.18±0.006	n.d.	104±2
	B3/12/86	2.51±0.69	2.38±0.15	0.14±0.04	4±0.02	329±33
	B3/10/88	1.24±0.02	3.85±0.01	0.26±0.03	n.d.	1007±47
Group III	S16	1.20±0.06	2.45±0.06	0.24±0.03	18±1	1392±52
	S20	0.71±0.006	1.21±0.03	0.46±0.01	15±0.6	219±3
	S23	1.50±0.06	0.91±0.07	0.11±0.01	n.d.	92±1
	S27	0.79±0.01	0.75±0.02	0.30±0.05	n.d.	137±3
	BCR 684	0.39±0.03	0.85±0.02	0.05±0.002	n.d.	579±19

n.d.: not detected

the IP fraction (r=0.979), and with aluminium extracted in the NAIP fraction (r=0.924). However, it is not correlated with the extracted amounts of Ca (r=–0.054), Fe (r=0.337) and Mn (r=0.195) in this fraction. These results can be explained considering that the extraction with NaOH releases phosphate bound to iron and manganese oxyhydrates by means of the substitution of the adsorbed phosphate ions by the hydroxyl ones. Phosphate release from aluminium oxyhydrates can also occur by dissolution mechanism due to the amphoteric nature of this element, explaining the relationship observed between the extracted amounts of aluminium and phosphorus in this fraction.

Apatite phosphorus fraction, AP

Phosphorus extracted in the AP-fraction is strongly correlated with XRF phosphorus total content (r=0.964) and with phosphorus extracted in the TP (r=0.944) and in the IP fractions (r=0.964). Although apatite phosphorus is defined as related to Ca, the correlation coefficient between P and Ca extracted in this fraction was 0.016. This could be explained by the occurrence of calcium, probably as calcium carbonate, that masks any possible relationship between phosphorus and calcium extracted in this fraction. As expected, no relationship was observed between apatite phosphorus and Al, Fe, or Mn (r=–0.309, 0.268 and –0.088, respectively). Very strong correlations were obtained between the extracted amounts of Fe and Mn in the AP and IP-fractions (r=0.998 and 0.999, respectively). These results together with data in Table 3 indicated that an important dissolution of the metal oxyhydrates takes place during the extraction, probably yielding an overestimation of the phosphorus extracted in the AP-fraction due to the release of occluded phosphorus.

Conclusions

Total phosphorus is accurately determined with this method. The relationships between the data obtained when the SMT protocol is applied show that the procedure distinguishes correctly between the organic and inorganic phosphorus in the samples studied. On the other hand, one of the drawbacks of the method is that the differentiation between the apatite and non-apatite fractions is not so accurate, due to the reagents employed that determine the releasing mechanism from the sediment.

Despite the limitations inherent to the method, the results indicate that the SMT protocol is a good approach for phosphorus fractionation in sediments. This, in addition to the fact that it is a validated procedure [28] easy to implement in a routine basis, make the SMT protocol tenable as a useful tool for the monitoring of phosphorus partitioning in sediments.

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