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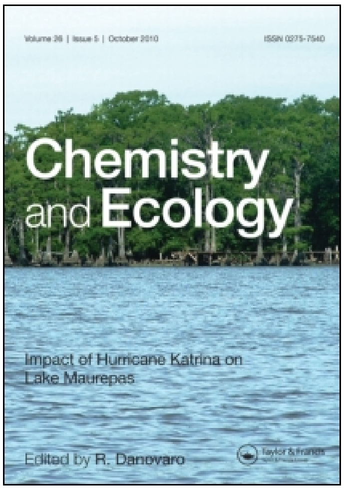

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Phosphate Analysis of Marine Sediments

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Phosphate Analysis of Marine Sediments

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Phosphate chemistry at the sediment–water interface could play a key role in the periodic eutrophication events characteristic of a N-W Adriatic coastal area. In order to establish a general knowledge of phosphate speciation in the sediments, we chose the sequential extraction procedure which gave most reproducible results as an analytical method. Comparison of data from the sequential procedure with that obtained with different methods using a single extraction step, indicates some inconsistencies due to the effects of chemical reagents on the sedimentary mineral composition.

INTRODUCTION

Several attempts have been made to assess the contribution from sediments of phosphate to the overlying water in natural sediment–water systems exposed to eutrophication. Since each environment has its own peculiarities related to its ecological components, one of the most reliable approaches involves bioassay studies of specific algal taxa responsible for the blooms, combined with sediment-phosphate analyses. Hegemann *et al.* (1983) wrote a critical review of the results of the investigations so far undertaken in this field, outlining the need for defining and applying more reliable and standardized methods in both related subjects (bioassays and sediment analyses). In this paper we deal only with the chemical analyses of sediment phosphates.

Some investigators have adapted the familiar chemical fractionation

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scheme for soil analysis outlined by Chang and Jackson (1957) to study the transfer of phosphate in sediment–fresh water systems (Petersen and Corey, 1966, Williams *et al.*, 1967; Wildung *et al.*, 1977). The procedure uses serial extractions by chemical solutions of increasing strength in order to solubilize phosphate anions differently sorbed to solid particles in the soil and ultimately those precipitated in the mineral phase. The limitations of this approach have been outlined by Wildung *et al.* (1977) and by Morse and Cook (1978). It is however generally accepted as a useful tool for distinguishing between the modes of occurrence of phosphates in sediments.

Data on marine sediments are very few and less contrasted since sediment dynamics and the environmental conditions of marine coastal waters preclude the dramatic ecological consequences often found in fresh-water and lacustrine systems. Moreover marine eutrophication seemed to be more likely limited by nitrogen than phosphate (Ryther and Dunstan, 1971). Anyway, given the large number of samples which are normally analyzed from the larger environment, sequential extraction procedures are troublesome and time-consuming. The general target has been therefore to develop and apply a method which is as simple as possible and allows quantifying the most important sedimentary phosphate fraction available for algal growth by analyzing one specific extractant solution (Kurmies, 1972; Aspila *et al.*, 1976; Golterman, 1977; Allan and Williams, 1978).

In this paper we report and discuss results obtained by analyzing marine sediment samples, covering the typical sedimentological composition of an eutrophicated coastal area, by three methods. The first two are single extraction procedures using 1 M HCl and a citrate-dithionite-bicarbonate mixture (CDB), which have been tested on fresh-water sediments by Aspila *et al.* (1976) and Williams *et al.* (1980), respectively. The last method is a fractionating scheme evolved to provide a general distribution pattern of sediment phosphate compounds.

On comparing the data, we discuss the selectivity of each extractant and its chemical effect on sediment mineral composition, together with its utility for assessing phosphates liable to be released to the overlying waters.

EXPERIMENTAL

Preliminary studies

In a first approach, we tried to distinguish between mineral phosphates and loosely bound, i.e. easily available, sediment phosphates by using two different extraction methods. The former was suggested by Aspila *et al.* (1976), and analyzes phosphates extracted by 1 M HCl after shaking for 16 hours. According to the authors this method, when applied to samples after ignition at 550°C, gives total P contents and by the differences of the two, organic P is obtained.

An experimental estimate of phosphate, which can be released to seawater under dynamic conditions, was obtained by analyzing phos-

TABLE I

Sedimentary phosphate contents (mg.kg^{-1} dry weight) extracted by the different solutions.

Extractant	Time (hrs)	Range (mg.kg^{-1})	Mean (mg.kg^{-1})	Std. dev.*
a) HCl 1 M	16	516.5–715.1	563.2	3.5
HCl 1 M**	16	529.2–680.0	606.8	10.0
b) ASW	2	2.1–22.0	13.3	0.4
c) NH_4Cl 1 M	0.5	0.0–10.8	5.7	0.2
NH_4F 0.5 M pH = 8.2	1	3.4–9.7	7.1	0.3
NaOH 0.1 M	17	n.d.	n.d.	n.d.
CDB pH = 8.2 (Ne citrate 0.3 M $Na_2S_2O_4$ 0.1 M $NaHCO_3$ 2.3 × 10^{-3} M)	0.1	110.4–209.1	148.7	5.6
HCl 1 M	16	516.0–715.1	576.8	10.8

* on triplicate analyses

a) Aspila *et al.* (1976) method. ** after ashing at 550°C for 2 hrs

b) Artificial Sea Water according to Strickland & Parsons (1972) bicarbonate buffered

c) Sequential procedure according to this paper.

TABLE II

Easily available phosphates (mg.kg^{-1} dry weight) from samples with different grain-size composition

Sample n.	1	2	3	std. dev.*
% sand	0.5	22.2	70.0	
% silt	35.0	53.6	5.7	
% clay	64.5	44.2	24.3	
a) ASW unbuffered ph = 6.10	7.3	3.9	3.0	0.2
b) ASW buffered pH = 8.00	9.1	4.5	3.5	0.2
c) distilled water pH = 5.39	2.4	1.8	n.d.	0.2
d) $NaHCO_3$ 2.3 × 10^{-3} M pH = 8.49	3.1	2.3	1.0	0.1

* On triplicate analyses for each sample.

phates extracted by artificial seawater, prepared according to Strickland and Parsons (1976). Table I a) and b), reporting ranges and average results, shows that the latter is about 2% of total P. Moreover bicarbonate buffer (Table II) affects phosphate concentrations in the extraction solution either because of the difference in pH and/or the extraction capacity of bicarbonate ions towards specifically adsorbed anions on clay colloid surfaces (Nagarajah *et al.*, 1968). Table II reports the results of some simple tests made on three samples, having different grain-size composition. Differences b)–a) and d)–c) are greatest for samples with the highest fine sediment fractions.

Recommended analytical procedure

Table I c) reports extractant compositions, shaking times and results obtained following a simple fractionating scheme for sediment phosphate determination, mainly taken from Petersen and Corey (1966). The solid/extractant ratios and the extraction solutions used were the same as the published procedures. Only shaking times and sample treatment before phosphate colorimetric analyses were different. In order to use the method of Murphy and Riley in each sequential step, the samples were treated according to John (1970), except for the CDB solutions. The best results were obtained by oxidation with concentrated, phosphate free, hydrogen peroxide as reported by Jackson (1958). The calibration curve was constructed by addition of the phosphate standards to the same volumes of CDB solution used for the samples and subsequent treatment with hydrogen peroxide.

Direct extractions with CDB were performed on another set of the same samples and analyzed. Iron, manganese and aluminum were determined on both sequential and single CDB extracts by Atomic Absorption Spectrophotometry, for comparative purposes.

For the last extraction we used 1 M HCl and shaking for 16 hrs, as suggested by Wildung *et al.* (1977). In these extracts Ca^{++} was also determined by A.A.S.

Materials studied

The 20 sediment samples analyzed were collected in a shallow area off the Emilia–Romagna coast about 50 km south of the Po River delta, at depths between 3 and 14 m.

Sampling procedures and material preservation between collection and analysis are described elsewhere (Giordani and Angiolini, 1983).

The samples covering the range of sediment texture in this area had different grain-size composition from sandy silt to silty-clay. Chemical analyses were carried out on 1 g of freeze-dried sample.

RESULTS AND DISCUSSION

Table I c) reports the averages and ranges of all the data, together with the standard deviations referred to triplicate analyses on each sample. The data obtained with artificial seawater more or less equals the sum of the first two extractions (NH_4Cl 1 N + NH_4F 0.5 N pH = 8.2) containing phosphates associated with carbonates, dissolved by ammonium chloride, plus those bound to aluminum. They include Al-phosphates in hydrated or hydroxylated forms, precipitated on oxides or alumosilicates, adsorbed and F-exchangeable (Jackson, 1958).

As shown in Table I, we did not detect any PO_4—P in 0.1 M NaOH extract. This reagent, like NH_4F, is supposed to remove sorbed phosphate ions, associated with Al and short range order Fe-rich complexes (Syers *et al.*, 1973) and also some organic compounds such as phospholipids.

This result seems to be characteristic of our Adriatic sea sediments. Allan and Williams (1978) found that NaOH extracted a 4% larger quantity of phosphates than CDB from fresh-water sediment samples. In the same way, Hieltjes and Lijklema (1980) extracted 98% of Fe—P and 91% of Al—P from synthetic iron and aluminum phosphates added to their samples. They appointed an extraction procedure which eliminated the CDB step. Salomons and Gerritse (1980) applied the method of Kurmies (1972), which is basically the same as Allan and Williams' (1978), to marine samples. Their results are different from ours. We can assume that in this sedimentary environment physico-chemical conditions (mainly pH and salinity) are adverse to the precipitation of NaOH soluble phosphates.

The CDB is a reduction-chelation reagent mixture, specific for phosphates released from iron oxides and also dissolves Mn oxides and alumina coatings. The extracted fraction or "reductant soluble" phosphate is insoluble in both acids and bases (Jackson, 1958). Its availability is strictly related to environmental reducing conditions. According to Williams *et al.* (1971), CDB also extracts some organic phosphorus compounds, which in lake sediments, can be a large amount

TABLE III

Sediment phosphate, iron, aluminum and manganese from direct (d) and sequential step (s) extraction using CDB (mg kg^{-1}).

	$[PO_4$—P]		[Fe]		[Al]		[Mn]	
	d	s	d	s	d	s	d	s
average	158	142	2660	3516	194	334	8.3	4.7
minimum	110	88	1549	1970	81	218	5.5	2.8
Maximum	209	271	4067	5420	276	446	11.6	6.4

(Marengo and Amantini, 1983). In our samples, the organic matter content is very low (about 0.4‰ org. C), compared with freshwater and other marine sediments (Salomons and Gerritse, 1980). Therefore the organic P in the CDB extracted phosphate should be minor and also the good linear correlation coefficient with Fe (0.759) and Al (0.787) concentrations would support this hypothesis. Organic phosphorus itself can become available after mineralisation.

Table III shows the data for phosphates and related metals (Fe, Al and Mn) in the reductant soluble fraction for direct and sequential extractions. It is interesting to observe that for average, minimum and maximum values, PO_4—p does not change very much (10‰); average and minimum phosphate values tend to be slightly higher in the direct extractions, while Fe and Al are much lower than in the sequential extraction. This seems to indicate that phosphate anions undergo a specific adsorption reaction with Al, Fe ions, with the formation of surficial bonds which only a reduction-chelation treatment can break. In the sequential extraction the alterations of the sedimentary matrix affect Fe, Al and Mn concentrations. For Fe and Al this difference is clearly due to the extraction of cations from some clay mineral lattices such as montmorillonite (Subramanian, 1975), illite (Lahann, 1978) and chlorite, which make up the finer sedimentary material in this area (Bagnari, 1980). According to Anderson and Jenne (1970), Al might come from amorphous alumosilicates and Fe from a more crystalline iron oxide phase or silicate impurities. The Mn content is very low and clearly does not represent the inner mineral texture of the sediments to an important extent.

The last fraction, extracted with 1 M HCl after shaking for 16 hours should provide the measure of Ca-bound phosphate. The concentration values are the same as those obtained directly by the method of Aspila *et al.* (1976), within the analytical error. The ratios Ca/P are very close to the ones reported by Martens and Harris (1970) for amorphous apatite (1.35). This fraction has been regarded as the less liable to be dissolved. Some recent bioassays with fresh-water algae have shown that it can supply important amounts of phosphates for their growth (Hegemann *et al.*, 1983).

The sum of all the fractions always exceeds total phosphate concentrations obtained by the method of Aspila *et al.* (1976), which include also organic P, by more than the sum of each analytical error. This confirms that 1 M HCl does not dissolve the "reductant soluble" PO_4—P, which is bound to iron hydroxides even after ashing at 550°C.

CONCLUSIONS

In this investigation we tried to get a general distribution pattern of sedimentary phosphates by a simple analytical sequential procedure. The results obtained by other methods, applied to sediments to assess potentially available phosphates for algal growth have been compared, taking into account the effects of chemical treatments on sedimentary mineralogical composition. It appears that single extraction procedures can be helpful in quantifying different forms of sediment phosphates which can be released under naturally occurring environmental conditions in marine ecosystems. However the main indication as to which method gives the most useful informations should come from bioassay studies on sediment-water systems reproducing as closely as possible the main ecological components (i.e. marine sediment, seawater and algal species involved in eutrophication phenomena.)

The application of standard methodologies would clarify the peculiarities of each sedimentary environment and would be very valuable in the investigation of factors controlling its natural equilibria.

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