

Phosphorus Retention Capacity of Sediments in Mandovi Estuary (Goa)

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Experiments carried out under controlled conditions to study P retention capacity of sediments indicate that the processes of adsorption and desorption of P are pH dependent. Adsorption of P is maximum (58-99%) at pH 4. Both the exchangeable P and ratio, (desorbed P/adsorbed P) are significantly higher at pH 10 than at pH 4 and 7.

Phosphate is the only plant nutrient anion which shows exchange with soils¹. The capacity of sediments to retain or release phosphorus (P) is one of the important factors which influence the concentrations of inorganic and organic P in the overlying waters. Large quantities of P are consistently found deposited in the sediments but often the quantities of soluble P found in the water are very small. If a mechanism could be discovered to increase the release of P from the sediments so that it could enhance the productivity of the overlying waters it would be a valuable contribution. The behaviour of labile inorganic phosphate in sediments is dominated by adsorption and desorption processes², which in turn depend on several factors such as texture of the sediment, pH, oxidation-reduction state, organic matter content, etc. Phosphate sorption and release from sediments are pH dependent^{2,3}.

Although several reports have been made on the effects of various physical and chemical parameters on the behaviour of sediments⁴⁻⁸, few only pertain to evaluation under controlled conditions of the amount of P exchanged between the sediments and water. Therefore, a study has been carried out on the P retention capacity of some tropical estuarine sediments (Mandovi estuary) under controlled conditions.

Materials and Methods

Fig. 1 shows the sampling locations in Mandovi estuary from where sediments were collected (April 1980) using a Van Veen Grab. The overlying water was collected with a Van Dorn bottle. Sediments were analysed for their textural characteristics⁹. Interstitial, adsorbed and total P in the sediments⁵ and reactive phosphate in the water¹⁰ were analysed. Organic matter was calculated by multiplying the organic carbon content¹¹ by 1.724 (ref. 1).

The notations of P used to facilitate discussion and understanding of the results are: inorganic P (P_i),

added P (P_a), adsorbed P (P_{ad}), desorbed P (P_d), adsorbed (net) P (P_{an}) and exchangeable P (P_e).

The processes of adsorption and desorption of P_i by estuarine sediments were studied in 0.1 M NaCl system¹² under different concentrations of P_a and pH levels.

Sediment samples (0.5 g dry wt) were transferred to pre-weighed 100 ml polyethylene tubes. Water samples (25 ml) from sts $M_1 - M_5$, which had been pre-analysed for P_i concentration were added, followed by 25 ml of 0.2 M NaCl solution, enriched with KH_2PO_4 to obtain a phosphate concentration equivalent to 1×10^2 , 1×10^3 and $5 \times 10^3 \mu\text{g.g}^{-1}$ of the sediment. Experiments were carried out at pH 4, 7 and 10. The tubes were mechanically agitated on a shaker for 12 h at room temperature ($\sim 30^\circ\text{C}$) after which the suspensions were centrifuged at 3000 rpm. Aliquots of the supernatant were taken for the determination of P_i adsorbed. The supernatant was removed as far as possible and the tubes were again weighed to determine the volume of solution entrapped in the residue.

Measurement of P_d from the sediments involved addition to the residue of an appropriate volume of 0.1 M NaCl solution to make the volume to 50 ml and the system was maintained at pH 4, 7 and 10. The 12 h extraction, recovery and removal of the supernatant

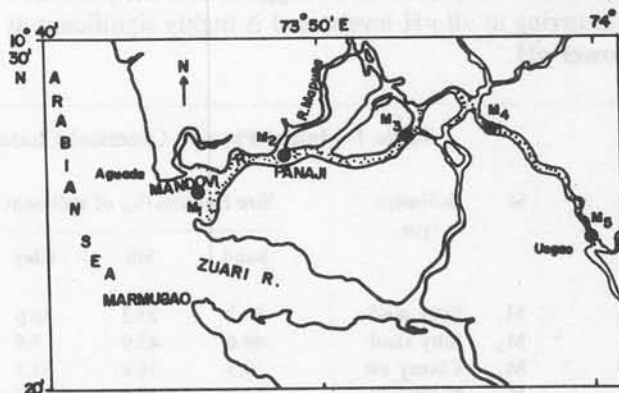


Fig. 1—Station locations

*Deceased

and P_i estimations were carried out as above. The residues were weighed immediately after centrifugation and decantation following the desorption step and again after drying at 110°C overnight. The amount of P_{ad} and P_d were calculated on basis of gram dry weight of sediment.

Results and Discussion

The initial physico-chemical characteristics of the sediments are given in Table 1. Interstitial and adsorbed phosphate concentrations showed considerable variations. No much variation in the total P concentration was observed. Relatively higher concentration of total P was observed in clayey silt. This agrees well with the results of Golterman⁶ who observed that the P content of the sediment primarily depends on particle size and increases with clay content.

The dependence of pH on the adsorption and desorption of P on sediment is well established¹³. Table 2 presents data on percentages of P_{ad}/P_a , P_d/P_{ad} , P_{an}/P_a . Adsorption of P at pH 4 is in the range 58 to 99% of P_a , which indicates that at $5 \times 10^3 \mu\text{g.g}^{-1}$ P_a level a maximum of $4300 \mu\text{g.g}^{-1}$ (86%) was adsorbed by the sediment at st M_2 as compared to the lowest value ($2900 \mu\text{g.g}^{-1}$) for sample at st M_3 (58%). The trend of adsorption at pH 7 is comparable with that of pH 4. At pH 10 a significantly lower rate of adsorption (10-79%) was observed. Meyer¹⁴ observed that in Bear Brook sediments adsorption is a rapid process particularly in the silty sediments which removed 93% of P from solutions within 5 min. Carritt and Goodgal¹³ studied the adsorption - desorption processes of P in estuarine sediments under different pH and found that the maximum adsorption occurred in pH 4-7. Maximum phosphate adsorption was observed between pH 5 and 7 (ref. 3).

Golterman⁶ suggested that the mechanism of sorption of phosphate on to the clay may be an exchange with other ions, preferably OH^- ions. An evaluation of present data suggests that the process is occurring at all pH levels, and is highly significant at lower pH.

Values of $(P_d/P_{ad})\%$ were in the range 1-27, 4-26 and 29-56 at pH 4, 7 and 10 respectively. Concentrations of P_d at different pH values are shown in Table 2. At $5 \times 10^3 \mu\text{g.g}^{-1}$ level of P_a , sample at st M_3 desorbed $783 \mu\text{g.g}^{-1}$ of P which was equivalent to 27% of the P_{ad} at pH 4. The same sample at pH 7 desorbed $1220 \mu\text{g.g}^{-1}$ (26%) as compared to $924 \mu\text{g.g}^{-1}$ (56%) at pH 10. This shows that maximum desorption takes place at higher values of pH.

P_e , calculated from the difference between P_{an} and total P_a , is shown in Fig. 2. The term 'exchangeable P' (P_e) is used in this study to denote that fraction of P which is not retained in the sediment during the adsorption-desorption steps at any specified pH. At P_a of $1 \times 10^2 \mu\text{g.g}^{-1}$, $(P_e/P_a)\%$ values ranged 2-8, 6-12 and 46-71 at pH 4, 7 and 10 respectively. More or less the same values were observed for P_a at $1 \times 10^3 \mu\text{g.g}^{-1}$.

Table 2—Adsorption and Desorption of Added P_i at pH 4, 7 and 10

St	$(P_{ad}/P_a)\%$			$(P_d/P_{ad})\%$			$(P_{an}/P_a)\%$		
	P_a								
	1×10^2			1×10^3			5×10^3		
	pH 4								
M_1	99	94	84	2	9	13	97	86	73
M_2	99	98	86	1	6	15	98	92	73
M_3	95	92	58	2	6	27	93	86	42
M_4	97	88	67	5	3	16	92	85	56
M_5	95	90	83	3	3	18	94	87	76
	pH 7								
M_1	94	92	82	6	9	14	88	84	71
M_2	99	89	88	4	11	19	95	79	71
M_3	100	99	94	9	18	26	91	81	70
M_4	98	95	87	6	17	22	92	79	67
M_5	96	93	89	7	10	19	89	84	72
	pH 10								
M_1	44	15	10	34	39	47	29	9	5
M_2	50	27	19	32	41	44	34	16	11
M_3	79	51	33	32	44	56	54	29	15
M_4	62	47	32	29	37	40	44	30	19
M_5	41	31	24	26	33	36	30	21	15

P_a = added P; P_{ad} = P adsorbed; P_d = P desorbed and P_{an} = adsorbed (net) P

Table 1—Initial Physico-Chemical Characteristics of Sediments in Mandovi Estuary

St	Sediment type	Size fraction (%) of sediment			P ($\mu\text{g.g}^{-1}$)			pH	Organic matter (%)
		Sand	Silt	Clay	Inter-stitial	Adsorbed	Total		
M_1	Silty sand	60.2	23.2	16.6	28.4	36.5	1660	7.91	5.21
M_2	Silty sand	49.6	42.9	7.5	30.8	34.8	1240	7.88	10.44
M_3	Clayey silt	8.5	56.8	34.7	18.4	46.2	2050	8.40	13.58
M_4	Sandy silt	32.6	50.9	16.5	34.7	24.1	1190	7.70	11.44
M_5	Silty sand	57.2	25.2	17.6	36.2	20.8	1430	7.11	9.46

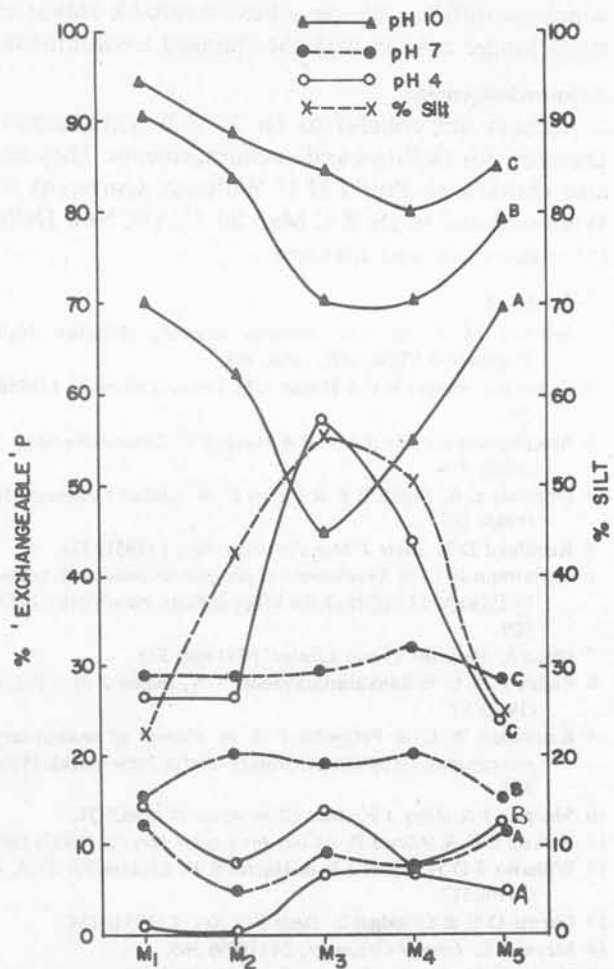


Fig. 2—Percentage P_e at pH 4, 7 and 10 for different levels of P_a [P_a levels ($\mu\text{g}\cdot\text{g}^{-1}$): A, 1×10^2 ; B, 1×10^3 and C, 5×10^3]

At P_a of $5 \times 10^3 \mu\text{g}\cdot\text{g}^{-1}$, these values ranged 24-58, 28-33 and 81 to 95 respectively at pH 4, 7 and 10.

Values of $(P_{an}/P_a) \%$ are shown in Fig. 3. Maximum retention is observed at pH 4 (42-98%) and 7 (67-95%) as compared to 10 (5-54%). Therefore, it can be concluded that the amount of P retained in the sediment varies with pH rather than the concentration of P_a . Maximum retention could be observed at pH 4 and minimum at pH 10.

A close relationship has been observed between the capacity of the sediments to adsorb and retain added P_i and the levels of total and inorganic phosphate accumulated in the sediments, and it has been suggested that P retention capacity of a sediment is an important factor determining the levels of phosphate which accumulates in sediments under natural conditions¹².

Harter¹⁵ measured the exchange capacity of clay samples and found the capacity to be relatively high and to increase with decreasing particle size. In the present study, clayey silt retained comparatively less P_a

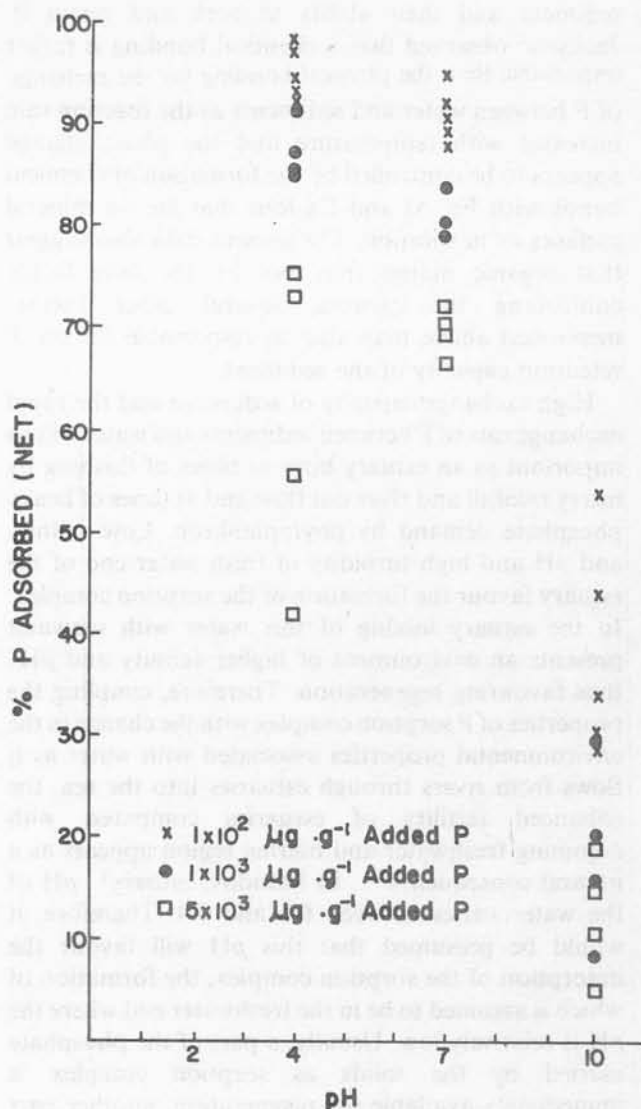


Fig. 3—Percentage P_{an} at different pH for different levels of P_a

at pH 4, whereas it retained more P at pH 10. Therefore, it can be suggested that the P retention capacity of the sediments varies with pH of the system rather than the particle size. Williams *et al.*¹² suggested that the sediments with CaCO_3 had a lower binding capacity than soils without CaCO_3 . Hayes *et al.*¹⁶ found that organic matter depressed P adsorption whereas iron increased it and that the adsorption capacity of sediments is directly related to the ratio of iron to organic matter.

The percentage of organic matter in Mandovi estuary sediments varies between 5.21 (st M₁) and 13.58 (st M₃). No direct correlation between the quantity of organic matter and the retention capacity of the sediments could be obtained in the present study. Harter¹⁵ observed a direct relationship between acid extractable aluminium, organic matter and to a lesser extent acid extractable iron content of the

sediment and their ability to sorb and retain P. Jackson¹ observed that a chemical bonding is rather responsible than the physical bonding for the exchange of P between water and sediments as the reaction rate increases with temperature and the phase change appears to be controlled by the formation of chemical bonds with Fe, Al and Ca ions that are on mineral surfaces or in solution. The present data also suggest that organic matter may not be the only factor controlling the process, several other factors mentioned above may also be responsible for the P retention capacity of the sediment.

High exchange capacity of sediments and the rapid exchange rate of P between sediments and water will be important in an estuary both at times of flushing by heavy rainfall and river out flow and at times of heavy phosphate demand by phytoplankton. Low salinity and pH and high turbidity of fresh water end of the estuary favour the formation of the sorption complex. In the estuary mixing of this water with seawater presents an environment of higher salinity and pH, thus favouring regeneration. Therefore, coupling the properties of P sorption complex with the change in the environmental properties associated with water as it flows from rivers through estuaries into the sea, the enhanced fertility of estuaries compared with adjoining freshwater and marine region appears as a natural consequence^{1,3}. In Mandovi estuary¹⁷ pH of the water varies between 6.5 and 8.4. Therefore, it would be presumed that this pH will favour the desorption of the sorption complex, the formation of which is assumed to be in the freshwater end where the pH is relatively low. Usually, a part of the phosphate carried by the solids as sorption complex is immediately available for regeneration, another part

which has diffused into the solids is available only after much longer contact with the changed environment.

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