

Factors influencing phosphate exchange across the sediment-water interface of eutrophic reservoirs

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Abstract

The results of a survey of the sediment chemistry of 7 East Anglian reservoirs are presented as part of a regional study on the assessment and control of eutrophication. The influence of water quality (dissolved oxygen, pH, temperature) on phosphate (PO₄) adsorption by sediment from hypertrophic Ardeigh Reservoir is also examined. Extractable phosphate-P (extr.-P) varied between 92 and 383 mg kg⁻¹ dry matter. Extractable P varied between 5.3 and 16.6% of the total phosphate-P (Tot. P) content and increased with the concentration of dissolved reactive phosphate-P (DRP) in the overlying water column. Organically complexed iron (organic Fe) was the determinand which correlated most closely with phosphate adsorption capacity, PAC ($r = 0.8$). Organic Fe was also related inversely to Extr. P. The rate and extent of PO₄ adsorption by Ardeigh Reservoir sediment increased with the initial concentration of DRP and adsorption equilibria were reached after 24 h. The equilibrium DRP concentration, [DRP], was 0.7 mg P l⁻¹ under aerobic conditions indicative of a high potential for PO₄ exchange. The rate and extent of PO₄ adsorption was greater at 7 °C than at 22 °C. PO₄ adsorption increased markedly with dissolved oxygen status. Ardeigh sediment exhibited a marked buffering capacity to a change in pH; however, PO₄ adsorption was greatest at an equilibrium pH of 5.6 and decreased progressively either side of this pH value.

Options for the artificial control of sediment PO₄ release are discussed in relation to the seasonal variation in sediment PO₄ exchange observed for Ardeigh Reservoir.

Introduction

Many attempts have been made to control the effects of eutrophication and a wide range of lake restoration techniques have been reported (Jorgensen, 1980; OECD, 1982). Restoration methods may be divided into two general cate-

gories, those requiring a reduction in the external nutrient load, and in-lake schemes which aim to accelerate nutrient outflow or prevent nutrient recycling. It has often been necessary to incorporate both of these approaches in order to achieve rapid improvement in water quality.

Sediments often play an important role in the

PO₄ cycle of lakes and the trophic response of a lake to a reduction in the external input of PO₄ is dependent, amongst other factors, on the extent to which PO₄ is recycled from the sediments. The time required for a lake to recover to a trophic status governed by the external PO₄ loading alone is dependent largely on the rate of internal PO₄ loading, the amount of sediment PO₄ available for release to the water column, and on the extent to which the internal PO₄ load is lost through the outlet. Particularly in shallow eutrophic lakes, which have a long history of high PO₄ loading, sediment release of PO₄ may severely delay, or even prevent, the recovery of the lake following external PO₄ control (Welch *et al.*, 1980; Ryding, 1981; Bostrom *et al.*, 1982). Thus, before embarking on an expensive PO₄ control programme, information is required on the rate of sediment PO₄ release following a reduction in the external PO₄ load, and on the potential of the sediments to release PO₄ at a rate sufficient to sustain algal growth.

In eastern England, eutrophication poses a severe threat to the quality of reservoir water used for potable supply, especially during the summer months (Hayes & Greene, 1984). Internal recycling of PO₄ appeared to be important and could confound any attempts to reduce external loading. The present study therefore examines the sediment chemistry of seven reservoirs in the region with two objectives. Firstly, the importance of sediment chemistry as a factor influencing the phosphate exchange processes of the sediments is

assessed. Secondly, the way in which water quality influences PO₄ adsorption at Ardeigh Reservoir, where eutrophication has proved especially troublesome, is examined.

Materials and methods

Two series of investigations were conducted. In the first, superficial sediments, collected from seven reservoirs in the Anglian Water region, were subjected to chemical analyses. Multiple linear regression analyses were used to determine the interrelationships between Tot. P, PAC, and Extr. P, and to assess the relative importance of various sediment chemistry determinands in influencing these three phosphorus characteristics. In the second series of investigations, the influence of [DRP], [O₂], temperature and pH on PO₄ adsorption by sediments was examined in laboratory experiments using superficial sediments collected from one particularly troublesome reservoir.

Sediment survey

Of the seven reservoirs studied, all except Ravensthorpe are pumped water storage schemes and receive high N and P loadings from river water. Using the criteria of OECD (1982), Ardeigh is hypertrophic and the others are eutrophic. The basic characteristics of the reservoirs are presented in Table 1.

Table 1. Physical and chemical characteristics of reservoirs surveyed (from Greene & Hayes, 1981).

Reservoir	National grid reference	Age (years)	Maximum capacity (m ³ × 10 ⁶)	Surface area top water level (ha)	Mean depth at top water level (m)	Hydraulic retention time (days)	Chlorophyll <i>a</i> concentration (mg m ⁻³)		Annual mean DRP concentration (mg m ⁻³ P)
							Maximum	Mean	
Ardleigh	TM 035281	12	2.2	56	3.9	210	85	32	210
Covenham	TF 345960	12	10.4	80	13.0	306	51	20	340
Rutland	SK 930070	6	124	1260	10.6	1314	88	17	24
Pitsford	SP 760695	26	17.7	300	5.9	423	29	6	9
Ravensthorpe	SP 678706	92	1.9	46	4.1	442	52	6	10
Grafham	TL 150680	16	59	638	9.7	440	41	7	760
Alton	TM 150361	6	9.6	158	6.1	480	35	13	10

Sediments were sampled by Ekman dredge during November 1979 at stations located at equal distances along the length of each reservoir. The depth of sediment collected was generally less than 10 cm. Samples were stored wet in sealed glass bottles at 4 °C. Prior to chemical analyses, the sediments were air-dried (20 °C) to constant weight, sieved through a 2 mm screen, and stored in polythene bags. The percentage moisture content of air-dried sediment was determined from the weight loss of a subsample after drying in an oven at 105 °C overnight. All results are expressed per unit weight of oven-dried matter.

Loss on ignition (LOI) was determined according to the method of Allen *et al.* (1974), and pH was measured by the procedure of Avery & Bascomb (1974). Extractable silica was determined by shaking 1.0 g sediment with 50 ml distilled water for 5 h followed by filtration and analysis of silica by the molybdosilicate method (APHA, 1976). Total N was determined by Kjeldahl digestion (Allen *et al.*, 1974) with analysis of ammoniacal N by direct nesslerisation (DOE, 1972). Extractable P was determined by a single extraction with 0.5 M NaHCO₃ (pH = 8.5) (Olsen *et al.*, 1954) followed by analysis of DRP by the ascorbic acid method (APHA, 1976).

A tentative estimate of phosphate adsorption capacity (PAC) was obtained by shaking 2 g sediment with 20 ml of a phosphate solution, containing 100 mg P l⁻¹ as K₂HPO₄, for 4 h followed by filtration and analysis of DRP by the ascorbic acid method (APHA, 1976). It is recognised that the rate and extent of PO₄ adsorption will vary with both the initial concentration of DRP and with the contact time. As such, the estimates of PAC obtained for the Sediment Survey are not intended to describe the kinetics of PO₄ adsorption, but merely to indicate the relative potentials of different reservoir sediments to adsorb further PO₄.

Tot. P was determined by digestion with a mixture of concentrated nitric and perchloric acids (4 : 1 v/v) followed by analysis of phosphate by the ascorbic acid method (APHA, 1976).

A sequential extraction procedure employing 3

extractants (sodium pyrophosphate, acid ammonium oxalate, and citrate dithionite) was used to characterise different fractions of iron, manganese, and aluminium. Sodium pyrophosphate, ammonium oxalate, and citrate dithionite are alleged to extract the organic, amorphous, and crystalline fractions respectively. This procedure, whilst developed initially for soils (McKeague & Day, 1966; McKeague, 1967; McKeague *et al.*, 1971) has also been used for sediments (Shukla *et al.*, 1971; Williams *et al.*, 1971; Hayes, 1978; Slater & Boag, 1978). Analyses of these metals were conducted by atomic absorption spectrophotometry (Varian AA-375). Estimates of total Fe and total Mn were calculated as the sum of the organic, amorphous, and crystalline forms of these metals. Subsequent analyses of Ardleigh Reservoir sediment indicated that the values obtained by the sequential procedure represented about 55% of the total iron and 75% of the total manganese values obtained using a mixture of nitric and perchloric acids (4 : 1 v/v).

Phosphate adsorption studies on Ardleigh Reservoir sediment

The surface sediment (top 2 cm) of Ardleigh Reservoir was sampled by scuba divers on 5th August, 1980 and stored in a sealed plastic container at 4 °C prior to analysis. Moisture content was determined as percent weight loss after drying a pre-weighed subsample of sediment overnight at 105 °C. Experiments were conducted on moist sediment, but the results are expressed per unit weight of oven-dried material. The effects of [DRP], pH, temperature, and [O₂] on PO₄ adsorption by Ardleigh Reservoir sediment were examined.

The experimental procedure used to examine the influence of [DRP] on PO₄ adsorption was similar to that described by Hwang *et al.* (1976). Undried sediment was shaken with 4 solutions of K H₂ PO₄ (2.5, 5.0, 10.0, 15.0 mg P l⁻¹) on an orbital shaker at room temperature (20 °C) using a sediment-solution ratio of 1 : 80 w/v. After pre-determined time intervals, a 10 ml aliquot of each

80 ml suspension was centrifuged at 440 g for 20 min and the [DRP] of the supernatant liquid analysed using the ascorbic acid method (APHA, 1976). This value was taken to represent the concentration of unadsorbed PO_4 remaining in solution. Cumulative PO_4 adsorption by the composite sample at varying initial added DRP levels and after various contact times, was determined according to the method of Hwang *et al.* (1976).

For example, for the composite sample and an added DRP level of 10.0 mg l^{-1} , cumulative phosphate adsorption was calculated as follows: At 0 h contact time: the nominal level of DRP in reactor solution = 10.0 mg l^{-1} .

At 2 h contact time before removal of 10 ml aliquot:

DRP in reactor solution = 4.48 mg l^{-1} .

DRP adsorbed by reactor solids = $0.88(10.0 - 4.48) = 0.44 \text{ mg} = 0.44 \text{ mg g}^{-1}$.

Weight of solids remaining after removal of 10 ml aliquot, assuming homogeneous suspension = $70/80 \times 1.00 \text{ g} = 0.88 \text{ g}$.

DRP adsorbed by reactor solids = $0.88 \times 0.44 = 0.39 \text{ mg}$.

At 4 h contact time before removal of 10 ml aliquot:

DRP in reactor solution = 2.35 mg l^{-1}

DRP adsorbed by reactor solids = $0.39 + 0.07(4.48 - 2.35) = 0.54 = 0.61 \text{ mg g}^{-1}$.

Weight of solids remaining after removal of 10 ml aliquot, assuming homogeneous suspension = $60/70 \times 0.88 = 0.75 \text{ g}$.

DRP adsorbed by reactor solids = $0.75 \times 0.61 = 0.46 \text{ mg}$.

A similar method was used to study the influence of $[\text{O}_2]$, temperature and pH on PO_4 adsorption except that the time course for PO_4 adsorption was not examined. Sediment suspensions (1:40 w/v) were shaken for 24 h prior to analysis of DRP. PO_4 adsorption at 7°C was compared with that at 22°C . The effects of pH and $[\text{O}_2]$ were examined at room temperature (20°C). PO_4 adsorption was followed at five pH levels, 4.0, 6.0, 7.5, 8.5, and 10.0. The pH of the suspensions was adjusted with 0.1 N NaOH or 0.1 N HCl. A pH buffer was not used to maintain pH constant

throughout the experiment, thus the treatments represent pH values at the start of the experiment only (initial pH). The pH measured at the end of incubation is considered to represent equilibrium pH, the difference between initial and equilibrium pH reflecting the buffering capacity of the sediment. The effect of $[\text{O}_2]$ on PO_4 adsorption was examined by comparing adsorption under aerated conditions with that under nitrogen-flushed conditions.

Results

Sediment survey

The results of the sediment survey are given in Table 2. Extr P represented between 5.5% and 16.5% of the Tot. P content. With the exception of Covenham there was little variation in PAC between reservoirs. The sediments adsorbed between 40% (Covenham) and 88% (Ardleigh) of the DRP added at a level of $1000 \text{ mg P kg}^{-1}$. The mean reservoir total Fe content was 30000 mg kg^{-1} and, excepting Ardleigh, the organic Fe content was less than the amorphous Fe content which, in turn, was less than the crystalline Fe content. On average, crystalline Fe represented about 55% of total Fe, and organic Fe and amorphous Fe represented about 16% and 29% of total Fe respectively. The mean reservoir total Mn concentration of 745 mg kg^{-1} was 40-fold lower than that for total Fe. On average, crystalline Mn represented about 53% of total Mn, and the organic and amorphous fractions each represented about 25%.

In the sediment of the seven reservoirs, oxalate Mn was closely correlated with oxalate Fe ($r = 0.77$, $p < 0.05$), and also with oxalate Al ($r = 0.97$, $p < 0.001$). Oxalate Al was closely related to oxalate Fe ($r = 0.90$, $p < 0.01$). The mean reservoir content of oxalate extractable-Fe, Al, and Mn was 9380 mg kg^{-1} , 500 mg kg^{-1} , and 283 mg kg^{-1} respectively, corresponding to a ratio of about 33 Fe : 2 Al : 1 Mn. Ravensthorpe was an exception to this trend, having a ratio of about 66 Fe : 2 Al : 1 Mn. Rutland Water had the

Table 2. Physical and chemical characteristics (means with SE in parenthesis) of sediments of reservoirs surveyed. Values are mg kg⁻¹ oven-dried sediment unless stated otherwise.

	Ardleigh	Covenham	Rutland	Pitsford	Ravensthorpe	Grafham	Alton
N	6	5	6	6	6	2	6
Loss on ignition (%)	12.3 (1.2)	4.8 (0.5)	11.6 (1.8)	11.2 (0.6)	12.8 (1.1)	9.15	12.1 (2.1)
Water-extractable silica (as Si)	102 (15)	117 (14)	110 (24)	91 (11)	117 (12)	139	66 (8)
pH	7.06 (0.04)	7.21 (0.03)	6.98 (0.02)	6.97 (0.04)	6.86 (0.05)	6.95	7.07 (0.04)
Tot. P	2250 (70)	1660 (210)	1910 (60)	1770 (110)	1880 (20)	2300	1690 (90)
Extr. P	214 (12)	267 (39)	129 (16)	118 (15)	99 (9)	383	92 (12)
PAC	876 (27)	398 (29)	820 (29)	834 (30)	855 (33)	725	817 (29)
Iron							
Organic	5431 (350)	1400 (60)	5820 (530)	5510 (580)	8080 (830)	2460	5440 (920)
Amorphous	8860 (710)	2890 (350)	9360 (1030)	9490 (450)	15240 (770)	5120	9440 (1120)
Crystalline	6100 (560)	8690 (460)	18330 (2720)	25570 (1430)	22840 (1110)	13200	20310 (4280)
Total	20400 (1120)	12980 (470)	33510 (3360)	40560 (1960)	46160 (1740)	20780	35200 (5070)
Manganese							
Organic	239 (42)	34 (4)	373 (18)	267 (69)	153 (19)	53	232 (30)
Amorphous	216 (33)	87 (7)	267 (39)	191 (34)	170 (20)	123	189 (27)
Crystalline	360 (52)	234 (19)	422 (30)	395 (46)	410 (34)	363	440 (82)
Total	815 (125)	355 (24)	1061 (64)	853 (141)	733 (73)	538	861 (108)
Oxalate iron	10760 (940)	2130 (280)	14120 (1720)	10370 (1030)	13580 (1110)	4120	10550 (1480)
Oxalate manganese	303 (41)	80 (11)	564 (46)	310 (66)	205 (27)	147	372 (43)
Oxalate aluminium	559 (41)	146 (15)	875 (126)	509 (43)	509 (63)	266	639 (168)
Total N	8220 (1190)	2870 (508)	4610 (480)	5740 (450)	8810 (660)	4560	6700 (1430)

highest oxalate extractable-Fe, Mn, and Al contents, whilst Covenham had the lowest.

Excepting Covenham, variation in Tot. P closely followed that for Extr. P. In general, the ratio of Extr. P to Tot. P increased with the mean annual concentration of DRP in the water column (Table 3). In contrast, the ratio of PAC to Tot. P decreased. Extr. P was closely correlated with DRP (Fig. 1) as follows:

$$\text{Extr. P (mg kg}^{-1}\text{)} = 0.38 [\text{DRP}]_y + 112$$

($r = 0.98$, $p < 0.001$)

where, $[\text{DRP}]_y$ represents the annual mean concentration of DRP in the overlying water column (mg m⁻³).

In Table 4, determinands are listed according to their contribution to the variation in each of

three dependent PO₄ characteristics. Determinants are ranked according to their closeness of association with a given PO₄ property. Extr. P and PAC were the two most important variables influencing Tot. P. Organic Fe was the determi-

Table 3. Inter-relationships between phosphate properties of the sediments and annual mean concentration of dissolved reactive phosphate (mg P m⁻³) in the overlying water column (values for DRP from Greene & Hayes, 1981).

Reservoir	Extr. P. (%) Tot. P	PAC (%) Tot. P	[DRP] _y
Graham	16.6	31.5	760
Covenham	16.1	24.0	340
Ardleigh	9.5	39.0	210
Rutland	6.8	43.0	24
Pitsford	6.7	47.0	9
Ravensthorpe	5.3	45.5	10
Alton	5.5	48.4	10

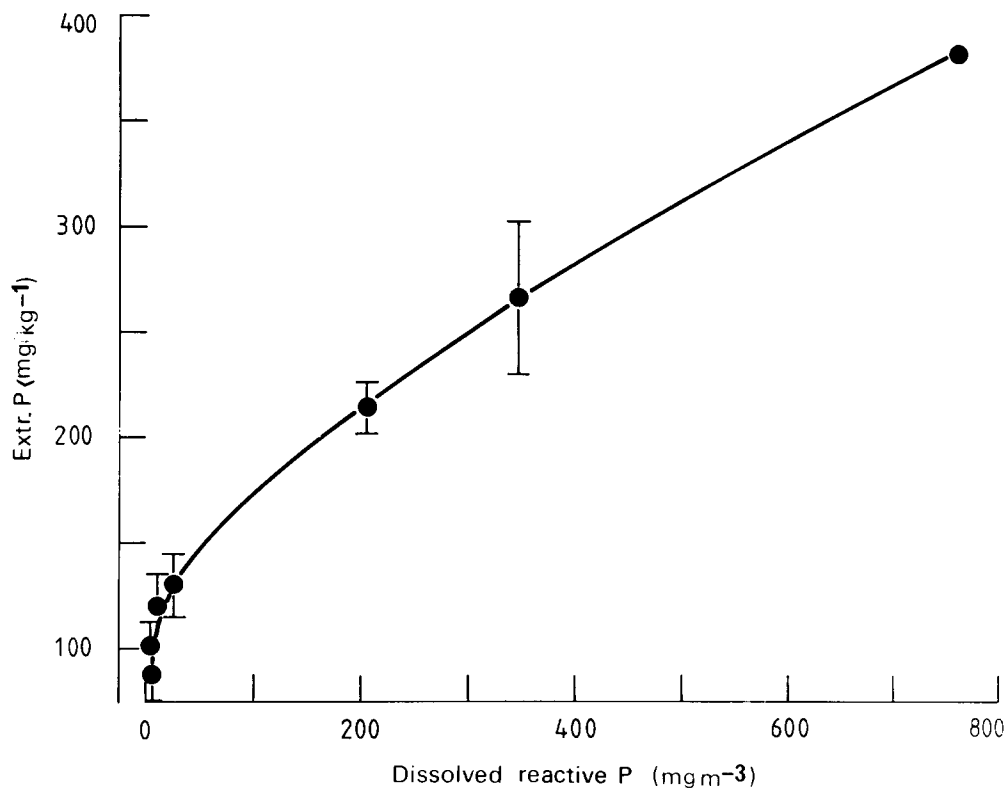


Fig. 1. Relationship between extractable P content (means \pm SE) of reservoir sediments and the annual mean DRP in the overlying water column.

Table 4. Influence of sediment chemistry determinands on phosphate properties of sediments of reservoirs, as measured by multiple correlation coefficients.

Extr. P	Dependent variable		
	PAC	Tot. P	
Tot. P	0.56	Organic Fe 0.80	Extr. P. 0.56
Organic Fe	0.82	LoI 0.86	PAC 0.81
Total	0.92	Total 0.95	Total 0.90

nand most closely related to PAC, with 64% of the variation in PAC being explained by variation in organic Fe. Inclusion of LOI increased the explained variation in PAC to 74%. Organic Fe was the second most important variable influencing Extr. P. Together, variation in Tot. P and organic Fe explained 67% of the variation in Extr. P.

Phosphate adsorption studies on Ardleigh Reservoir sediments

Both the amount of PO_4 adsorbed and the rate of PO_4 adsorption for any given contact time increased with initial [DRP] (Fig. 2). Adsorption equilibria were established after 24 h.

In order to construct PO_4 adsorption isotherms (Fig. 3) the concentrations of DRP remaining after an incubation period of 24 h were taken as representative of equilibrium conditions. The gradient of the initial stage of the curve is often used as a measure of the sediment's phosphate buffering capacity (Slater & Boag, 1978). In the case of Ardleigh sediments, an increase in equilibrium [DRP] resulted in a large increase in PO_4 adsorption, particularly at PO_4 concentrations below 1 mg P l^{-1} , indicating a high phosphate buffering capacity. It should be noted that the

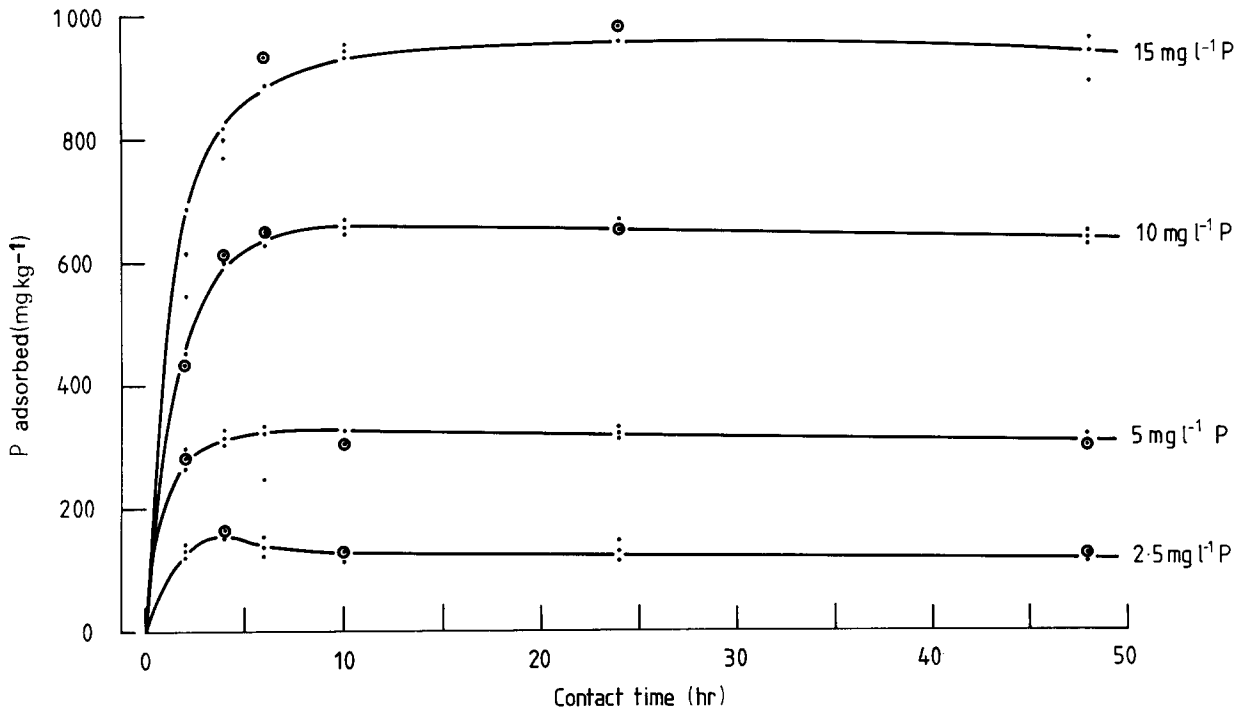


Fig. 2. Effect of contact time and initial DRP concentration on PO₄ adsorption by Ardleigh Reservoir sediment (curves connect the means of triplicate treatments).

values for PO₄ adsorption do not include PO₄ which is already bound to the sediment prior to the experiment. Consequently, the ordinate of the

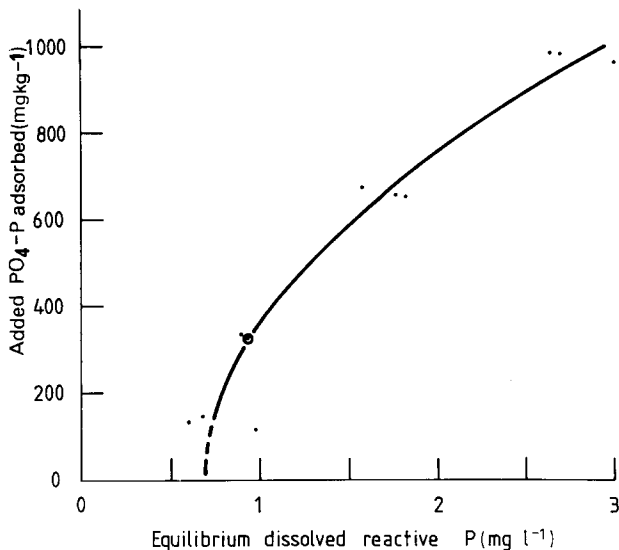


Fig. 3. Phosphate adsorption isotherm for Ardleigh Reservoir sediment (curves connect the means of triplicate treatments).

adsorption curves represents the net amount of added DRP which was adsorbed during the experiment and not the total amount of PO₄ adsorbed by the sediment. Thus the point at which the curve intersects the x-axis (the equilibrium phosphate concentration, Taylor & Kunishi, 1971) represents the concentration of DRP that exists in equilibrium with sediment particles when there has been no net release or uptake of added PO₄. The adsorption curve for Ardleigh sediment (Fig. 3) connects the mean values for triplicate treatments and, if extrapolated, it intersects the x-axis at about 0.7 mg P l⁻¹, indicating a high PO₄ release potential for the sediments.

At equilibrium DRP concentrations above about 0.6 mg P l⁻¹, adsorption was greater at 7 °C than at 22 °C (Fig. 4). The effect of temperature on PO₄ adsorption increased with equilibrium [DRP]. At PO₄ concentrations below 0.6 mg P l⁻¹ adsorption was greater at 22 °C than at 7 °C.

In the dissolved oxygen study, reduced conditions (final oxygen concentration 4–39% satu-

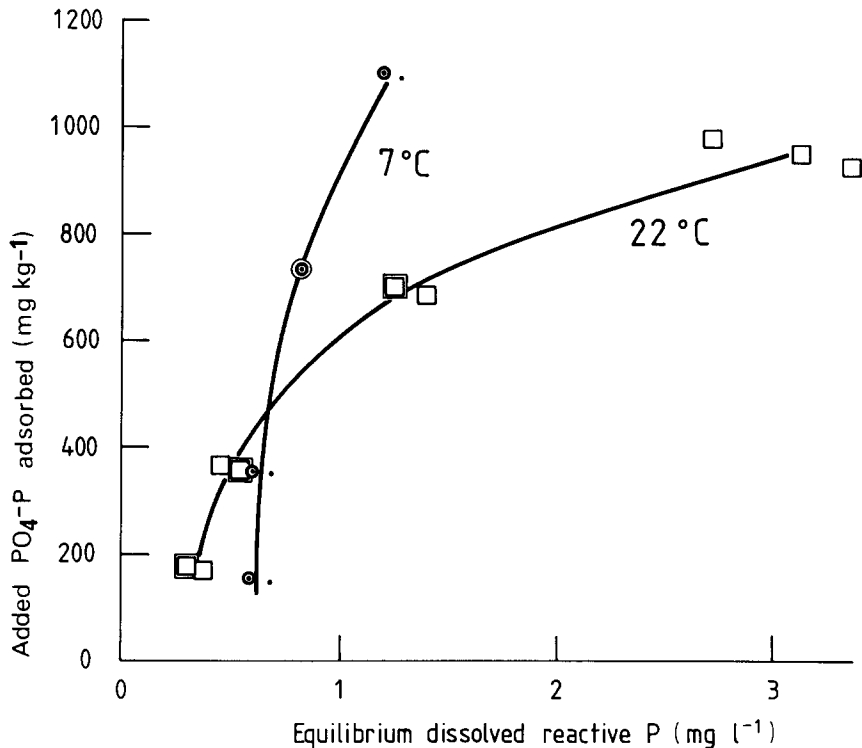


Fig. 4. Effect of temperature on PO₄ adsorption by Ardleigh Reservoir sediment (curves connect mean values for triplicate treatments).

ration) were produced by nitrogen flushing the atmosphere overlying the sediment suspension. Test vessels were sealed throughout the experiment. Dissolved oxygen concentrations in most of the reduced suspensions were less than 10% saturation while in the oxidised sediment suspensions they ranged from 68 to 75% saturation at the end of incubation. Inter-replicate variation in [O₂] was much greater in the reduced suspensions. More PO₄ was adsorbed by oxidised sediment than by reduced suspensions, and in both systems adsorption increased with initial [DRP] (Fig. 5). With an initial [DRP] of 2.5 mg P l⁻¹ the reduced sediment released PO₄.

Ardleigh sediment exhibited considerable buffering capacity to a change in pH, and consequently, a pH change induced, by HCl or NaOH addition, at the start of incubation was greatly reduced by the end (Fig. 6). The pH of the sediment suspensions was considered to have reached equilibrium by the end of incubation. At

the two higher initial DRP levels, PO₄ adsorption was greatest at pH 5.6 and decreased progressively with increasing pH change either side of this value (Fig. 7). At the two lower initial DRP concentrations (2.5, 5.0 mg P l⁻¹) adsorption varied little over the pH range 5.6 to 8.0.

Discussion

The levels of Extr. P, PAC and Tot. P, reported in the present study, are similar to those for some other lakes (Shukla *et al.*, 1971; Williams *et al.*, 1971; Jacobsen, 1977; Ku *et al.*, 1978; Slater & Boag, 1978). Williams *et al.* (1980), reported that PO₄ varied between 8 and 50% of the total PO₄ content of sediments from Lake Ontario and Lake Erie. Klapwijk *et al.* (1982), working on sediments from four Dutch lakes, found that available PO₄ varied between 0.4 and 36% of the total PO₄ content, Tot. P levels ranging from 1000

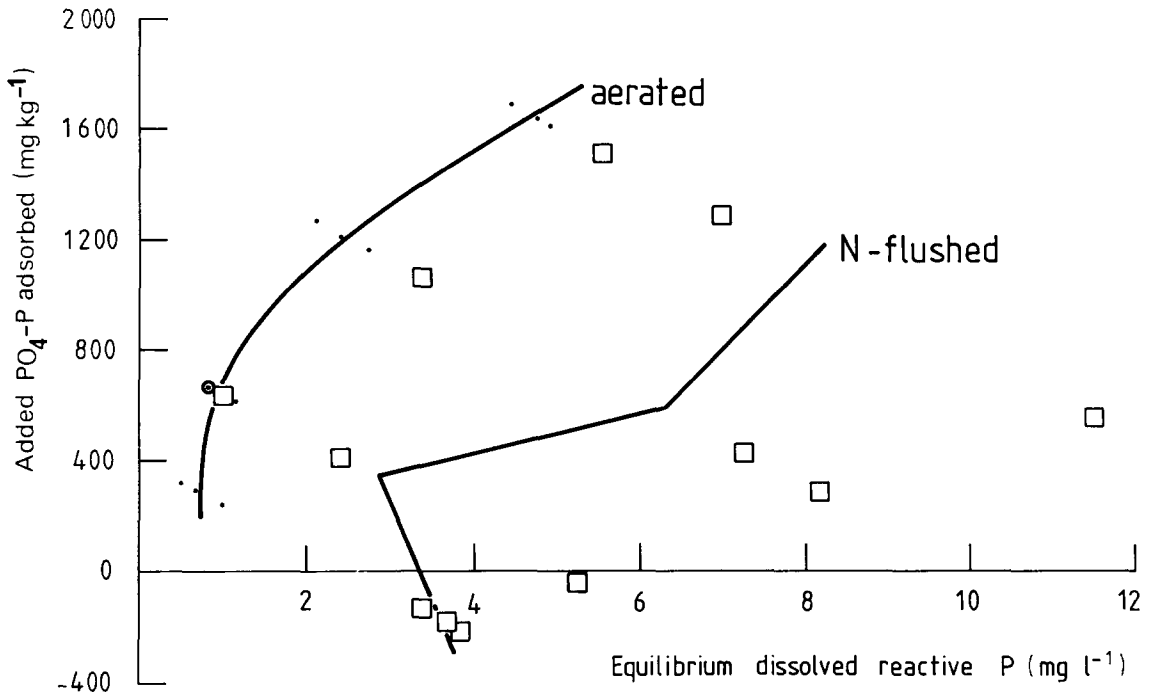


Fig. 5. Effect of dissolved oxygen on PO_4 adsorption by Ardleigh Reservoir sediment (curves connect mean values of triplicate treatments).

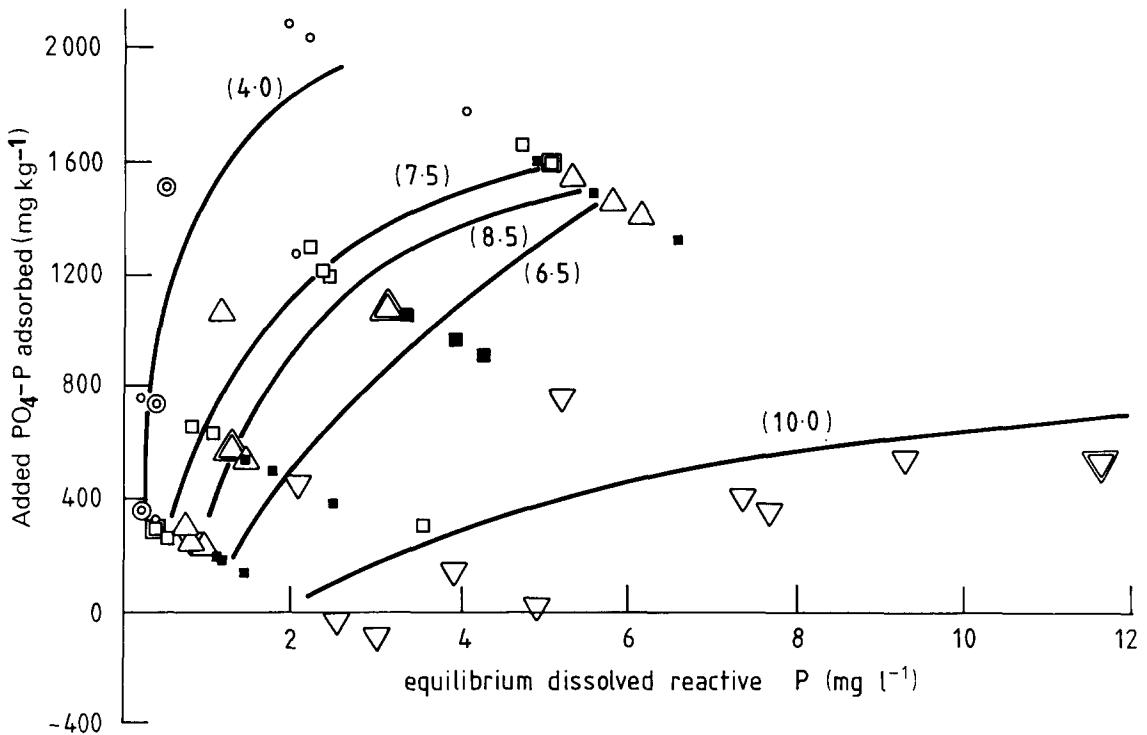


Fig. 6. Effect of pH on PO_4 adsorption by Ardleigh Reservoir sediment (initial pH values are given in parentheses and curves connect means of triplicate treatments).

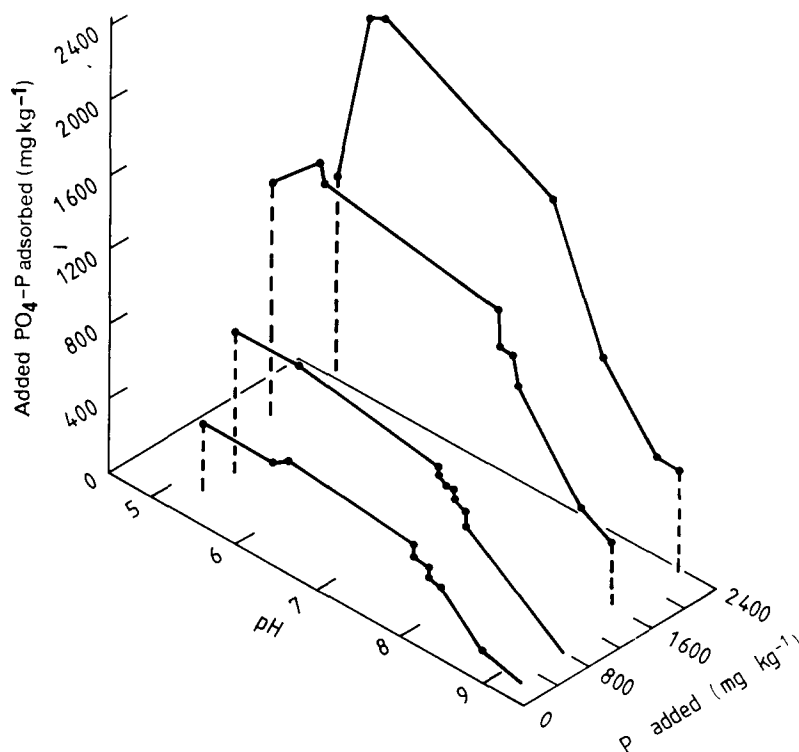


Fig. 7. Relationship between equilibrium pH and phosphate adsorption by Ardleigh Reservoir sediment.

to 4000 mg kg^{-1} . Generally, Extr. PO_4 as a percent of total PO_4 varies considerably from lake to lake according to the type of sediment (Bostrom & Pettersson, 1982; Klapwijk *et al.*, 1982). In the present study Extr. P followed closely the mean annual DRP concentration of the overlying water column which, in turn, reflects the intensity of water management problems experienced with each reservoir (Redshaw, 1983). Assuming that equilibrium exists between external PO_4 loading and lake PO_4 concentration (OECD, 1982), this relationship suggests that, at least for Anglian reservoirs, the Extr. P content of the sediments (i.e. potential for sediment PO_4 release) is related directly to the external PO_4 loading.

Klapwijk *et al.* (1982) reported that the total $\text{PO}_4\text{-P}$ content of sediments from 4 Dutch lakes was related directly to the net PO_4 loading on the lakes, and that the ratio of available $\text{PO}_4\text{-P}$ to total $\text{PO}_4\text{-P}$ was related closely to the total $\text{PO}_4\text{-P}$ content of the sediments. Lijklema and Hieltjes (1982) proposed that, for shallow lakes, the con-

centration of sediment PO_4 is an exponential function of external PO_4 loading. Consequently following a reduction in external PO_4 loading, one may expect a non-linear decrease in the concentration of PO_4 in the sediment and interstitial water, and therefore, a disproportionate decrease in the rate of sediment PO_4 release.

Chemical composition was a major factor influencing the PO_4 exchange potential of Anglian reservoir sediments. In particular, the content of organic iron was related closely to both PAC and Extr. P, reflecting the importance of iron in controlling the potential for sediment PO_4 release in these reservoirs. The precise speciation of organic Fe as extracted by pyrophosphate is, as yet, uncertain, although it probably incorporates amorphous iron oxyhydroxides complexed by low molecular weight organic substances (W. Adams, pers. comm.). This is consistent with the suggestion that organically complexed Fe^{3+} and Al^{3+} are the sites most likely for PO_4 adsorption on organic matter surfaces (Syers *et al.*, 1971).

Amorphous Fe has been shown to play an important role in determining the ability of sediments to accumulate PO_4 in the environment and to adsorb PO_4 in the laboratory (Shukla *et al.*, 1971; Williams *et al.*, 1971; Jacobsen, 1977; Slater & Boag, 1978). Shukla *et al.* (1971) and Williams *et al.* (1971) concluded that a gel complex, consisting largely of hydrated iron oxide along with smaller amounts of organic matter, aluminium, and associated silicates, and inorganic PO_4 was the major contributor to inorganic PO_4 adsorption by non-calcareous and calcareous sediments from Wisconsin lakes.

In the present study, the DRP concentration of the water column was related directly to the sediment ratio of Extr. P to Tot. PO_4 , and inversely to the sediment ratio of PAC to Tot. PO_4 . These results suggest that the percentage saturation of PO_4 adsorption sites in the sediment decreased with the concentration of PO_4 in the overlying water column. This hypothesis is strengthened by the inverse relationship between Extr. P and PAC and suggests that, by increasing the iron content of the sediments, it should be possible to increase the PAC of the sediments and thereby reduce the potential for sediment PO_4 release.

The results of the PO_4 adsorption experiments on Ardleigh Reservoir sediment support the hypothesis that iron is the major element controlling the availability of sediment PO_4 in Anglian reservoirs. Adsorption was greatest at pH 5.6 and decreased rapidly either side of this value. This pattern is similar to that reported for other lakes where PO_4 adsorption is controlled predominantly by the solubility of iron and aluminium (McPherson *et al.*, 1958; Gummerman, 1970; Ku *et al.*, 1978). An increase in sediment pH leads to a reduction in PO_4 adsorption by amorphous iron and goethite, but simultaneously the formation of hydroxyapatite or calcium phosphate increases (Jacobsen, 1977). Ku *et al.* (1978) reported that protonation of surface iron and aluminium in clays, oxides and hydroxides (promoted by decreasing pH) creates more positive sites to enhance PO_4 binding.

In the present study the effect of dissolved oxygen on PO_4 adsorption was as great as that of pH.

Adsorption under reduced conditions was more than 50% lower than that under oxidised conditions, reflecting the importance of iron as a factor influencing PAC. Norvell (1974) reported PO_4 adsorption of up to 1860 mg kg^{-1} for anaerobic sediment and suggested that the mechanism responsible for anaerobic PO_4 adsorption was a combination of precipitation and adsorption by calcium, iron and manganese. Gummerman (1970) concluded that the response of PO_4 adsorption to a reduction in O_2 concentration depends on the amount of PO_4 bound to potentially reducible iron.

When examining the effects of temperature on PO_4 adsorption in the present study no attempt was made to maintain constant dissolved oxygen concentrations. Thus, the reduction in adsorption recorded at the higher temperature (22°C) may have been due to reduced oxygen levels associated with increased activity of sediment bacteria. Using similar DRP concentrations to those of the present study, Ku *et al.* (1978) demonstrated greater adsorption at 11°C than at 20°C and reported that the effect of temperature on PO_4 adsorption was greater at pH 7.0 than at pH 5.5. In contrast, Gummerman (1970) demonstrated an increase in adsorption with temperature (4°C compared with 22°C) for sediments from central Lake Erie and western Lake Superior. Holdren & Armstrong (1980) demonstrated an increase in sediment PO_4 release rate with increasing temperature over the range 2°C – 23°C .

The equilibrium [DRP] for Ardleigh sediment was about 0.7 mg P l^{-1} . This is considerably higher than values ranging between 0 and 0.4 mg P l^{-1} reported for three Australian and two Wisconsin (USA) lakes (Slater & Boag, 1978) and highlights the importance of Ardleigh sediments as a potential source of PO_4 .

Ardleigh Reservoir receives a high external input of PO_4 and exhibits many of the features classically associated with hypertrophic water bodies (Redshaw, 1983). Detailed PO_4 budgets indicate that, whilst the sediments act as a net annual sink for P, a large net release of sediment PO_4 occurs during the summer. The high phosphate release potential of Ardleigh sediment, as

phate release potential of Ardleigh sediment, as observed in the present study, may severely limit the initial impact of external PO_4 control on the trophic status of the reservoir.

Phosphate adsorption by Ardleigh sediment was lowest under conditions of high temperature, high pH, and low O_2 . Such conditions are typical of Ardleigh Reservoir water quality during the summer months and may explain the release of sediment PO_4 during this period (Redshaw, 1983).

In order to reduce the potential for sediment PO_4 recycling in Ardleigh Reservoir it may be necessary to combine chemical treatment of the sediments, using iron, with the maintenance of favourable water quality conditions for sediment PO_4 adsorption (low temperature, low pH, and high O_2). Until the availability of sediment PO_4 is reduced, the sediments of Ardleigh Reservoir may continue to act as a potential source of PO_4 for algal growth.

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