

Using sediments to assess the resistance of a calcareous lake to diffuse nutrient loading

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With 4 figures and 4 tables

Abstract: The capacity of lake sediments to retain phosphorus can provide an important buffer to eutrophication. Concentrations of total phosphorus (TP) in the surface sediment of a shallow calcareous lake (Lough Carra, Ireland) varied significantly across three basins and were correlated strongly with iron and manganese, but correlated inversely with calcium carbonate. The concentrations of phosphorus in the surficial sediments of each basin were observed to reflect the mean annual TP of overlying waters, such that the North Basin > South Basin > Mid Basin. Phosphorus sorption experiments on the most TP-enriched sediments predicted a saturation concentration of 0.15 mg P g⁻¹. Geochemically similar sediments from the northern basin had slightly lower measured TP concentrations (0.10 mg P g⁻¹), while those sediments with higher Fe concentrations had up to 0.54 mg P g⁻¹. Decreasing Fe:P in the upper sections of sediment cores taken from each lake basin show clearly a reduction in the ability of the lake sediments to bind P, reducing the resistance of the lake to eutrophication. The reduced capacity of the sediments to adsorb P should be viewed as a warning signal that indicates increasing risk to water quality and current high conservation status of Lough Carra. The risk that the lake could “flip” to an alternative state, with high concentrations of phytoplankton and a loss of extensive charophyte beds, requires that measures are effected that will prevent or reduce nutrient loads to the lake. This will necessitate a reversal of the current trend of increasing catchment pressures from intensification of agriculture and increased rural housing.

Key words: marl lakes; phosphorus; stable states; sorption; sediments.

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Introduction

Lake sediments, acting as sinks for diffuse nutrient inputs, primarily phosphorus (P), can provide an important buffer against eutrophication (SØNDERGAARD *et al.* 2003, ENGSTROM & WRIGHT 1984). Sediment retention or loss of P can be a major factor for nutrient recycling, especially in shallow lakes (SCHEFFER 1997, SØNDERGAARD *et al.* 2003, KALFF 2002). The ability of calcareous lakes to buffer phosphorus loading is associated with co-precipitation of P and calcium carbonate from the water column (OTSUKI & WETZEL 1972, SØNDERGAARD *et al.* 2003). The retention of P within the marl sediments depends largely, however, on the presence of iron and manganese hydroxides (GOLTERMAN 1988, GONSIORCZYK *et al.* 2001).

Early experiments by MORTIMER (1941) revealed the importance of the redox state of iron and manganese in sediments for P absorption and release. In shallow polymictic lakes, P is bound by oxidised sediments. Mobilization of P can, however, occur below the sediment surface, or at the sediment-water interface under low oxygen concentrations, which are often reduced further by abundant organic matter and accentuated by high summer temperatures. This can lead to a post-depositional upward movement of elements (CARIGNAN & FLETT 1981). MACKERETH (1966) used molar Fe:Mn ratios to suggest redox conditions at the time of deposition and post-deposition, based on preferential depletion of Mn in anaerobic environments owing to its greater mobility (ENGSTROM & WRIGHT 1984). The reconstruction of redox conditions can, therefore, validate inferences of nutrient variations attributable to the source as opposed to diagenetic changes within the sedimentary chemical stratigraphy.

The importance of calcareous waterbodies has been recognized internationally by being listed as an Annex I habitat under the 'Habitats Directive' (92/43/EEC) of the European Union. In addition, five other habitat types of conservation importance under the directive have been identified within the catchment of Lough Carra, the lake which is the focus of this study. Diffuse nutrient loading to Lough Carra has increased over time (IRVINE *et al.* 2003), owing primarily to intensification of agriculture and considerable increases in the size of the cattle population in the lake catchment since the early 1970s. Highly significant associations among three independent data sources; sedimentary total phosphorus (TP), diatom-inferred epilimnetic TP and TP loads calculated from historical census data suggest strongly that TP profiles found in three sediment cores reflect increased eutrophication of the water column since this time (DONOHUE *et al.*, unpubl.). In this study, we used a spatial surface sediment survey, laboratory sorption experiments and sediment cores to assess the current ability of sediments in Lough Carra to buffer diffuse nutrient loading by binding available P.

Methods

Study site

Lough Carra is a shallow polymictic calcareous lake in the west of Ireland (Fig. 1) and is the largest marl lake in the country, covering an area of approximately 1610 hectares at an elevation of 18.9 m a. s. l. (Table 1). The lake has been managed as a wild brown trout (*Salmo trutta* L.) fishery since the 1950s. The shoreline of Lough Carra is highly indented and forms three well-defined basins: Castleburke Basin (North Basin), Castlecarras Basin (Mid Basin) and Twin Islands Basin (South Basin) (Fig. 1). The catchment is located on Upper Carboniferous limestone, and soils consist of brown earths (68%), grey-brown podzolics (25%) and basin peats (7%) and are of limestone glacial till origin (KING & CHAMP 2000). Limestone rock outcrops occur frequently around the lake shore. Land use on the catchment comprises primarily grass production for sheep and cattle grazing.

The north end of the lake is fed by the North Basin River (unnamed river), which traverses low lying agricultural land and is considerably wider (approximately 3–4 times) once it has flowed through the small Lough Beg (surface area: 3.4 ha; Fig. 1). The Mid Basin does not have a fluvial input. In the southern basin, the Mullingar and Clooneen Rivers feed into the lake. It is also believed that the lake is spring fed (DÚCHAS 2002), although recent estimates suggest that groundwater supply account for <5% net annual throughflow (DONOHUE, unpublished data). The Keel Canal is the sole outflow, located at the south-western end of the lake. Lough Carra is currently classified as mesotrophic, with evidence of a gradual decline in water quality since sampling began on the lake in 1975 (MCGARRIGLE et al. 2002).

Sampling

The sampling of surface sediments was undertaken at randomly selected sites within each basin in May 2002 (Fig. 1). Seven sites were sampled in both the Mid and South Basins, while nine were sampled in the North Basin. Additional sampling of fluvial and inlet sites was done in June 2002. Surficial sediments (0–1 cm) were collected using an Ekman grab sampler and stored in sterile 150 ml plastic containers. Sediment cores and a bulk sediment grab were taken in July 2002. One core was taken from an area of known maximum depth in each basin using a 5 cm diameter modified Livingston core sampler. Each core was taken ashore following its extraction and segmented into 1 cm intervals. Samples were stored in individual zip lock polyethylene bags and refrigerated at 4 °C. Sample locations were logged using GPS.

Sediment chemistry

Sediment was oven-dried upon returning from the field. Quantification of total phosphorus (TP) concentrations followed the ascorbic acid method of JOHN (1970), after microwave nitric acid digestion using a CEM[®] MDS–2000 microwave. The loosely-bound or bioavailable phosphorus (BAP) was analysed following JOHN (1970) after extraction with iron oxide-impregnated filter paper, which estimates the fractionation of

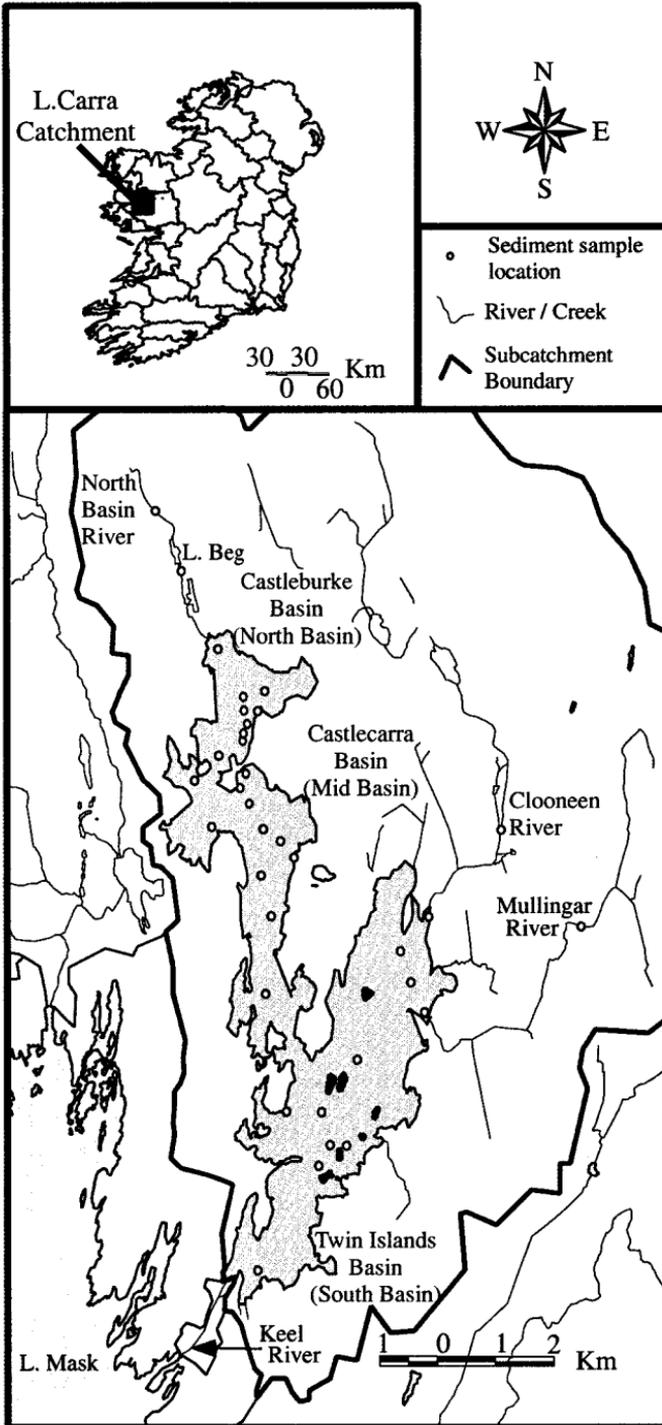


Fig. 1. Study site location map of Lough Carra, Co. Mayo, Ireland.

Table 1. Morphometry of Lough Carra and catchment (updated from KING & CHAMP 2000).

Longitude (°W)	9.227
Latitude (°N)	53.698
Altitude (m ASL)	18.9
Lake Catchment Area (km ²)	114
Lake Surface Area (km ²)	16.1
Volume (m ³)	2.8 × 10 ⁷
Shoreline Length (km)	70.5
Water Residence Time (yrs)	0.79
Maximum Length (km)	9.6
Maximum Width (km)	2.5
Mean Depth (m)	1.75
Maximum Depth (m)	20
Percentage of Lake Bed in Depth Zone:	
0 – 3 m	86.7
3 – 6 m	6.3
>6 m	7.0

loosely-bound P (KUO 1996, LIN et al. 1991). Lake sediment P comprises both labile (loosely-bound and biogenic) and refractory (mineral and organic) components. The labile fraction is bioavailable and comprises CaCO₃-P, Fe-P and biogenic P (PENN et al. 1995). The method described by LIN et al. (1991) quantifies loosely-bound P in soils, and has been shown to represent biologically-available P through laboratory comparisons with established methods for available soil P.

Sediment pH was determined using a combination electrode and standard pH meter with a 50%–50% by volume mixture of sediment to deionised water. The percent organic matter (ALLEN 1989) and percent carbonate (RABURNHORST 1988) were determined through loss-on-ignition at 550 °C and 1000 °C, respectively. Percent abundance of total organic carbon (TOC) and total nitrogen (TN) were determined by elemental analysis on a LECO[®] CNS-1000. Following microwave nitric acid digestion in the CEM[®] MDS-2000 microwave, concentrations of calcium (Ca), magnesium (Mg), iron (Fe) and manganese (Mn) were determined by the direct air-acetylene flame method (CLESCERI et al. 1989) using a Perkin Elmer[®] Atomic Absorption Spectrophotometer 3100 with an addition of 0.4% lanthanum to control interferences. Quality control standards, laboratory duplicates and laboratory blanks were analysed with each run of samples for each method. Each quality assurance method was observed to be within acceptable ranges (± 5%) for each analysis.

Phosphorus sorption experiments

The equilibrium absorption of phosphorus onto sediments in a laboratory setting has been observed previously to reflect a Langmuir sorption isotherm (FROELICH 1988, PANT & REDDY 2001, JENSEN & ANDERSEN 1992, HUPFER et al. 2000, HOUSE & DENISON 2000). The phosphorus sorption properties of a bulk surface sediment sample from the North Basin were determined through the Langmuir relationship. Portions of

1 g of wet sediment were suspended in 400 ml artificial lake water at a temperature of 18 °C and a pH of 8.16 (representative of Lough Carra), with seven orthophosphate concentrations ranging from 0 to 930 µg L⁻¹. Soluble reactive phosphorus (SRP) was added as KH₂PO₄, and initial concentrations were verified using the Molybdate Reactive Phosphorus method on a Shimadzu® UV-1601 spectrophotometer (EISENREICH et al. 1975). Artificial lake water was made by adding the following salts to demineralised water: [NH₄] = 0.01 mM, [SO₄] = 0.5 mM and [HCO₃] = 2 mM. Each PO₄ concentration was replicated three times. Samples were shaken for 24 hours and SRP then quantified after filtration through Whatman® 0.45 µm filter papers.

The sorbed P per unit weight of sediment (SP), which is the difference between the initial and final SRP concentrations, and the final concentration of SRP (C_e), the equilibrium concentration, were plotted against each other. The Langmuir Equation was used as the representative sorption isotherm:

$$SP = [SP_{\max} \cdot K \cdot C_e] / [1 + (K \cdot C_e)] \quad (1)$$

where SP_{max} is the theoretical sorption maximum of the sediment (mg g⁻¹) and K is the Langmuir constant or bonding energy of the sediment (L g⁻¹). At low C_e concentrations (< 10 µM), the Langmuir isotherm resembles a linear isotherm permitting the calculation of the sorption parameters using least squares (FROELICH 1988, JENSEN & ANDERSEN 1992). The point at which no desorption or adsorption is taking place (x-intercept) is the equilibrium P concentration (EPCo, mg L⁻¹) and the slope of the relationship represents a linear adsorption coefficient (LAC, L g⁻¹) or buffering intensity. The sediment P concentration at the EPCo represents a native absorbed P (NAP, mg g⁻¹) and can be calculated as (FROELICH 1988):

$$NAP = (EPCo)(LAC) \quad (2)$$

Finally, a linear form of the Langmuir Equation can be used to determine the SP_{max} and K values, such that:

$$C_e/SP = [C_e/SP_{\max} + 1] / (K \cdot SP_{\max}) \quad (3)$$

From the linear plot of C_e/SP vs. C_e, the reciprocal of the slope is SP_{max} and the intercept is 1/(K · SP_{max}).

Results

Surface sediment chemistry

The highest concentrations (*n* = 9, mean ± 95 % C. I.) of surface sediment BAP (0.05 ± 0.01 mg g⁻¹) and TP (0.29 ± 0.06 mg g⁻¹) were found in the North Basin, with the lowest found in the Mid Basin (0.02 ± 0.01 mg g⁻¹ and 0.09 ± 0.04 mg g⁻¹, respectively; *n* = 7). The North Basin sediments also contained the highest concentrations of total iron, total magnesium and total manganese, while those from the South Basin (*n* = 7) had the highest concentrations of total calcium (and % calcium carbonate) of the three basins (Table 2). The molar

Table 2. Characteristics (mean \pm 95% CI) of surface sediments from the North, Mid and South Lough Carra basins. TP = total phosphorus, BAP = Biologically Available Phosphorus, Fe = total iron, Ca = total calcium, Mg = total magnesium, Mn = total manganese, % OM = % organic matter, % OC = % organic carbon, % CaCO₃ = % calcium carbonate, Ca:P = total calcium : total phosphorus molar ratio and Fe:P = total iron : total phosphorus molar ratio. * Significant difference among basins (ANOVA; $p < 0.05$) for profundal sediments. Other sample sites are Carra Bridge (CB); Lough Beg (BEG); Mullingar River (MUL); Cloonee River (CLN) (Fig. 1). Water column TP from DONOHUE (unpublished data; July 2001–July 2002).

	North Basin				Mid Basin			South Basin					
	Lentic		Lotic		Lentic		BEG	Lentic		Inlet (MUL)	CLN	Lotic	
	Profundal (n = 9)	Inlet	CB		Profundal (n = 7)	Profundal (n = 7)		Profundal (n = 7)	Inlet (CLN)				
Surface Sediment Chemistry													
Depth (m)*	11.69 \pm 3.10	–	–	–	4.40 \pm 3.52	7.21 \pm 2.97	–	–	–	–	–	–	–
pH*	7.69 \pm 0.11	7.53	7.80	7.33	7.97 \pm 0.09	7.78 \pm 0.22	7.43	7.46	7.46	7.67	7.46	7.46	7.46
TP (mg g ⁻¹)*	0.29 \pm 0.06	0.10	0.13	0.36	0.09 \pm 0.04	0.18 \pm 0.08	0.25	0.25	0.25	0.37	0.25	0.25	0.25
BAP (mg g ⁻¹)*	0.05 \pm 0.01	0.03	0.01	0.02	0.02 \pm 0.01	0.04 \pm 0.02	0.06	0.02	0.02	0.02	0.02	0.02	0.02
Fe (mg g ⁻¹)*	3.31 \pm 0.80	1.15	4.91	7.32	0.84 \pm 0.45	1.76 \pm 0.57	1.96	6.48	6.48	7.00	6.48	6.48	6.48
Ca (mg g ⁻¹)	264.3 \pm 23.0	260.9	166.3	189.0	257.1 \pm 23.5	292.4 \pm 19.4	256.1	206.6	206.6	148.6	206.6	206.6	206.6
Mg (mg g ⁻¹)	1.93 \pm 0.18	1.70	2.10	3.96	1.68 \pm 0.12	1.57 \pm 0.34	0.79	5.17	5.17	3.55	5.17	5.17	5.17
Mn (mg g ⁻¹)*	0.11 \pm 0.01	0.13	0.14	0.22	0.05 \pm 0.01	0.10 \pm 0.02	0.83	0.16	0.16	0.27	0.16	0.16	0.16
% OM	10.2 \pm 1.2	4.3	2.8	15.9	8.2 \pm 2.1	8.4 \pm 1.8	5.1	4.3	4.3	18.4	4.3	4.3	4.3
% OC	9.3 \pm 0.7	7.5	2.7	9.6	8.7 \pm 1.0	8.7 \pm 0.5	8.8	7.1	7.1	9.6	7.1	7.1	7.1
% CaCO ₃	82.3 \pm 5.4	72.1	42.7	58.9	82.3 \pm 7.9	88.5 \pm 3.0	79.2	56.0	56.0	55.8	56.0	56.0	56.0
Ca:P	857 \pm 387	1970	1020	410	2942 \pm 1205	2150 \pm 1744	800	634	634	311	634	634	634
Fe:P	6.4 \pm 0.7	6.2	21.3	11.4	5.6 \pm 2.0	6.3 \pm 1.7	4.4	14.3	14.3	10.3	14.3	14.3	14.3
C:N	17.5 \pm 1.4	23.1	17.3	20.0	17.4 \pm 2.6	20.3 \pm 3.6	20.1	37.8	37.8	25.6	37.8	37.8	37.8
Water Column Total Phosphorus ($\mu\text{g L}^{-1}$)													
Mean	11.6 \pm 2.2	–	35.3 \pm 12.2	–	9.1 \pm 1.9	10.6 \pm 2.9	–	–	–	2124 \pm 2.9	40.5 \pm 6.2	–	–
Min	6.9	–	11.0	–	4.7	5.0	–	–	–	13.2	17.3	–	–
Max	28.4	–	114.6	–	28.0	37.7	–	–	–	44.9	73.6	–	–

Table 3. Pearson Product-Moment Correlation Coefficients (r) for parametric data ($n=23$). * $p < 0.05$ and ** $p < 0.01$.

	TP	BAP	Fe	Ca	Mg	Mn
TP	0.711**	1.000				
BAP	0.676**	0.899**	1.000			
Fe	0.723**	0.949**	0.837**	1.000		
Ca	-0.118	-0.306	-0.280	-0.231	1.000	
Mg	0.587**	0.557**	0.512*	0.576**	-0.418*	1.000
Mn	0.716**	0.887**	0.815**	0.862**	-0.004	0.528**

Fe:P ratio was greatest in the North Basin (Table 2), but a Kruskal-Wallis test indicated there was no significant difference among basins ($\psi = 2.10$; $p = 0.35$). Molar Ca:P ratios were lowest in the North Basin and highest in the Mid Basin (Table 2), and varied significantly among the three basins ($\psi = 10.94$, $p = 0.004$). The molar C:N ratio for the surface sediments did not, however, vary significantly among basins ($\psi = 1.45$; $p = 0.49$) and ranged from 12 to 26. Nonvascular aquatic plants have low C:N ratios (4–10), whereas vascular land plants, which contain cellulose, have C:N ratios of 20 and greater (MEYERS & ISHIWATARI 1993). Thus C:N ratios of Lough Carra surface sediments are typical of a mixture of both autochthonous and allochthonous material.

There was a strong significant difference in overall sediment chemistry among the three basins (MANOVA; Wilks $\lambda = 0.066$, approx. $F_{20,22} = 2.64$, $p = 0.016$; Table 2). Percentages (% OM, % OC and % CaCO_3) were included in this parametric analysis, as they were normally distributed. LSD post hoc tests indicated that the main interbasin variability occurred between the North and Mid Basins (Table 2). The North and South Basins had, however, significantly different concentrations of sedimentary TP ($p = 0.026$), Fe ($p = 0.004$) and Mg ($p = 0.035$).

Significant correlations for the entire lake (Pearson Product-Moment Correlations; $p < 0.01$ and $n = 23$ in each case) were found between TP and Fe, TP and Mn, BAP and Fe and BAP and Mn (Table 3). All relationships between parametric variables were significant (Table 3), with the exception of those involving Ca. TP and BAP also correlated significantly with % organic matter and inversely with % CaCO_3 , while BAP also showed a highly significant correlation with % organic carbon (Table 4).

Surface sediment chemistry from the fluvial and inlet areas of the Lough Carra catchment (Table 2) showed similar relationships between physico-chemical variables to the lake surface sediment. Higher concentrations of Fe, Mn and %OM prevailed in the tributary sediments yielding higher TP and BAP concentrations than the respective inlet areas, where higher CaCO_3 abundance was present.

Table 4. Spearman Rank Correlation Coefficients (r_s) for non-parametric data ($n=23$). * $p < 0.05$ and ** $p < 0.01$.

	OM	% OC	% CaCO ₃	Ca:P	Fe:P
% OM	1.000				
% OC	0.959**	1.000			
% CaCO ₃	-0.842**	-0.837**	1.000		
Ca:P	-0.645**	-0.558*	0.533*	1.000	
Fe:P	-0.382	-0.374	0.259	0.100	1.000
pH	-0.251	-0.178	0.194	0.697**	0.153
Depth	0.216	0.112	-0.293	-0.754**	0.192
TP	0.642**	0.542*	-0.498*	-0.981**	-0.081
BAP	0.693**	0.622**	-0.582**	-0.880**	-0.125
Fe	0.458*	0.385	-0.398	-0.890**	0.291
Ca	-0.513*	-0.533*	0.622**	0.416	0.353
Mg	0.262	0.229	-0.418	-0.599**	0.119
Mn	0.395	0.273	-0.218	-0.850**	0.157

Geochemical stratigraphy

The sedimentary geochemical profiles from the three Lough Carra basins have very similar total phosphorus trends (Fig. 2). Marked increases in TP in the upper 10 cm was consistent among each core. This trend was perhaps more pronounced in the North and South Basins, which receive the fluvial inputs from the surrounding catchment. Concomitant with the TP trend was a significant positive correlation between the Fe:Mn molar ratios and Fe concentration (North: $r = 0.77$, $p < 0.01$; Mid: $r = 0.87$, $p < 0.001$; South: $r = 0.79$, $p < 0.05$). Also evident is the positive correlation down-core of TP and %OM for all three basins (combined: $r = 0.85$, $p < 0.01$), suggestive of a presence of refractory organic P.

Phosphorus sorption experiments

The bulk sediment sample for the sorption experiments had low geochemical concentrations relative to the characteristics of other sediment samples from the North Basin from where it was collected (with Fe and Mn concentrations of, respectively, 1.16 mg g^{-1} and 0.005 mg g^{-1} , compared with ranges of 1.17 to $5.58 \text{ mg Fe g}^{-1}$ and 0.09 to $0.14 \text{ mg Mn g}^{-1}$ for North Basin surface sediments), and was more representative of sediments from the South and Mid Basins. Results of the laboratory sorption experiments should be viewed as being at the lower end of the range of sorption capacities for the Lough Carra sediments.

The impact of microbial activity and subsequent uptake of P during the experiment was not addressed directly. Possible bacterial impacts include photo-

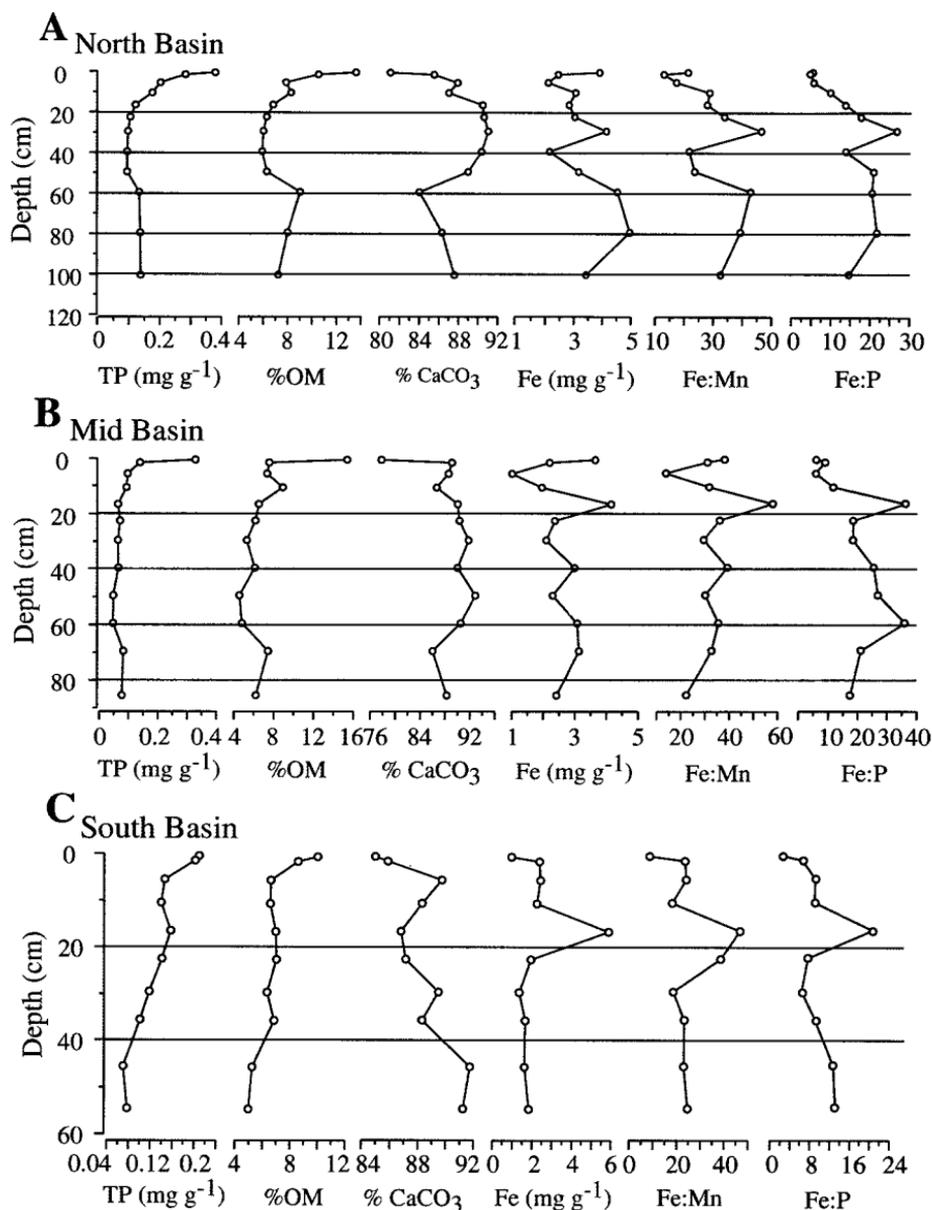


Fig. 2. Sedimentary records from Lough Carra (A) North (Castleburke) Basin, (B) Mid (Castlecarra) Basin and (C) South (Twin Islands) Basin.

synthetic heterotrophs which utilise P during the oxidation of organic matter. Specific P uptake rates of bacteria have not, however, been well studied, preventing us from concluding that the removal of P during the experiments was

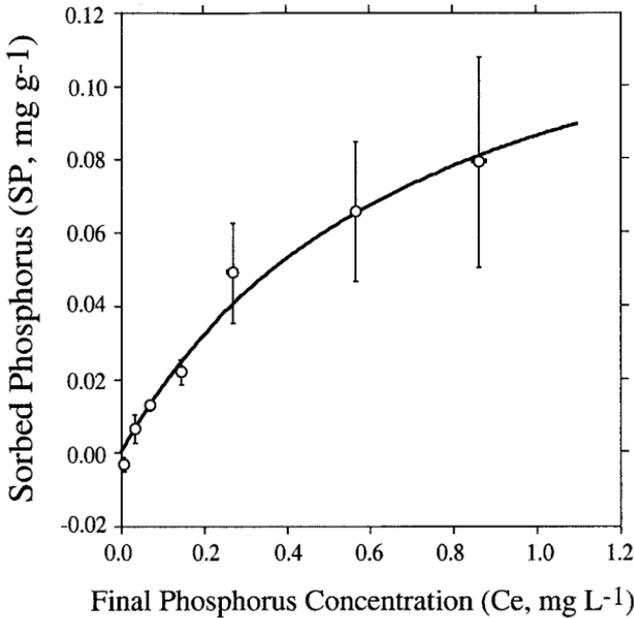


Fig. 3. Experimental P sorption data fitted to a Langmuir sorption isotherm as per Eqn. 1 ($r^2 = 0.98$). Error bars show 95 % CI.

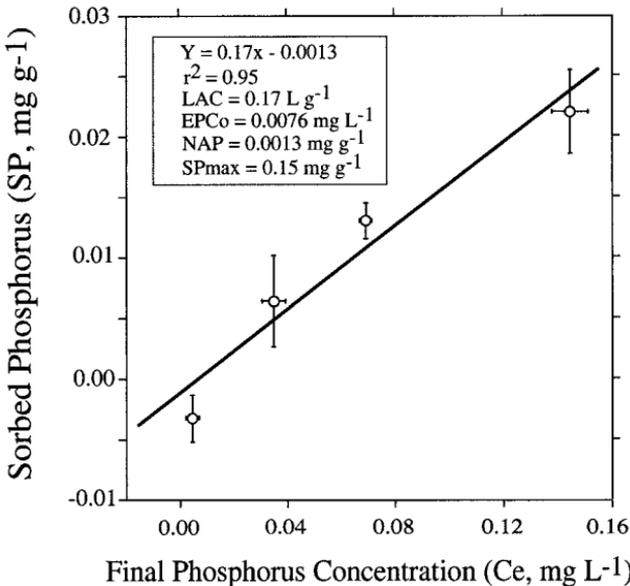


Fig. 4. Linear isotherm fitted to sorption data. P sorption properties gleaned from the linear relationship include: linear adsorption coefficient (LAC), equilibrium phosphorus concentration (EPCo) and native adsorbed phosphorus (NAP; Eqn. 2). SP_{max} (maximum sorbed phosphorus) is taken from a linear form of the Langmuir Isotherm (Eqn. 3). Error bars show 95 % CI.

solely due to physical and chemical adsorption. The artificial nature of the experiment water and low percent organic matter (~ 10 %) in the sediment used in the experiment suggest however that microbial impacts, if any, would have been minimal.

A Langmuir isotherm was fitted to the sorption experiment data (Fig. 3) with a regression $r^2 = 0.98$ ($p < 0.00001$). The lower end experimental P concentrations were used to calculate the equilibrium sorption properties as described by a linear isotherm and least squares regression (Fig. 4). The water column TP concentration where no absorption or desorption takes place (EPCo) was found to be $7.6 \mu\text{g L}^{-1}$. In comparison with bi-weekly water monitoring data from 2001/2002 (Table 2), this concentration was exceeded over 81 % of the time in the North Basin and over 61 % of the time throughout the lake. In particular, TP pulses during winter months (November through mid-January) reached over $28 \mu\text{g L}^{-1}$ in the North and Mid Basins and $38 \mu\text{g L}^{-1}$ in the South Basin. Of note is the maximum sorbed P concentration (SP_{max}), of 0.15 mg P g^{-1} which represents saturation concentration. Surficial sediments from the North Basin, similar to those tested, exhibited a slightly lower TP concentration than the SP_{max} .

Discussion

Basin heterogeneity and the water column

Despite Lough Carra being shallow and polymictic, our results indicate that there are three geochemically distinct basins within the lake system. Molar C : N ratios ranging from 12 to 26 and catchment water monitoring (Table 2) suggest that allochthonous material and inorganic nutrient inputs to both the North and South Basins from the riverine network are important for lake basin sediment heterogeneity. Wind-induced resuspension and redistribution of sediments could also affect basin heterogeneity. It is clear that the North Basin has the highest sedimentary TP concentrations and associated higher Fe and Mn sediment concentrations. The rankings of water column TP concentrations for the respective basins are reflected in the surface sediment (Table 2; North > South > Mid). That the equilibrium phosphorus concentration of sediments was exceeded over 81 % of the time in the North Basin from which the experimental sediments were taken during our 12 month monitoring period suggests that water-column TP concentrations provide excess P for adsorption by sediments for the majority of the year, until the maximum sorbed P concentration of 0.15 mg P g^{-1} is reached. Surface sediments from the fluvial inputs to both basins (North Basin River: $0.36 \text{ mg TP g}^{-1}$; Clooneen River: $0.37 \text{ mg TP g}^{-1}$; Mullingar River: $0.25 \text{ mg TP g}^{-1}$) provide potential for considerable TP pulses during spates (Table 2) irrespective of likely additional mobilisation of P from within the lake

catchment. Mobilisation of P during spate events in rivers has been shown previously to be extremely important in the nutrient balance of the Lough Mask system (DONOHUE et al. 2005), within which Lough Carra is located.

Our results suggest that the labile fraction (BAP) of seston P ranged from 12–24% of the TP, and that Lough Carra sediments are relatively Fe-deprived (Table 2). Redox-sensitive P release from the largely oxic Lough Carra sediments is expected to be low (SØNDERGAARD et al. 2003) and, therefore, phosphorus release is most likely during wind resuspension. The large pool of refractory P and the significant positive correlation between TP and %OM suggests the majority of in-lake TP is lost to a sediment archive.

As noted in other studies from calcareous lakes (GONSIORCZYK et al. 2001, GOLTERMAN 1988, HUPFER et al. 2000), CaCO_3 in Lough Carra appears to have little impact on the retention of P in the surface sediments. This is not to say carbonates are not important for co-precipitation and for loosely binding P during calcite formation in Lough Carra (OTSUKI & WETZEL 1972), but rather that Fe and Mn hydroxides and phosphate precipitates (such as vivianite, $\text{Fe}_3(\text{PO}_4)_2$) appear to be responsible for the majority of post-depositional P retention, even though these are likely to be comparatively modest owing to the overall low concentrations of Fe and Mn in surface sediments (ANDERSON et al. 1993, SØNDERGAARD et al. 1996).

Historical phosphorus loading

The known diagenetic effects of microbial activity and redox conditions have led many investigators to approach sedimentary TP profiles with caution (ENGSTROM & WRIGHT 1984). Indeed, some studies have shown a mobilization of phosphorus through diffusion from the deeper, reduced zones of sediment to the upper oxidized layers (ISTVÁNOVICS 1988, CARIGNAN & FLETT 1981). In Lough Carra, however, strong and statistically significant agreement among three independent proxies of TP (diatom-inferred epilimnetic TP, modelled TP loads based on historical census data and sediment TP concentrations; DONOHUE et al., unpubl.) suggests strongly that evidence of nutrient enrichment are not confused by an upward migration of phosphorus in the sediment profile. Further, it has been suggested that an inverse correlation between Fe:Mn and [Fe] minima reflects a redox influence (MACKERETH 1966). Concentrations of iron should be lowest in strongly reducing environments, while Mn should be even lower, owing to a greater mobility (ENGSTROM & WRIGHT 1984). The significant positive correlation between Fe:Mn and [Fe] in Lough Carra is suggestive of changes in source material rather than changes in redox states within the lake sediments.

Phosphorous sink capacity and stable state equilibria

Laboratory experiments have suggested that surface sediments exhibit sorption properties which can be explained by Langmuir Isotherms (JENSEN & ANDERSEN 1992). As such, there is a theoretical capacity of the oxic sediments to bind and retain P in a sedimentary archive. Should this capacity be exceeded, then the ability of the sediments to act as a sink for P has essentially been negated. The theoretical maximum sorption concentration of 0.15 mg P g^{-1} calculated from sorption experiments is only slightly above TP concentrations of geochemically similar surface sediments ($\sim 0.10 \text{ mg P g}^{-1}$). The experiments suggest, therefore, that sediments in the North Basin of the lake (the most P enriched) are nearing saturation.

JENSEN et al. (1992) suggested that the ability of aerobic sediments to retain PO_4 is reduced significantly for an Fe:P molar ratio below 15. This is owing to a reduction in the ability of the sediments to bind P from the water column as the free sorption sites approach capacity (MORTIMER 1941, JENSEN et al. 1992). The range of surface sediment Fe:P across all three basins was 5.6 to 6.4, suggestive of considerably limited capacity for the sediments to retain excess P influxes to the lake. Once maximum sorption concentration is exceeded and Fe:P ratios approach zero, the retention of P would be minimal. Sediment core data shows that, historically, all three basins had Fe:P ratios of approximately 15 or greater (Fig. 2). The trend of decreasing Fe:P up the sediment profile highlights a decrease in the capacity of the sediment to bind P and reduced ecological resistance to eutrophication.

The theory of alternate stable state equilibria in lakes has been used to describe abrupt shifts in water quality and aquatic vegetation (IRVINE et al. 1989, SCHEFFER et al. 1993, 2001). Shallow lakes can have two alternate equilibria: a clear water macrophyte dominated system and a turbid, algal dominated system. In a situation where the sediments can no longer aid the maintenance of a macrophyte-dominated clear water state, by buffering the increased P loading, the additional P remains biologically available. A loss in resistance of the aquatic system increases the potential for a rapid shift to an alternate turbid state (SCHEFFER et al. 2001).

Given the pressures within the catchment and the increased agricultural intensification and development of rural housing, the prognosis for the ecological quality of the lake is not good, unless effective measures are introduced to reduce those pressures. Although the site is of immense conservation importance and has statutory protection under a number of European Union environmental directives, adequate protection is unlikely to be afforded unless there is acceptance by both the local government authority and among catchment users and stakeholders that current activities are degrading the site. If nutrient inputs into the lake continue to increase there will be both short-term and long-term

damage. If the pressures are sufficient to effect a switch to an alternate stable state, with a dominance of phytoplankton and loss of submerged plants, restorative measures are likely to be both expensive and uncertain. For Lough Carra, prevention is certainly a better, and still feasible, option.

Conclusions

Examination of the geochemical composition of surface sediments from the calcareous Lough Carra clearly shows three distinct basins. Those basins which receive fluvial inputs from the surrounding catchment reflect enriched concentrations of phosphorus in the water column and sediments. The chemical stratigraphy of sediment records from each basin has faithfully archived the increasing P load over time. Early warning signals of shifts in alternate stable states are difficult to obtain (SCHEFFER et al. 2001). The reduced capacity of the lake sediments to absorb P should be interpreted as one such 'warning signal'. Indeed, monitoring evidence (MCGARRIGLE et al. 2002) suggests that Lough Carra has already exhibited signs of nutrient enrichment. There is little doubt that this protected system will be irrevocably altered, should the trophic status continue to be impacted by diffuse nutrient pollution.

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