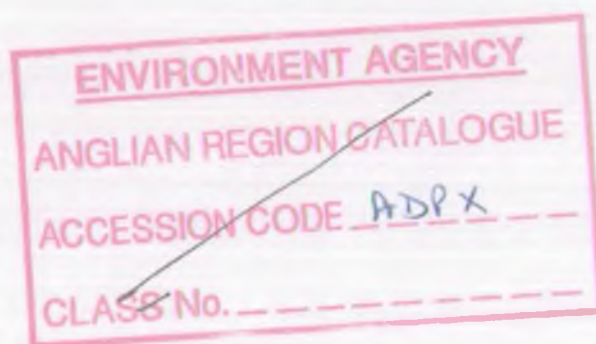


The extent of phosphorus release in the Norfolk Broads

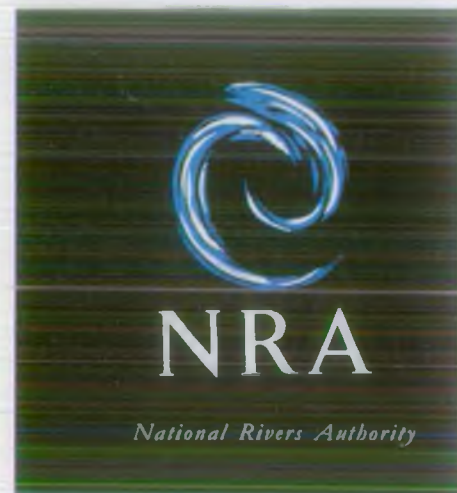
Report for 1991



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Anglian Regional Operational Investigation 518

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1. INTRODUCTION

During 1991, additional laboratory experiments and analysis of interstitial phosphorus, ferrous iron and sulphide concentrations were carried out on sediment cores from various broads to further investigate the extent of sediment phosphorus release and, if possible, to determine the factors affecting it. In particular, sediment from Cockshoot, Cromes and Ranworth Broads was studied with the aim of finding a sediment which might be suitable for large scale ferric dosing.

In order to obtain some idea of the potential for release in different sediments, analysis of total phosphorus, iron and sulphide content of sediments throughout the Broads was continued, together with analysis of the phosphorus fractions in the sediment.

As reported previously (Jackson, 1991), a number of tanks of Hoveton Little Broad sediment were dosed with ferric chloride in 1990. Cores were taken from the iron-dosed and control sediment tanks to analyse the ferrous iron and total iron content one year after dosing and to study any possible deleterious effects on the benthic invertebrates.

2. METHODS

2.1 Sampling strategy

From April to September 1991, sediment cores were taken from Ranworth Broad at approximately monthly intervals. Sediment cores were also taken from Cockshoot Broad for the first four months of this period and from Cromes Broad for the first two months. On each occasion, the variation with sediment depth in the concentration of soluble phosphorus, sulphide and ferrous iron in the interstitial water, pH and redox potential were determined for sediment cores from each site. From May onwards, incubation experiments were carried out on three replicate sediment cores from each of the sites to determine whether the sediment was releasing phosphorus. At the end of each incubation experiment the sediment cores were sieved and the chironomid larvae and tubificid worms sorted from the sediment, preserved in industrial methylated spirits and counted at a later date.

In order to investigate the spatial variability in the composition of the pore water, ten sediment cores were taken from within a 20 m² area of Ranworth Broad in September 1991. The variation in the interstitial ferrous iron content with depth in each of the cores was determined. Ferrous iron concentration was analysed because it was deemed to be the most variable component; it was not possible to measure soluble phosphorus and sulphide as well as ferrous iron in this number of cores.

The variation in pore water content across the length of Ranworth Broad was also studied, by taking cores from a series of points. The interstitial ferrous iron content in each of the cores was determined and, in addition, the soluble phosphorus concentration was measured in one core from the eastern end of the broad and one core from just west of the centre of the broad.

Sediment cores were sampled from Alderfen Broad, Burnt Fen and Woodbastwick Dyke for interstitial analysis, to obtain an indication of the sediment type at these sites.

Sediment cores were also taken from each of the high iron-dosed and control sediment tanks, to determine the distribution of ferrous iron a year after iron dosing and to measure the total iron and phosphorus content. In order to investigate whether iron-dosing had affected the benthic invertebrates in the sediment tanks, five sediment cores were taken from each of the iron-dosed and control tanks, sieved and the invertebrates sorted and counted.

Duplicate cores, for total sediment analysis, were taken from Ranworth Broad. In these cores the variation with depth of total phosphorus, iron and acid-volatile sulphide was determined for the top 12 cm of sediment, together with the sediment phosphorus fractions.

2.2 Sampling technique

As the Broads are less than 2 m deep, it was possible to collect undisturbed sediment cores using a simple corer consisting of a wooden pole (2.5 m long) to which a perspex tube, 50 cm long and 6.9 cm internal diameter, was attached. The perspex tubes were pre-drilled with 3-mm diameter holes (after Davison *et al* 1982) in a spiral pattern at 1 cm intervals along the length of each tube. Before collecting sediment cores, the holes were sealed with transparent waterproof tape. The tubes were clipped into the corer and pushed into the sediment to the required depth, the top of the tube was sealed with the plunger and brought to the surface where the base of the tube was sealed with a rubber bung. The plunger was then removed from the top of the tube and replaced with another bung. The sediment core was then unclipped from the corer and transported to the laboratory in a cool box, protected from the light by black polythene.

Samples of benthic algae were collected using a similar device to that described above but with a much smaller perspex sample tube (1.6 cm internal diameter and 20 cm long). A mini sediment core was sampled in a similar manner to that for the large corer and brought to the surface. The overlying water was removed by extruding the sediment using a polypropylene rod inserted into the base of the sample tube, until the sediment surface was level with the top of the sample tube. The top 1 cm of sediment was then extruded into a screw-capped sample container, washing the sample in with ultrapure water.

2.3 Analysis of the overlying water

Samples for soluble phosphorus analysis were collected in 10-ml plastic syringes and filtered on site into sample tubes through 0.45- μ m membrane filters held in Swinnex filter units. Soluble phosphorus was analysed using the molybdenum blue method (Murphy and Riley, 1962), as modified by Stephens (1963).

Total phosphorus was analysed using the sulphuric acid/nitric acid digestion method (Standing Committee of Analysts, 1981).

Chlorophyll *a* was determined by extraction in 90% acetone using the method in Golterman and Clymo (1969).

2.4 Analysis of benthic algal chlorophyll

The sample of surface sediment was diluted to 50 ml with ultrapure water. A 10 ml aliquot was removed with a syringe and filtered through a Swinnex filter unit containing

a 25-mm diameter Whatman GF/C filter. Chlorophyll was extracted from the filtered sediment by grinding the filter in 90% acetone, after the method of Parsons and Strickland (1963), and determined using the spectrophotometric equations of Lorenzen (1967). The chlorophyll and phaeophytin concentration per unit area of sediment was then calculated.

2.5 Analysis of pore water

Following the method of Davison *et al* (1982), samples of sediment were removed from the core through the sample holes using 60-ml disposable syringes with 12 gauge stainless steel needles. To avoid oxidation and changes in ferrous iron, the syringe and needle were purged with nitrogen prior to use. Pore water was extracted from the sediment by filtering it directly from the syringe through 0.45- μ m membrane filters (Millipore Corp., type HV) with Whatman GF/D pre-filters held in Swinnex filter units; these also being flushed with nitrogen. For soluble phosphorus, ferrous iron and sulphide analysis: pore water samples were filtered directly into nitrogen-purged reagents via a 50-mm, 19 gauge needle held below the surface of the reagent. Sample volume was measured by carrying out this procedure on a balance.

Ferrous iron was analysed using the simplified bathophenanthroline method of Nürnberg (1984) with, however, 0.5 mM bathophenanthroline as opposed to 5 mM, which was found to be too concentrated to completely dissolve.

Soluble reactive phosphorus was measured, as for the overlying water, using the molybdenum blue method of Murphy and Riley (1962), as modified by Stephens (1963), and adapted for use with small sample volumes. Where ferrous iron was absent in the pore water, it was assumed that this was due to the presence of hydrogen sulphide and the filtered pore water was therefore bubbled with nitrogen, prior to the addition of the reagent, to drive off the hydrogen sulphide as hydrogen sulphide interferes with the molybdenum blue method of phosphorus analysis (Nürnberg, 1984).

Soluble sulphide was determined using an adaptation of the colorimetric procedure of Davison and Lishman (1983). The original method was devised for the measurement of acid-volatile sulphide released from sediment by the addition of hydrochloric acid. This was adapted for the analysis of soluble sulphide in pore water. Pore water (0.5-1.0 ml) was filtered directly into 10 ml of nitrogen-purged zinc acetate in a stoppered sample tube. The amount added being determined by weight. Immediately after addition of the sample, 0.25 ml of 50% hydrochloric acid and 0.25 ml of NN-diethyl-p-phenylene-diamine sulphate reagent were added and the tube stoppered. After 2 minutes, 0.25 ml of ammonium sulphate reagent was added and the tube re-stoppered. The colour was allowed to develop for 15 minutes and then the sulphide concentration was determined colorimetrically as ethylene blue.

2.6 Eh and pH measurement

An additional core was collected from each site to determine the pH and redox potential of the sediment. The redox profile of the top 10 cm of each sediment core was measured using an array of platinum electrodes after Mortimer (1941) and a calomel reference electrode. pH was measured directly in the sediment using a specially designed long penetration combination pH electrode (Russell pH Ltd.). The Redox potential (E) was corrected for the potential of the reference electrode, which = 250.8 mV at 20°C, giving a value of Eh ($Eh = E - 250.8$ mV). Eh was converted to Eh₇ using the equation $Eh_7 = Eh - 58.1 \times (\text{Sample pH} - \text{pH}_7)$.

2.7 Analysis of total sediment phosphorus and iron

Total phosphorus was analysed using an adaptation of the ignition method of Andersen (1976) and total iron determined using an adaptation of the spectrophotometric method of Davison and Rigg (1976). To avoid using the potentially hazardous perchloric acid digestion method, sediment organic matter was destructured by ignition. The residue was then boiled in 10 ml of 1 M hydrochloric acid on a hot plate for 15 minutes to convert all the inorganic phosphorus to ortho-phosphate (Andersen, 1976). In order to measure total iron on the same sample: the acid extracts were then gently evaporated to dryness, allowed to cool, then the residue dissolved in 20 ml of 5.93 M hydrochloric acid and transferred to a centrifuge tube (Davison and Rigg, 1976). The colour development is stable for at least 48 hours and maximum extraction into the acid was found after 36 hours, which was when the absorbance was read, after first centrifuging the extract solutions. Owing to the high iron content of the sediments, most of the extracts required 25-50 fold dilution with 5.93 M hydrochloric acid. Analysis of the extracted total phosphorus was based on the molybdenum blue method (Murphy and Riley, 1962), using the optimised mixed reagent concentration of John (1970): an aliquot of the extract was removed, diluted with ultrapure water to give a final dilution of 25 fold, and the reagent added. To avoid having to neutralise the solution, the acid content of the soluble phosphorus reagent was adjusted to account for the acid content of the extract, giving a concentration of 0.45 N acid in the final solution, which was shown to be the optimum acidity for the reaction (John, 1970).

2.8 Analysis of acid-volatile sulphide in sediment

Acid volatile sulphides are those present as iron sulphides which produce the black colour in anoxic sediment. Following the method of Davison and Lishman (1983), the sulphide was liberated from the sediment, in a sealed system of syringes, by the addition of hydrochloric acid, reacted with zinc acetate to give zinc sulphide, which, after the addition of reagents, was detected spectrophotometrically as ethylene blue.

2.9 Analysis of sediment phosphorus fractions

Certain phosphorus fractions in the sediment are more likely to be available for phosphorus release, particularly the iron-bound phosphorus fraction (Williams *et al.*, 1971); whereas, phosphorus bound as apatite is unlikely to be available for release. This method (Nürnberg, 1988) sequentially fractionates the sediment phosphorus into: bicarbonate-dithionite extractable phosphorus, ie the mainly iron-bound phosphorus component; sodium hydroxide extractable phosphorus, ie phosphorus bound to aluminium and metals in humic acids; and hydrochloric acid extractable phosphorus, ie that bound as apatite. The sum of the phosphorus concentrations from the three sequential extractions is equal to the total inorganic phosphorus concentration. The method followed was that of Nürnberg (1988) with the exceptions that subsequent to each extraction the residue was washed with 1 M sodium chloride (Williams *et al.*, 1976) not the extract solution and also the extract solutions were not membrane filtered after centrifugation.

2.10 Laboratory experiments

Sediment cores were incubated in a culture cabinet at the ambient temperature of the broad surface sediment with continuous light of $60 \mu\text{E m}^{-2} \text{s}^{-1}$. The cores were placed in a flow-through system using filtered water collected from Ormesby Broad during the first half of the year and chemically defined water in the latter half of the year, when the broad water became too turbid with phytoplankton. Water was pumped into the cores 1 cm above the sediment surface at the rate of 120 ml hr^{-1} . The overflow in each core

was set 8 cm above the sediment giving a volume of 300 ml and an exchange time of 2.5 hours. Water was not recirculated around the system to avoid a gradual build up of phosphorus thus maintaining the greatest concentration gradient between the sediment and the overlying water. This continual removal of phosphorus-rich water from above the sediment was intended to mimic the effect of algal uptake of phosphorus in the broad and allow an estimation of the maximum rate of release. Cores were normally incubated for approximately 100 hours. Samples were taken at frequent intervals from the overflow of each core and the soluble reactive phosphorus concentration determined using the molybdenum blue method of Murphy and Riley (1962) as modified by Stephens (1963). Phosphorus concentration in the inflowing water was also monitored. From these measurements, the rate of phosphorus release from the sediment was calculated.

2.11 Production of chemically defined water for incubation experiments

Data was obtained from the Harmonised Monitoring Scheme on the composition of the major chemical ions in the River Bure at Horstead Mill in January 1991. A chemically defined medium was developed which resembled the River Bure water as closely as possible (Table 2.11.1).

Table 2.11.1 Comparison of the major ion concentration in the River Bure at Horstead Mill with the Artificial Water.

	River Bure (mM)	Artificial Water (mM)
Carbonate Alkalinity	1.998	0.881
Chloride	1.904	1.904
Silicate	0.173	0.173
Sulphate	1.478	1.577
Sodium	1.227	1.227
Potassium	0.099	0.099
Magnesium	0.354	0.354
Calcium	3.927	2.077
Manganese	0.001	
Iron	0.004	
Phosphorus	0.004	
Ammonia	0.006	

Phosphate, nitrate, ammonia, iron and manganese were omitted from the artificial water, since these ions could interfere with sediment phosphorus release. The appropriate quantities of analar-grade chemicals were dissolved in ultrapure water for use in the incubation Experiments

3. 1989 RESULTS

Sediment cores were taken from a number of sites in the Broads during 1991 and the variation with depth of interstitial phosphorus, ferrous iron and sulphide concentration determined. The average interstitial concentrations of these determinands (Table 3.1) show the extent of the variability between and within sites.

Table 3.1 Average concentration of interstitial soluble phosphorus, ferrous iron and sulphide (averaged over the top 12 cm of sediment); average ratio of ferrous iron to soluble phosphorus (by weight); and average sediment phosphorus release rate (mean of 3 cores) for sediment from a number of sites throughout Broadland, sampled during 1991.

Site	Date	Average SRP (mg/l)	Concentration Fe ²⁺ (mg/l)	S ²⁻ (mg/l)	Fe:P	Release Rate (mg/m ² /d)
Alderfen (1) (middle)	25/7/91	2.288	0.000	0.910		ND
Alderfen (2) (Near Outflow)	25/7/91	2.156	0.000	0.708		ND
Alderfen (3) (Near Inflow)	25/7/91	3.166	0.000	5.295		ND
Burnt Fen	25/7/91	0.567	2.463	0.000	4.36	ND
Cockshoot	15/4/91	0.050	0.087	0.000	2.13	0.0 ± 0.2
	13/5/91	0.488	0.000	0.681		1.4 ± 1.2
	17/6/91	0.333	0.111	0.109	1.77	0.0 ± 0.2
	29/7/91	0.777	0.000	0.428		6.0 ± 8.9
Cromes	15/4/91	0.160	0.054	ND	17.25	0.1 ± 0.01
	15/5/91	0.079	0.143	0.736	20.57	0.7 ± 0.3
Ranworth	15/4/91	2.564	0.330	ND	5.91	0.4 ± 0.2
	13/5/91	0.821	0.253	0.405	0.84	4.1 ± 3.0
	17/6/91	1.230	0.104	1.075	0.22	9.2 ± 3.0
	1/7/91	0.546	0.332	0.094	3.38	35.6 ± 16.0
	29/7/91	0.910	0.035	0.328	1.97	37.4 ± 15.4
	13/8/91	0.474	0.713	0.455	3.70	8.4 ± 6.0
	19/8/91	1.046	0.674	1.705	1.56	18.5 ± 31.2
	9/9/91	1.660	2.125	0.528	1.93	16.9 ± 19.1
Woodbastwick Dyke	6/8/91	0.530	0.000	18.707		ND
	6/8/91	0.201	0.000	10.332		ND

ND Not determined

3.1 Ranworth Broad

3.1.1 Sediment variability within the sampling area

A number of sediment cores (ten) were taken from a 20 m² area near the eastern end of Ranworth Broad (Sample point 2 on Figure 3.1.1.1) on 11 September 1991. The interstitial ferrous iron content of eight of these cores (cores 1 to 8) was analysed within 6 hours of sampling and the ferrous iron content of the remaining 2 cores (cores 9 and 10) was measured 24 hours later. In each core, pore water was sampled at 1-cm intervals in the top 6 cm of sediment and at 2-cm intervals for the next 6 cm of sediment.

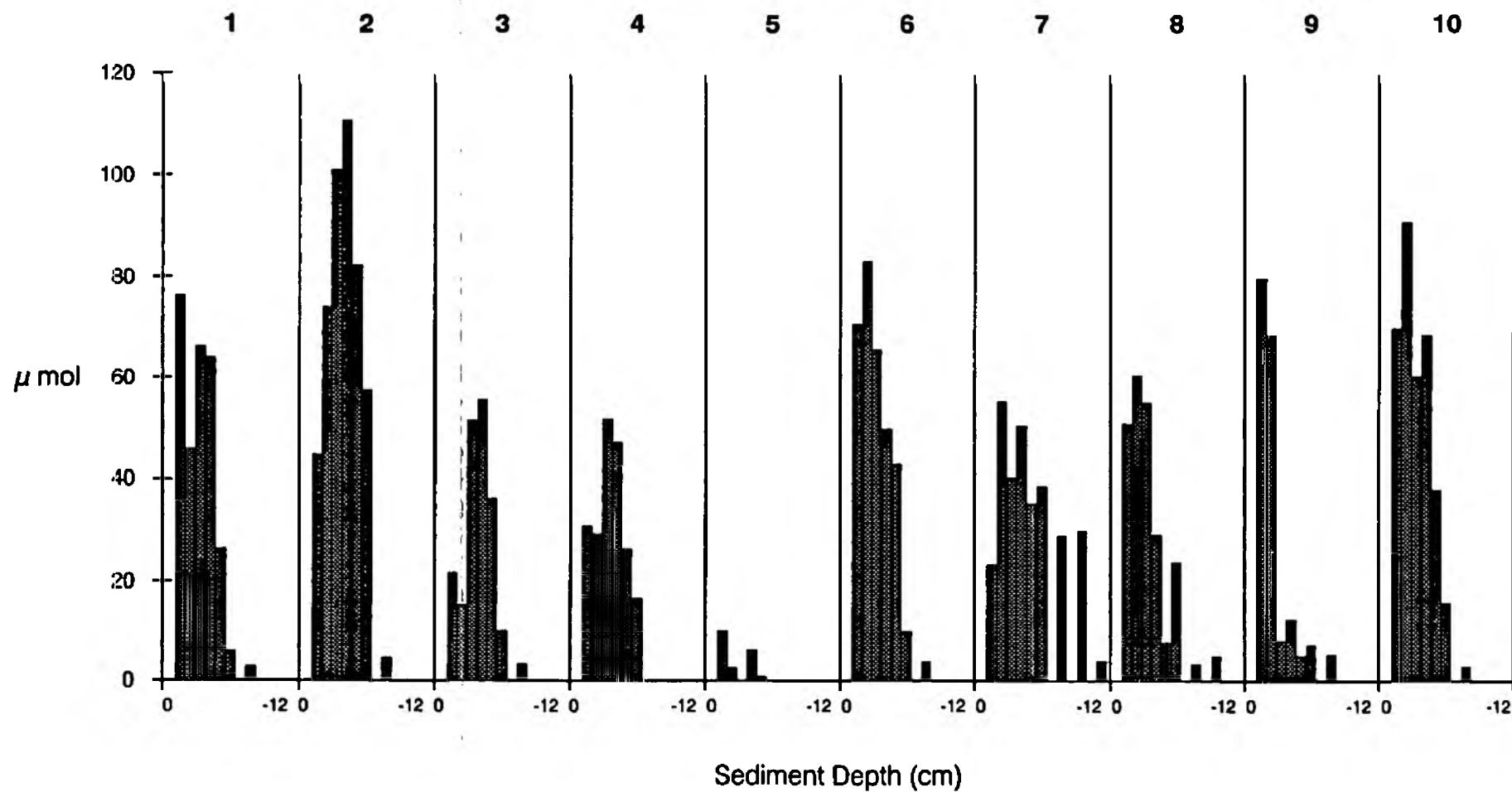


Figure 3.1.1.2 Ranworth Broad 11/9/91 - Variation in interstitial soluble phosphorus with depth between 10 cores taken from within a 20 m² area of the Broad.

Profiles of interstitial ferrous iron concentration in each of the ten cores are shown in Figure 3.1.1.2. With the exception of core 5, there was very little difference in the ferrous iron content of the cores. There was also no apparent difference between those cores analysed within 6 hours (cores 1 to 8) and those analysed 24 hours later (cores 9 and 10). The very low interstitial ferrous iron concentration in core 5 may be a result of patchiness in the chemical composition of the sediment and it is possible that this core was taken from a different "patch" to the other nine cores.

3.1.2 Sediment variability along a transect of Ranworth Broad

On 18 September 1991, sediment cores were taken from eight points between the Conservation Centre at the eastern end of the broad and the western end (Figure 3.1.1.1). The cores were all analysed within 6 hours of sampling. In each core, pore water was sampled at 1-cm intervals in the top 6 cm of sediment and at 2-cm intervals for the next 6 cm of sediment. The ferrous iron concentration of the pore water samples was determined for each of the cores (Figure 3.1.2.1).

High ferrous iron concentrations were measured in the sediment cores from sample points 1 and 2, whereas very little ferrous iron was detected in the cores from the rest of the broad. The eastern end of Ranworth Broad is connected to the River Bure and hence the high ferrous iron content of the sediment in this part of the broad is probably due to deposition of river-born sediment which presumably is relatively high in iron. Analysis of sediment from the lower part of the River Bure for total iron and phosphorus etc will be carried out at some stage.

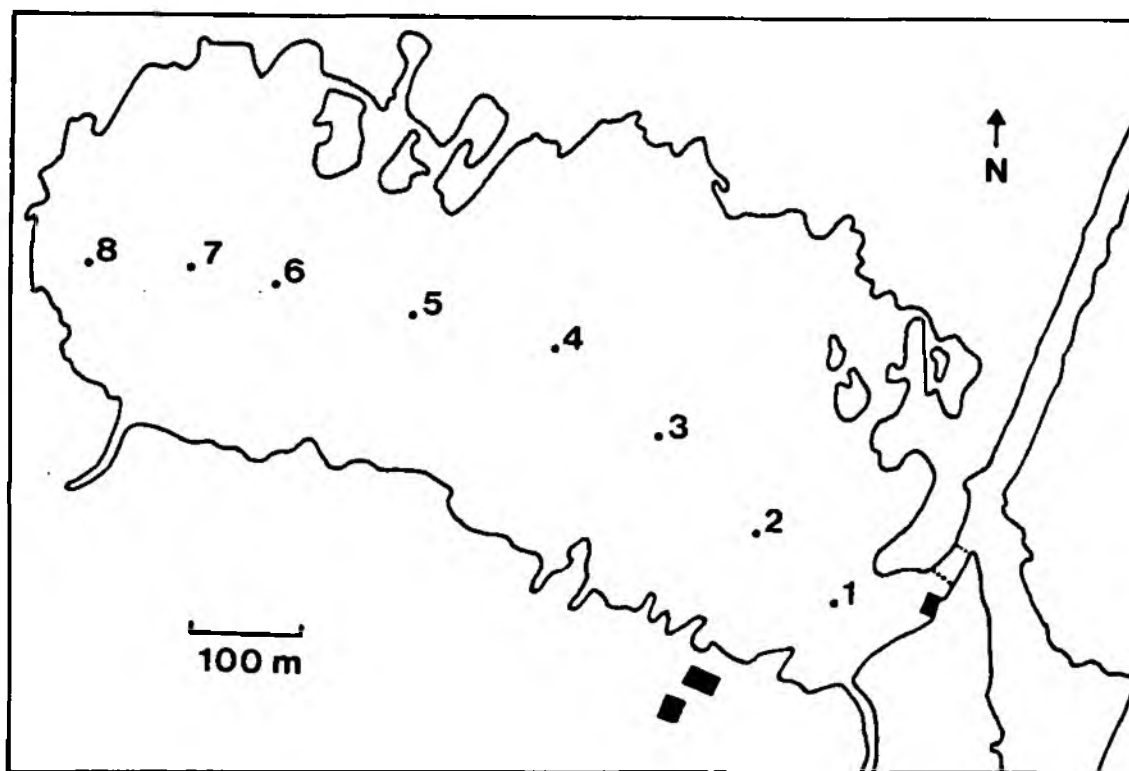


Figure 3.1.1.1 Sample sites in Ranworth Broad

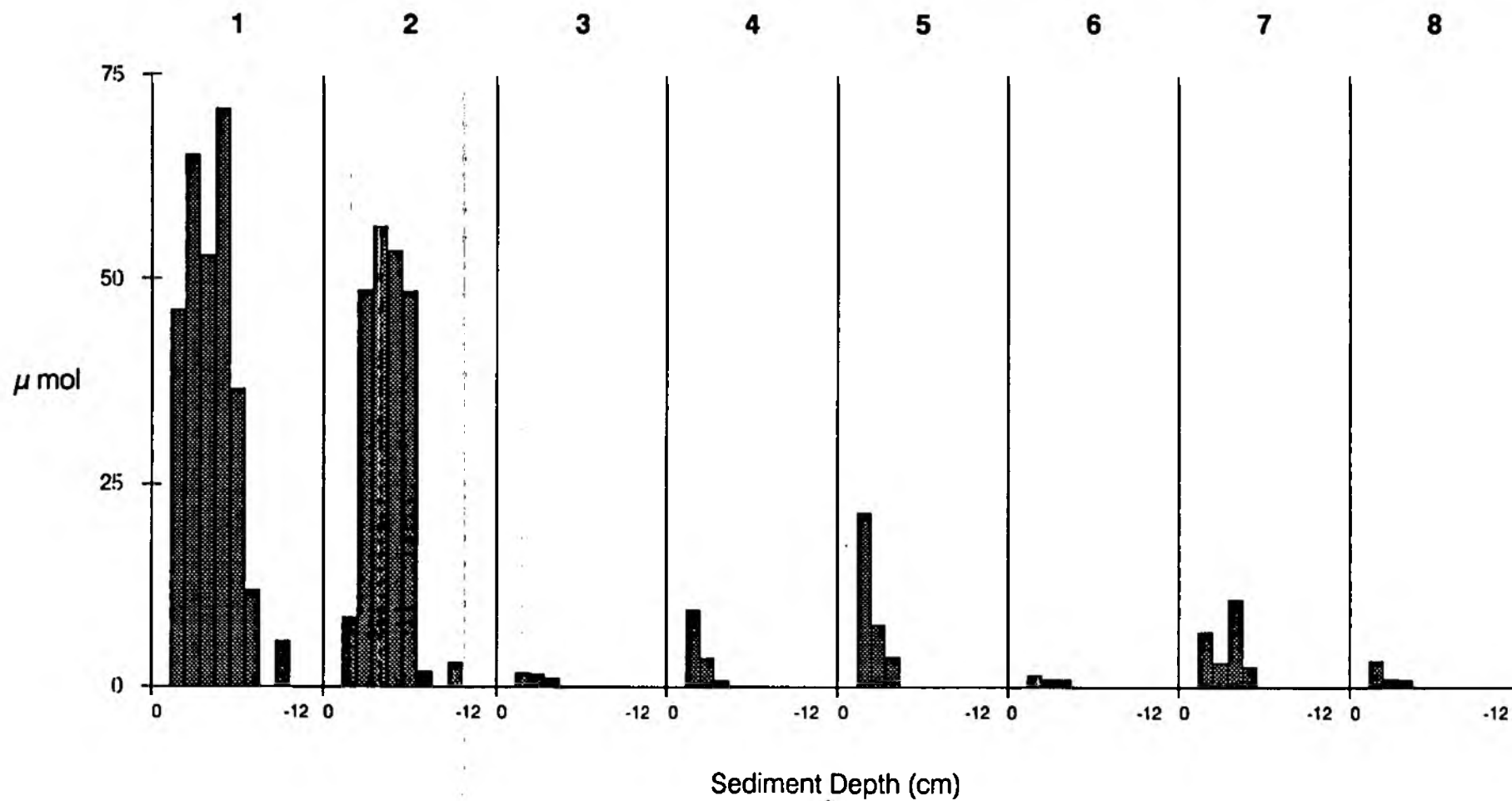


Figure 3.1.2.1 Ranworth Broad 18/9/91 - Variation in interstitial soluble phosphorus with depth on a transect across the Broad.

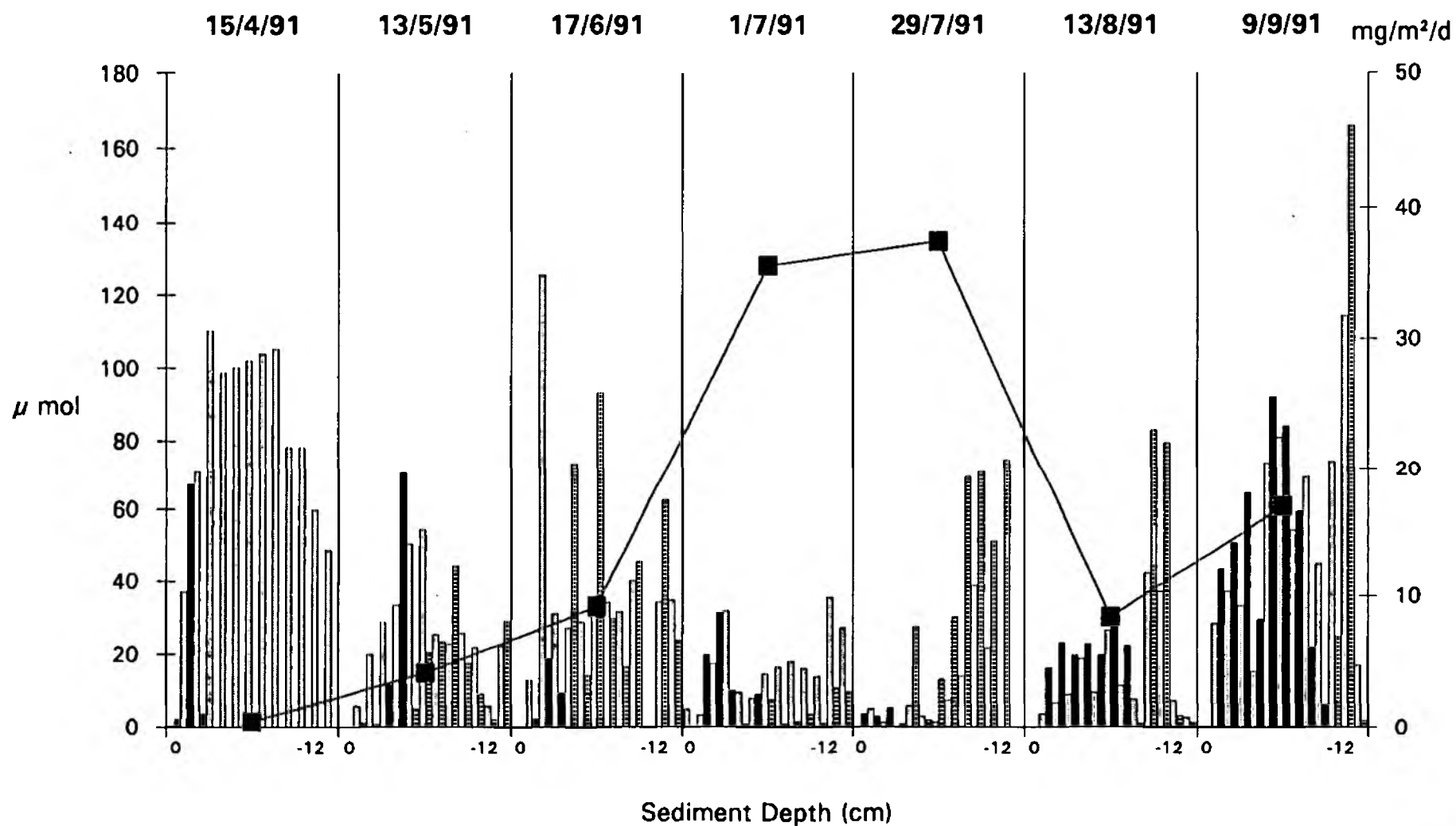


Figure 3.1.3.1 Ranworth Broad 1991 - Variation in interstitial soluble phosphorus (⊞), ferrous iron (■) and soluble sulphide (≡) concentration with sediment depth compared with the experimentally determined rate of phosphorus release (-■-).

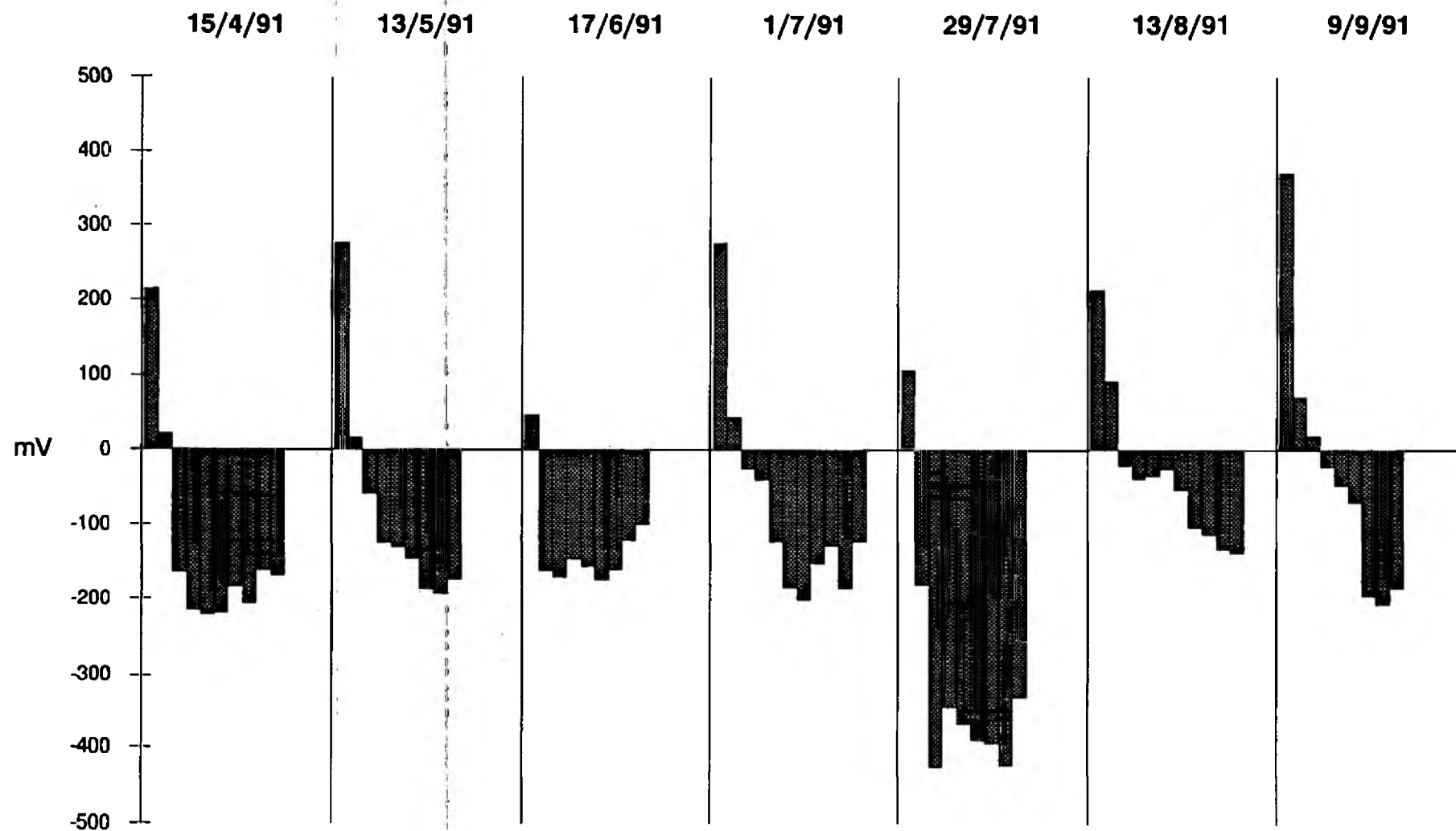


Figure 3.1.3.2 Ranworth Broad 1991 - Variation in redox potential with depth

3.1.3 Temporal variation in the pore water composition of Ranworth Broad sediment

Sediment cores were sampled from sample point 2 at approximately monthly intervals between April and September. In April, when the phosphorus concentration was very high, no phosphorus release was detected. The greatest sediment phosphorus release rate was measured in July (Figure 3.1.3.1), when the interstitial soluble phosphorus concentration was very low. On 1 July, the total soluble phosphorus concentration in the top 10 cm of a sediment core was 0.157 mg and the average amount of phosphorus released during a 90 hour experiment with sediment cores sampled on this date was 0.499 ± 0.255 mg. Similarly, on 29 July, the soluble phosphorus content of the top 10 cm was 0.237 mg and the average amount of phosphorus released during a 94 hour experiment was 0.551 ± 0.228 mg. This indicates that during a period of phosphorus release, soluble phosphorus is lost from the sediment almost as quickly as it is remobilised from the solid phase into the soluble phase within the sediment, resulting in a relatively low phosphorus concentration in the pore water. Conversely, during April no phosphorus was released from the sediment, allowing remobilised soluble phosphorus to build up in the sediment, resulting in a relatively high interstitial phosphorus concentration.

The lack of significant sediment phosphorus release in April and May may be attributed to a combination of high ferrous iron concentration in the top 1 cm of sediment, giving a high Fe:P ratio (Table 3.1), and the very low numbers of *Chironomus* sp. in the sediment (Table 3.2). Significant phosphorus release was detected during June through to September even when high ferrous iron concentrations were measured in the sediment (Figure 3.1.3.1). During this period, relatively high densities of *Chironomus* sp. were present in the sediment (Table 3.2). These large chironomid larvae can burrow 10-15 cm into the sediment and, as a result of their ventilating action, are able to transport phosphorus-rich pore water from beneath the zone containing ferrous iron; which would otherwise precipitate out the phosphorus at the sediment surface.

The very low concentration of ferrous iron in the sediment on 29 July was also associated with an extremely negative redox potential throughout the sediment (Figure 3.1.3.2), indicating very reducing conditions. This may be a result of increased microbial degradation of organic matter as relatively high sulphide concentrations were also measured on this occasion. In August and September, high concentrations of ferrous iron were found to a depth of at least 7 cm (Figure 3.1.3.1) and were associated with relatively high redox potentials (Figure 3.1.3.2), indicating relatively oxidised conditions.

Table 3.1.3.1 Chlorophyll a and phaeophytin concentration per unit area of the surface of Ranworth Broad sediment during 1991.

Date	Chlorophyll a ($\mu\text{g}/\text{cm}^2$)	Phaeophytin ($\mu\text{g}/\text{cm}^2$)
15/4/91	45	75
13/5/91	17	53
17/6/91	19	39
1/7/91	16	38
29/7/91	ND	
13/8/91	ND	
9/9/91	19	41

The chlorophyll *a* concentration in the surface sediment in April was significantly greater than in the following months (Table 3.1.3.1). A large amount of filamentous blue green algae was observed on the sediment surface on this occasion and the chlorophyll *a* concentration in the overlying water was $111 \mu\text{g l}^{-1}$, as determined during the routine monitoring of the River Bure. By 20 May, the chlorophyll *a* concentration in the Broad water was $225 \mu\text{g l}^{-1}$ and remained at about this level through until September. The water was obviously clear enough early in the year to allow the blue green algae to flourish on the sediment surface; whereas, from May onwards, the algae in the overlying water did not allow sufficient light through to the sediment for the blue greens. The blue green algal layer on the sediment surface during April may be another factor in preventing sediment phosphorus release at this time.

3.1.4 Composition of Ranworth Broad sediment

Duplicate cores were taken from Site 2 in Ranworth Broad (Figure 3.1.1.1) and the total phosphorus, iron and sulphide composition analysed and expressed as concentration per unit weight of dry sediment and compared with values obtained previously (Jackson, 1991) from other locations (Table 3.1.4.1).

Table 3.1.4.1 Total phosphorus, iron, acid-volatile sulphide and inorganic phosphorus (mg g^{-1} dry weight) content and percentage loss on ignition (L.O.I.) of sediment from various sites within Broadland. Values are the mean of the concentrations in the top 10 cm of sediment, measured at 1 cm intervals.

Site	Tot. P (mg g^{-1})	Tot. Fe (mg g^{-1})	Tot. S^{2-} (mg g^{-1})	Tot. P(i) (mg g^{-1})	L.O.I. (%)
Barton Broad (Site 3)	1.213 1.087 1.130 0.944	18.7 16.3 22.5 21.5	0.858 ND 0.719 ND	0.476 0.394 ND	19.3 19.0 20.4 18.7
Cockshoot Broad	2.230 1.969	13.7 14.0	0.707 0.977	0.901 0.717	48.7 44.6
Cockshoot Dyke	1.619 1.300	20.9 22.9	1.813 1.423	0.369 0.383	50.9 42.9
Hoveton Little	1.016 1.015	14.6 13.9	0.097 ND	0.406 0.444	16.9 15.9
Martham Broad	2.061 2.103	90.4 99.0	ND ND	1.488 1.557	30.1 29.2
Ranworth Broad	1.017 1.071	18.7 19.2	1.894 2.043	0.273 0.383	22.0 21.7
S. Walsham	1.447 1.239	26.1 30.3	3.619 3.652	0.365 0.487	30.5 19.4

ND Not determined

These values were also expressed as total concentration in the top 10 cm of sediment core (Table 3.1.4.2), which indicates the amount of phosphorus present in each sediment core and enables the calculation of total phosphorus and iron per unit area of sediment. The various fractions of the phosphorus component of Ranworth Broad sediment were also determined and again compared with values obtained previously from other sites (Tables 3.1.4.3 to 3.1.4.5).

The composition of Ranworth Broad sediment is very similar to that of sediment from South Walsham Broad, with a high acid-volatile sulphide content and a moderately high total phosphorus and iron content. The percentage composition of the various phosphorus fractions in the sediment of these two broads are also very similar (Table 3.1.4.5): in both sediments, most of the phosphorus is present in the organic fraction. The similarity in these sediments is presumably due to their proximity to each other and to the River Bure.

Table 3.1.4.2 Total phosphorus, iron, acid-volatile sulphide and inorganic phosphorus content (mg) of the top 10 cm of duplicate cores (374 cm³) and average percentage water content of sediment from various sites within Broadland.

Site	Tot. P (mg)	Tot. Fe (mg)	Tot. S ²⁻ (mg)	Tot. P(i) (mg)	Water Content (%)
Barton Broad (Site 3)	44.3 41.3 62.7 48.7	706.9 639.7 1309.9 1177.4	ND ND 37.1 ND	17.4 13.9 ND ND	90.7 90.2 85.6 87.7
Cockshoot Broad	48.0 43.1	296.0 315.1	14.7 23.4	18.4 15.5	94.5 94.1
Cockshoot Dyke	33.3 34.1	442.1 645.8	37.7 36.2	7.7 10.6	94.5 93.4
Hoveton Little	36.4 30.8	528.9 465.0	ND ND	14.1 13.1	90.9 92.0
Martham Broad	50.2 63.2	2478.8 3010.2	ND ND	28.7 42.3	93.2 92.0
Ranworth Broad	58.3 56.9	1076.6 1040.8	112.9 115.1	15.6 17.3	85.4 86.3
S. Walsham	44.9 39.8	813.9 954.4	108.6 112.1	10.4 15.1	92.0 91.9

ND Not determined

3.2 Cockshoot Broad

There was a large variation in the composition of the sediment pore water in Cockshoot Broad between April and July 1991 (Figure 3.2.1). In April, the soluble phosphorus and

Table 3.1.4.3 Average concentration (mg g⁻¹ dry weight) in the upper 10cm of sediment of total, organic and inorganic phosphorus and the inorganic phosphorus fractions sequentially extracted by dithionite-bicarbonate, sodium hydroxide and hydrochloric acid. The various phosphorus fractions are also expressed as a percentage of the total phosphorus. The average ratio of total iron to total phosphorus in the top 5cm of sediment is also shown together with the percentage loss on ignition, averaged over the top 10cm.

Site	Core	Total P	Org. P	Inorg. P	Inorganic P			Fe:P	L.O.I. (%)
					DB-P	NaOH-P	HCl-P		
Barton Broad - site 1 (near R. Ant inflow)	A	1.609	1.061 65.9%	0.549 34.1%	0.403 25.0%	0.121 7.5%	0.025 1.6%	17.7	25.6
	B	1.321	0.791 59.9%	0.530 40.1%	0.379 28.7%	0.121 9.2%	0.030 2.3%	19.3	25.5
Barton Broad - site 2 (centre of broad)	C	1.197	0.808 67.5%	0.388 32.4%	0.309 25.8%	0.061 5.1%	0.018 1.5%	15.0	19.7
	D	1.063	0.778 73.2%	0.285 26.8%	0.182 17.1%	0.071 6.7%	0.034 3.2%	15.4	19.2
Barton Broad - site 3 (South of pontoon)	E	1.213	0.738 60.8%	0.476 39.2%	0.310 25.6%	0.062 5.1%	0.104 8.6%	14.9	19.3
	F	1.087	0.693 63.8%	0.394 36.2%	0.219 20.1%	0.067 6.2%	0.108 9.9%	13.4	19.0

Table 3.1.4.4 Average concentration (mg g⁻¹ dry weight) in the upper 10cm of sediment of total, organic and inorganic phosphorus and the inorganic phosphorus fractions sequentially extracted by dithionite-bicarbonate, sodium hydroxide and hydrochloric acid. The various phosphorus fractions are also expressed as a percentage of the total phosphorus. The average ratio of total iron to total phosphorus in the top 5cm of sediment is also shown together with the percentage loss on ignition, averaged over the top 10cm.

Site	Core	Total P	Org. P	Inorg. P	Inorganic P			Fe:P	L.O.I. (%)
					DB-P	NaOH-P	HCl-P		
Cockshoot Broad	A	2.235	1.334 59.7%	0.901 40.3%	0.207 12.1%	0.444 19.9%	0.187 8.4%	5.5	48.7
	B	1.927	1.210 62.8%	0.717 37.2%	0.188 9.8%	0.328 17.0%	0.201 10.4%	6.2	44.6
Cockshoot Dyke	A	1.394	1.024 73.5%	0.369 26.5%	0.069 4.9%	0.138 9.9%	0.163 11.7%	10.1	50.9
	B	1.230	0.916 74.5%	0.383 31.1%	0.094 7.6%	0.100 8.1%	0.189 15.4%	15.1	42.9
Hoveton Little Broad	A	1.016	0.610 60.0%	0.406 40.0%	0.206 20.3%	0.077 7.6%	0.123 12.1%	13.8	16.9
	B	1.015	0.571 56.3%	0.444 43.7%	0.237 23.3%	0.077 7.6%	0.130 12.8%	11.5	15.9

ferrous iron content of the sediment was very low and no phosphorus release was detected (interstitial sulphide was not analysed on this occasion). The sediment redox potential in April was high, with the potential not dropping below -50 mV even at a sediment depth of 10 cm (Figure 3.2.2). One month later, the interstitial phosphorus concentration had increased considerably, as had the sulphide concentration and the redox potential had fallen to less than -150 mV; however, there was virtually no sediment phosphorus release. By June, the sediment composition had returned to a similar state to that in April but with a higher interstitial phosphorus concentration. In July, the soluble phosphorus content of the pore water had increased still further and, like the sediment sampled in May, the sulphide content was high and the redox potential (Figure 3.2.2) less than -200 mV; sediment phosphorus release was detected but at a very low rate.

Every effort was made to ensure that sediment cores were taken from approximately the same point in the Broad on each occasion. The large variation in the composition of the pore water is therefore assumed to be temporal not spatial.

Although virtually no phosphorus release was measured during the incubation experiments, the fluctuation in interstitial phosphorus concentration indicates that release was occurring but was not detected owing to the nature of the sampling regime. Cockshoot Broad sediment has a relatively low total iron content (Table 3.1.4.1) and very little of this is available as ferrous iron, as shown by the interstitial concentration; hence, the sediment has a minimal capacity to retain phosphorus. Therefore most of the phosphorus which is remobilised from the particulate to the soluble phase would be rapidly released into the overlying water. Such release would only be detected by very frequent sampling.

Sediment phosphorus release has been shown to be augmented by the presence of large chironomid larvae, particularly *Chironomus* sp. (Granéli (1979), Jackson and Phillips, 1990). However, in April when the density of *Chironomus* sp. in Cockshoot Broad was relatively high (Table 3.2), there was very little interstitial phosphorus available for release. Conversely, in September when the interstitial phosphorus and sulphide concentration was high, there were virtually no invertebrates at all in the sediment. Hence, no obvious effect of chironomids was determined in any of the incubation experiments. Chironomid larvae may still have had an impact on the rate of phosphorus release in the Broad, since it has been suggested that there may have been pulses of release at times other than when the sediment was sampled.

3.3 Cromes Broad

Sediment cores were sampled from Cromes Broad on 15 April and 13 May 1991. The interstitial phosphorus concentration in the sediment was very low on both occasions (Figures 3.3.1 and 3.3.2) and, although the ferrous iron concentration was relatively low in the surface sediment, the ratio of Fe:P was very high (Table 3.1). It is unlikely that this sediment would release phosphorus, even though large numbers of *Chironomus* sp. were measured in the sediment (Table 3.1). Because of this, sampling was discontinued at this site.

Table 3.1.4.5 Average concentration (mg g⁻¹ dry weight) in the upper 10cm of sediment of total, organic and inorganic phosphorus and the inorganic phosphorus fractions sequentially extracted by dithionite-bicarbonate, sodium hydroxide and hydrochloric acid. The various phosphorus fractions are also expressed as a percentage of the total phosphorus. The average ratio of total iron to total phosphorus in the top 5cm of sediment is also shown together with the percentage loss on ignition, averaged over the top 10cm.

Site	Core	Total P	Org. P	Inorg. P	Inorganic P			Fe:P	L.O.I. (%)
					DB-P	NaOH-P	HCl-P		
Martham Broad	A	2.061	0.574 27.9%	1.487 72.1%	0.999 48.5%	0.244 11.8%	0.244 11.8%	37.5	30.1
	B	2.103	0.546 26.0%	1.557 74.0%	0.983 46.7%	0.308 14.6%	0.266 12.6%	44.4	29.2
Ranworth Broad	A	1.016	0.744 73.1%	0.273 26.9%	0.103 10.0%	0.060 6.0%	0.110 10.9%	18.5	22.0
	B	1.107	0.724 67.7%	0.383 32.4%	0.175 14.1%	0.072 6.3%	0.137 12.1%	17.7	21.7
South Walsham Broad		1.447	1.082 74.8%	0.365 25.2%	0.183 12.6%	0.087 6.0%	0.095 6.6%	17.3	30.5
		1.239	0.752 60.7%	0.487 39.3%	0.222 17.9%	0.141 11.4%	0.124 10.0%	28.7	19.4

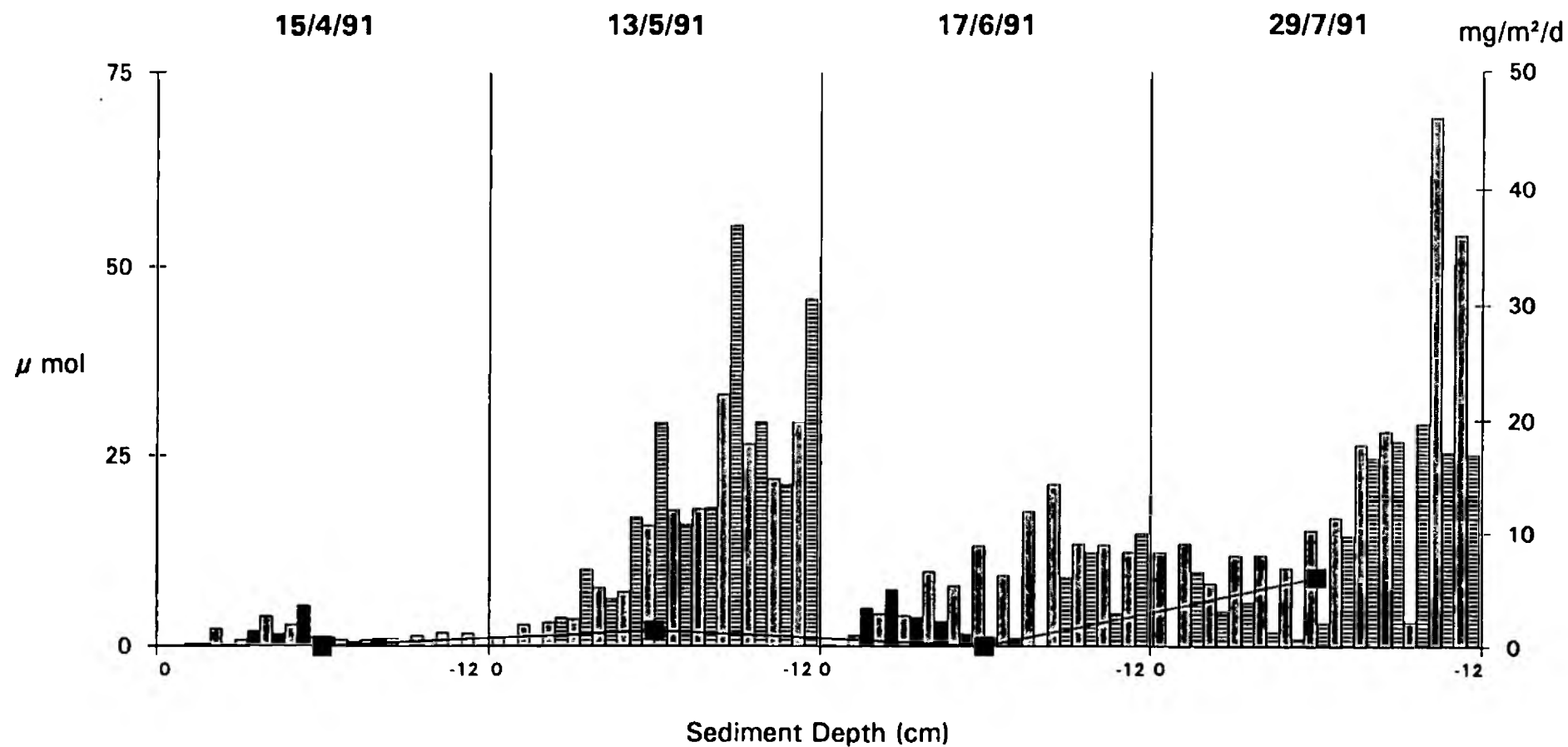


Figure 3.2.1 Cockshoot Broad 1991 - Variation in interstitial soluble phosphorus (▨), ferrous iron (■) and soluble sulphide (≡) concentration with sediment depth compared with the experimentally determined rate of phosphorus release (-▨-).

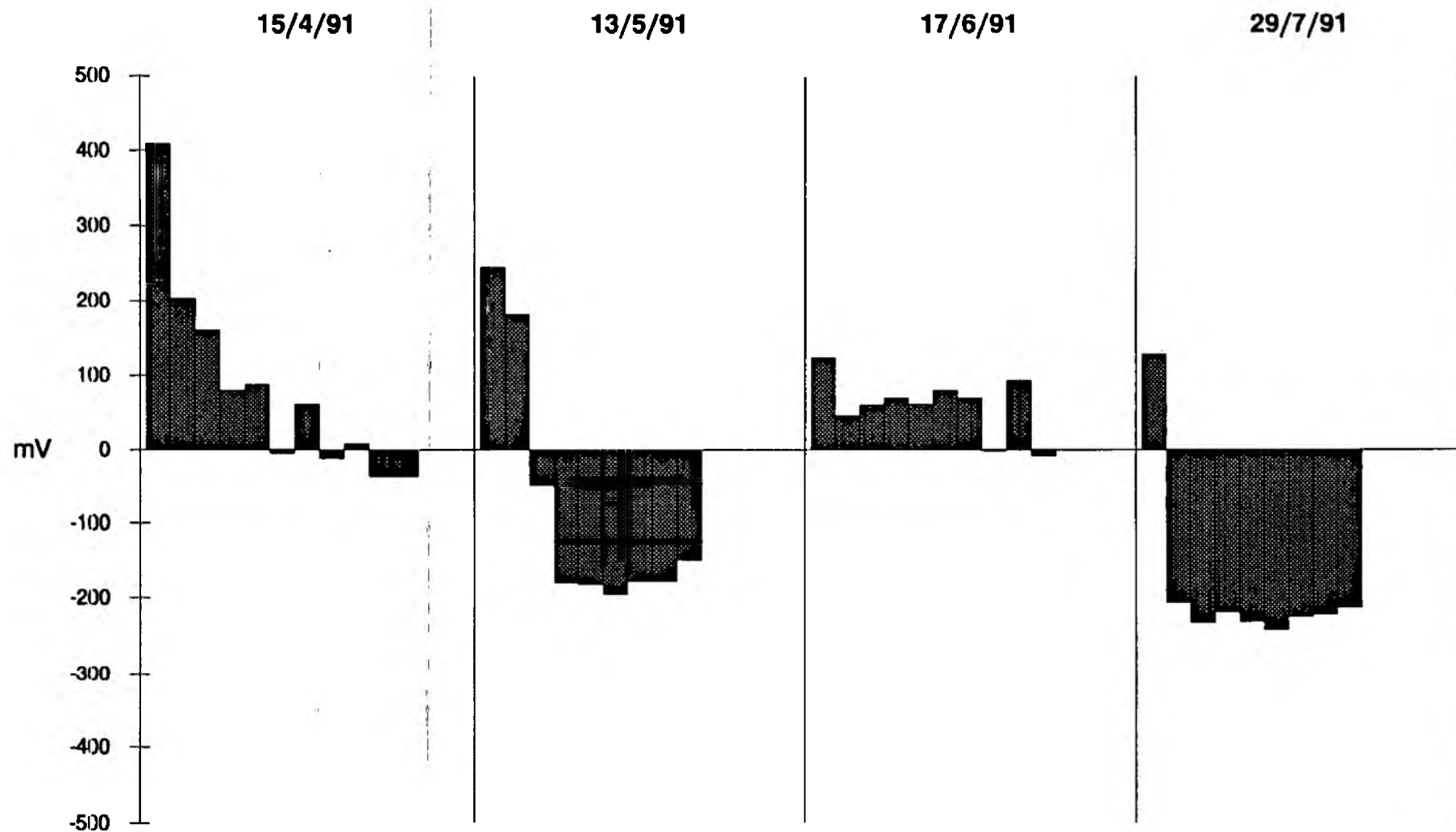


Figure 3.2.2 Cockshoot Broad 1991 - Variation in redox potential with depth.

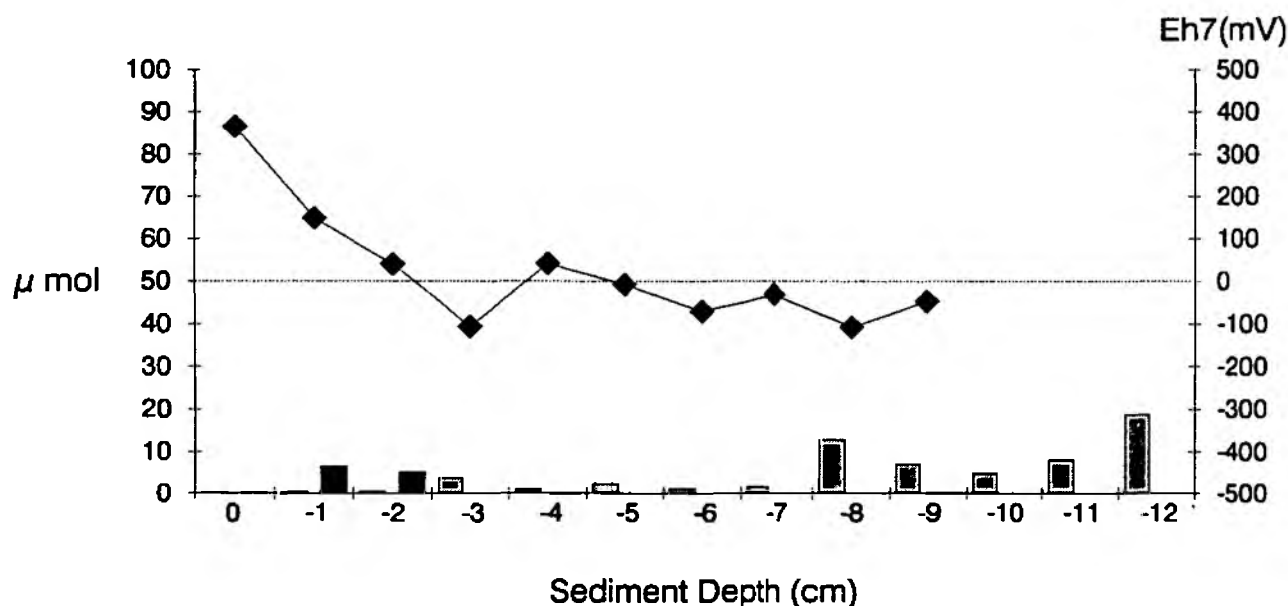


Figure 3.3.1 Cromes Broad 15/4/91 - Variation in interstitial soluble phosphorus (▨) and ferrous iron (■) concentration and redox potential (—♦—) with depth.

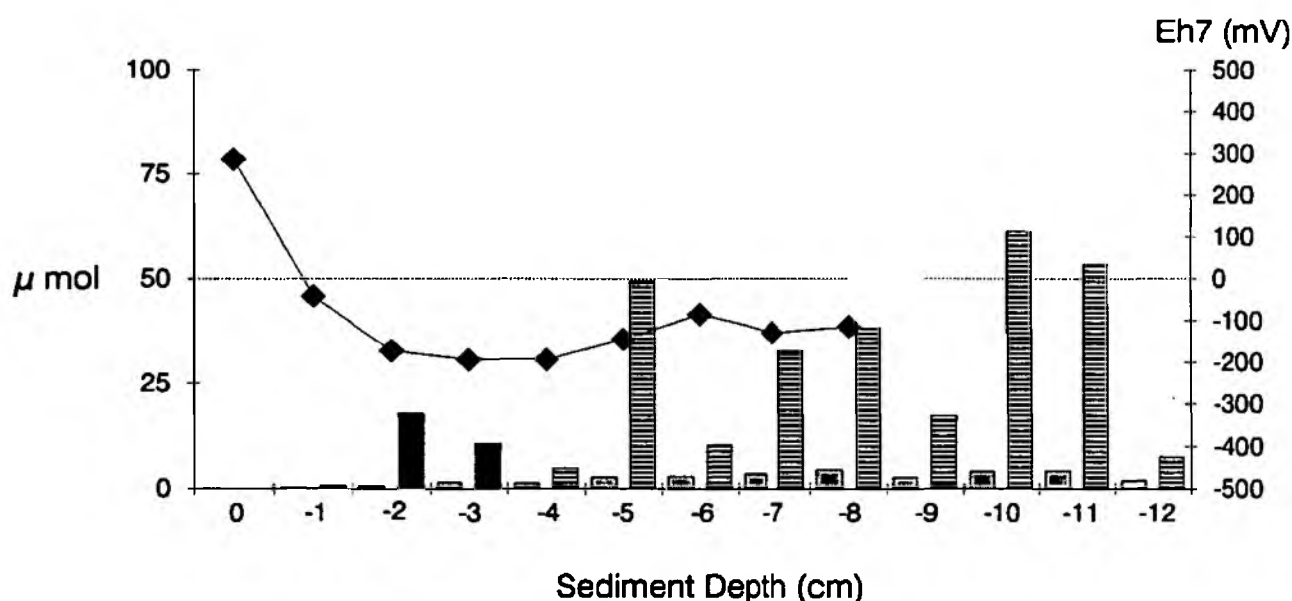


Figure 3.3.2 Cromes Broad 13/5/91 - Variation in interstitial soluble phosphorus (▨), ferrous iron (■) and soluble sulphide (≡) concentration and redox potential (—♦—) with depth.

3.4 Alderfen Broad

Sediment cores were sampled from three points in Alderfen Broad on 25 July 1991: from a site near the middle of the broad; from a site near the outflow at the southern end of the broad; and from a site near the northern end. The interstitial soluble phosphorus concentration was very high at all three sites (Figure 3.4.1). The redox potential was relatively low throughout the broad and soluble sulphide was found throughout each of the cores but was particularly high in the sediment sampled from

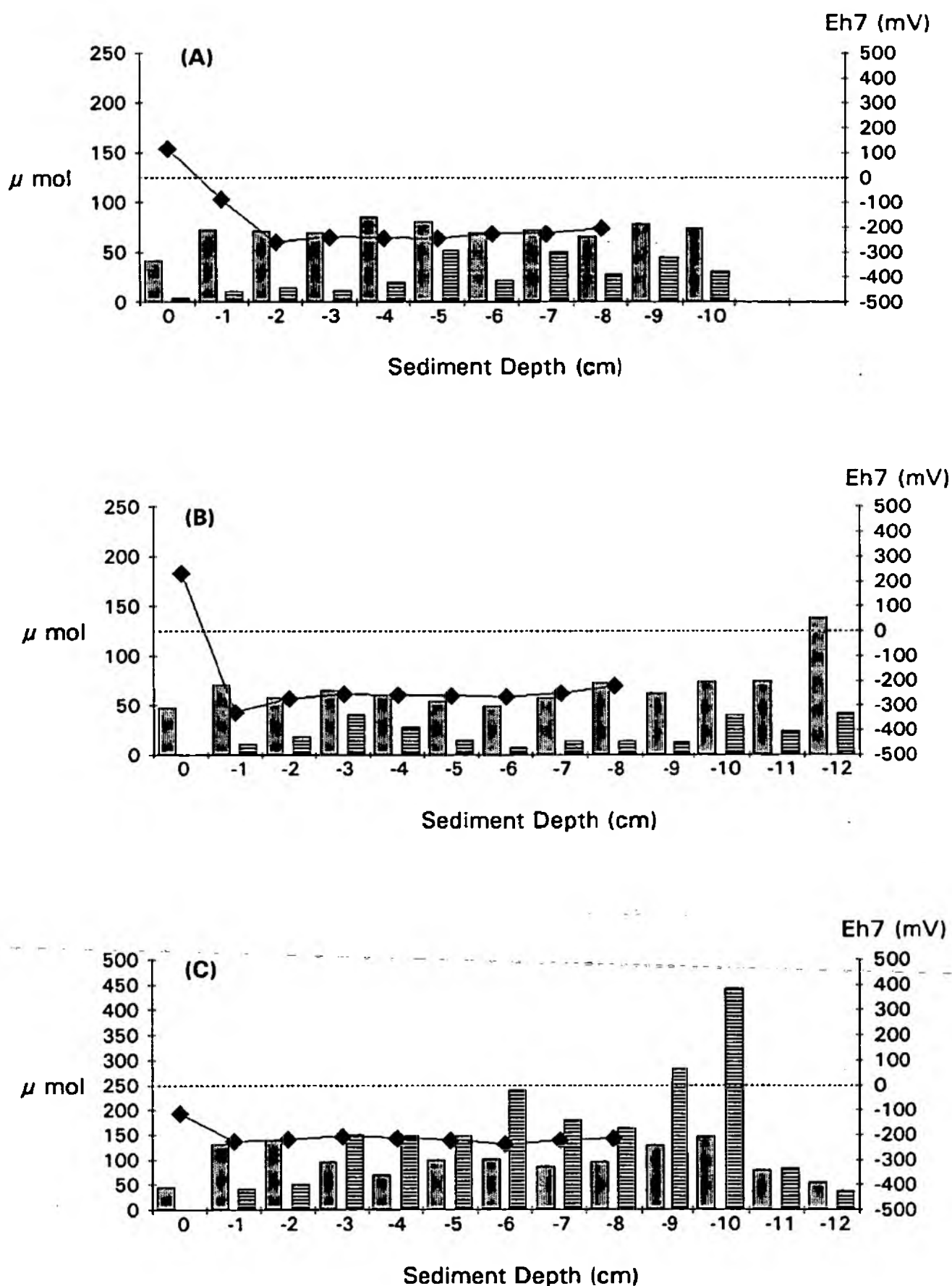


Figure 3.4.1 Alderfen Broad 25/7/91 - Variation in interstitial soluble phosphorus (▨) and soluble sulphide (▤) concentration and redox potential (—♦—) with depth in cores from: (A) the middle of the broad; (B) near the outflow at the southern end of the broad; and (C) the northern end of the broad.

near the inflow. No phosphorus release experiments were carried out on Alderfen sediment; however, the soluble phosphorus content of the overlying water is always very high, indicating significant phosphorus release. The high phosphorus and sulphide content of the pore water and complete absence of ferrous iron suggests that there is nothing to prevent phosphorus release. Assuming that phosphorus release is occurring; the steep concentration gradient of interstitial phosphorus indicates that soluble phosphorus is being remobilised from the particulate fraction at a very rapid rate.

3.5 Burnt Fen

Burnt Fen was sampled on 25 July 1991. The sediment pore water had a relatively high soluble phosphorus content and a very high ferrous iron content (Figure 3.5.1) throughout the top 12 cm of the core; giving an average Fe:P ratio of 4.36 (Table 3.1). The high interstitial phosphorus concentration is probably due to phosphorus which has been remobilised from the particulate phase being trapped in the sediment as a result of the high Fe:P ratio. The redox potential in the surface sediment is relatively high and oxidation of ferrous iron to ferric would prevent phosphorus being released.

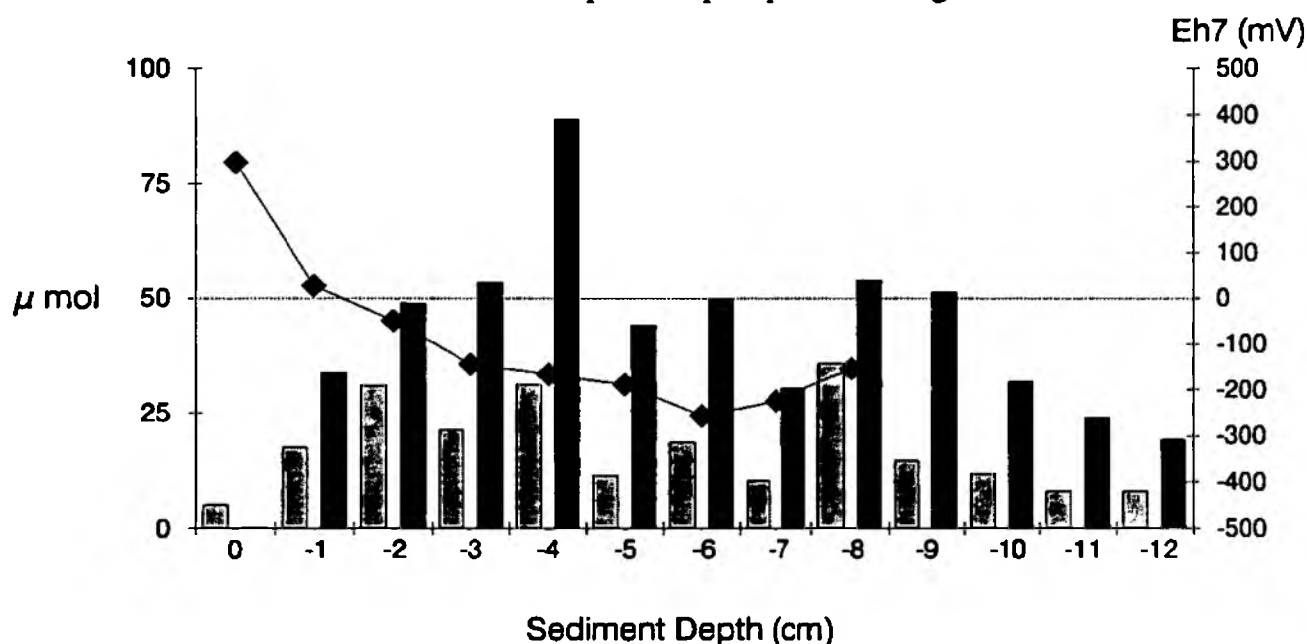


Figure 3.5.1 Burnt Fen 25/7/91 - Variation in interstitial soluble phosphorus (▨) and ferrous iron (■) concentration and redox potential (-♦-) with depth.

3.6 Woodbastwick Dyke

Sediment cores were taken from two points along Woodbastwick Dyke on 6 August 1991. Both cores contained very low concentrations of soluble phosphorus and extremely high concentrations of soluble sulphide and had very low redox potential (Figures 3.6.1 and 3.6.2). Any phosphorus in this sediment is likely to be released as there is no iron to retain it in the sediment. However, the release rate would be extremely low as very little interstitial phosphorus was detected in the sediment.

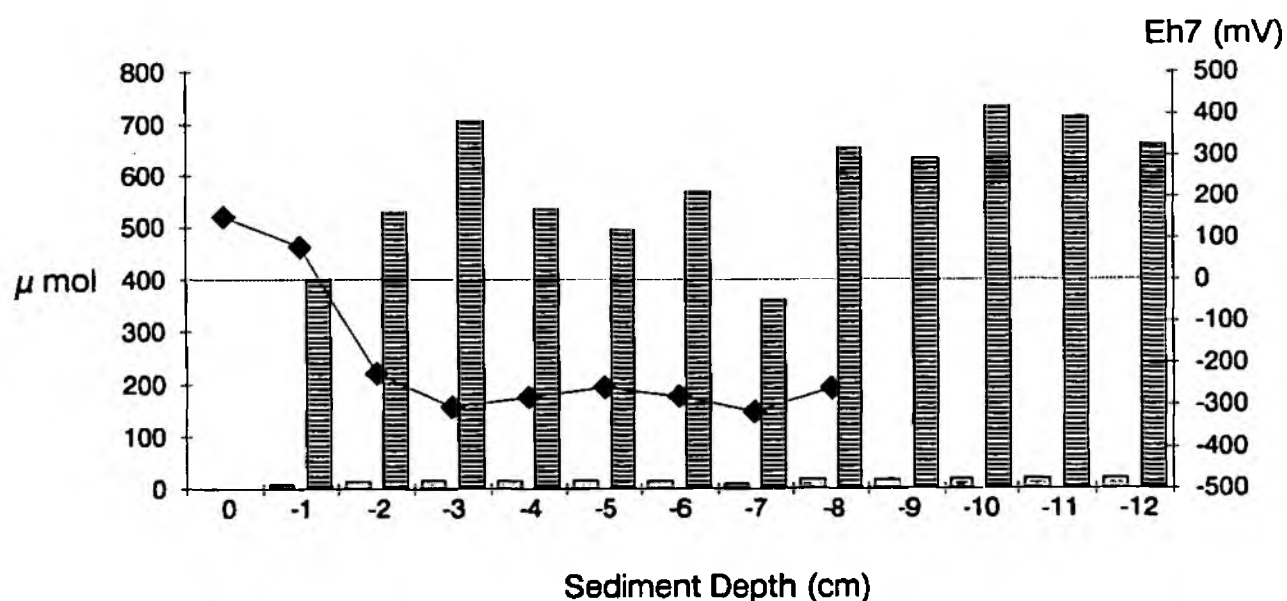


Figure 3.6.1 Woodbastwick Dyke 6/8/91: Site A - Variation in interstitial soluble phosphorus (▨), and sulphide (≡) concentration and redox potential (-♦-) with depth.

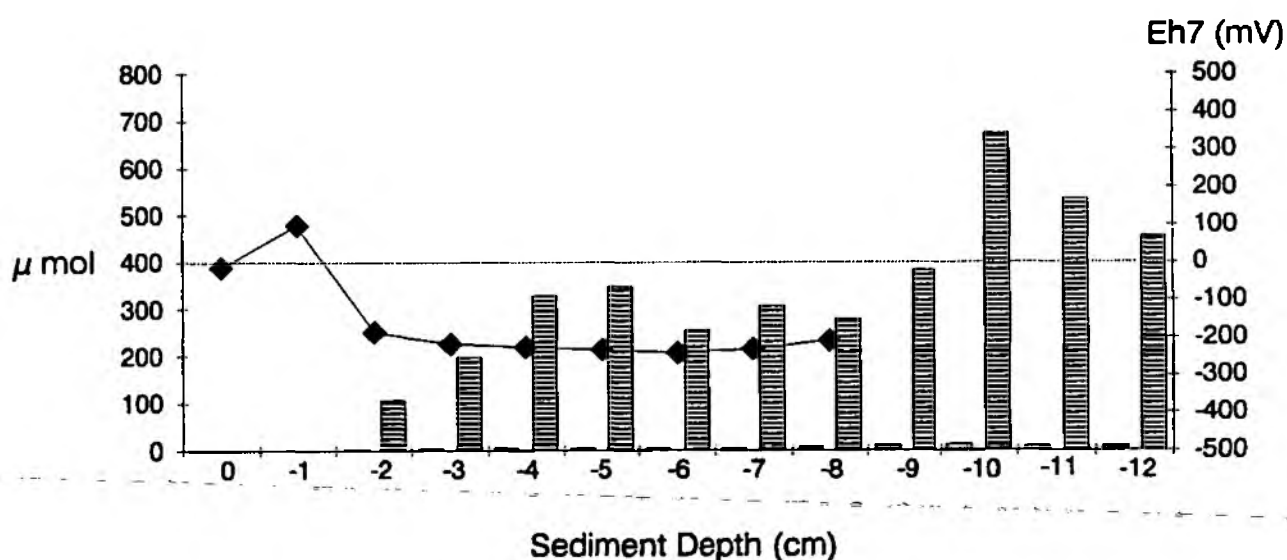


Figure 3.6.2 Woodbastwick Dyke 6/8/91: Site B - Variation in interstitial soluble phosphorus (▨), and sulphide (≡) concentration and redox potential (-♦-) with depth.

3.7 Sediment Tanks

As reported previously (Jackson, 1991), the 1-m² tanks of Hoveton Little Broad sediment were dosed with ferric chloride in late July 1990, by injecting the iron solution into the sediment. Analysis of the phosphorus, sulphide and ferrous iron content of each of the tanks was carried out just prior to dosing. Approximately one year after dosing, in

June and July 1991, the pore water of sediment from the control tanks and from the 100 g Fe m⁻² dosed tanks was again analysed for phosphorus, sulphide and ferrous iron content (Table 3.7.1) and the numbers of invertebrates counted in one core from each tank (Table 3.7.2). In October 1991 a more extensive study of the benthic invertebrates was carried out, five sediment cores were taken from each of these tanks and the benthic invertebrates counted (Table 3.7.3). The total phosphorus and iron content of the sediment in these tanks was also determined in November 1991 (Table 3.7.4).

Control tank 1 showed very little change in interstitial composition over the year (Figure 3.7.1). There was also little change in the interstitial phosphorus content of control tank 12 between 1990 and 1991 (Figure 3.7.2); although, the soluble sulphide content decreased ten-fold. The decrease in sulphide concentration could be a result of growth of *Chara* in this tank, covering 50% of the sediment surface area, which may have aerated the sediment due to the presence of its numerous rhizoids. The redox potential of tank 12 sediment was higher than that of tank 1 sediment.

Table 3.7.1 Concentration of interstitial soluble phosphorus, ferrous iron and soluble sulphide (averaged over the top 10 cm) and the concentration gradient of soluble phosphorus across the sediment surface of (a) cores sampled from the sediment tanks between 12/7 and 20/7 1990 (before iron dosing) compared with that of (b) cores sampled between 26/6 and 16/7 1991 (one year after iron dosing).

Tank Number		Soluble Phosphorus (mg l ⁻¹)	Ferrous Iron (mg l ⁻¹)	Soluble Sulphide (mg l ⁻¹)	Sol. P Conc. Gradient (mg l ⁻¹ cm ⁻¹)
1 Control	a	0.330	0.000	1.923	0.053
	b	0.508	0.000	1.777	0.117
2 Dosed	a	0.935	0.000	2.627	0.091
	b	0.536	9.221	0.000	0.133
4 Dosed	a	0.287	0.000	1.317	0.026
	b	0.165	8.235	0.000	0.031
7 Dosed	a	0.193	0.000	0.655	0.002
	b	0.388	9.934	0.000	0.020
8 Dosed	a	0.275	0.000	3.429	0.068
	b	0.052	3.604	0.000	0.000
12 Control	a	0.609	0.000	4.360	0.169
	b	0.493	0.036	0.433	0.000

Addition of 100 g m⁻² ferric chloride to the sediment (Tanks 2,4,7, and 8) produced no significant change in the average soluble phosphorus content of the pore water, with the exception of Tank 8 where there was a five-fold decrease. Before dosing, the sediment pore water of these tanks contained no ferrous iron and had relatively high concentrations of soluble sulphide; a year after dosing, the pore water contained no soluble sulphide and had a high ferrous iron concentration.

Although the ferrous iron content of the dosed sediment tanks was still relatively high a year after dosing, there was no significant difference in the total iron content of the control and dosed sediment tanks, calculated either as per unit dry weight (Table 3.7.2) or as the total per unit area (Table 3.7.3). The tanks were dosed with the equivalent of 374 g Fe m⁻² and hence the dosed tanks should contain this much more total iron than the control tanks. The lack of difference between the dosed and control tanks may be due to either variability in the iron content of the sediment prior to dosing or to patchiness in the iron dosing.

Table 3.7.2 Total phosphorus and iron (mg g⁻¹ dry weight), iron to phosphorus ratio (by weight) and percentage loss on ignition (L.O.I.) of sediment from the iron-dosed and untreated (control) tanks. Values are the mean of the concentrations in the top 10 cm of sediment, measured at 1 cm intervals.

Tank Number	Tot. P (mg g ⁻¹)	Tot. Fe (mg g ⁻¹)	Fe:P	L.O.I. (%)
Control Tanks				
1	0.692	17.75	25.8	19.9
5	0.730	14.22	19.5	13.9
11	0.689	16.29	23.7	19.5
12	0.823	14.02	17.3	12.4
Fe-dosed Tanks				
2	0.836	19.48	23.4	15.6
4	0.785	17.00	21.7	14.4
7	0.786	18.95	24.1	13.4
8	0.912	27.26	30.3	21.2

Table 3.7.3 Total sediment phosphorus and iron per unit area (g m⁻²)

Tank Number	Tot. P (g m ⁻²)	Tot. Fe (g m ⁻²)	Water Content (%)
Control Tanks			
1	7.3	183.3	89.9
5	12.2	241.0	84.4
11	6.6	152.6	90.9
12	13.6	232.5	84.7
Fe-dosed Tanks			
2	12.1	284.7	86.4
4	13.3	288.5	84.2
7	12.8	312.9	84.8
8	7.5	216.9	91.9

Table 3.7.4 Comparison of benthic invertebrate density (Numbers m⁻²) in July 1991 in sediment tanks dosed with (Tanks 2, 4, 7 and 8) and without (tanks 1, 5, 11 and 12) ferric chloride (100 g m⁻²).

Species	Control Tanks				Fe-dosed Tanks			
	Tank 1	Tank 5	Tank 11	Tank 12	Tank 2	Tank 4	Tank 7	Tank 8
CHIRONOMINAE								
Chironomus sp.	0	800	0	10700	270	7090	530	0
Kiefferulus sp.	3610	270	0	0	0	270	270	0
Microtendipes sp.	0	0	0	0	0	0	400	0
Tanytarsini	0	0	0	0	0	0	270	800
TANYPODINAE	400	800	270	1340	270	940	800	1330
TUBIFICIDAE	2540	2140	3210	21900	6020	5480	18300	1600

Table 3.7.5 Comparison of benthic invertebrate density (Numbers m⁻²) in sediment tanks dosed with (Tanks 2, 4, 7 and 8) and without (tanks 1, 5, 11 and 12) ferric chloride (100 g m⁻²). Values in parenthesis = standard deviation of 5 cores.

Species	Control Tanks				Fe-dosed Tanks			
	Tank 1	Tank 5	Tank 11	Tank 12	Tank 2	Tank 4	Tank 7	Tank 8
<i>Pisidium</i> sp.	0	270 (190)	0	0	0	0	7540 (3000)	480 (640)
<i>Potamopyrgus jenkinsi</i>	0	0	0	0	960 (410)	0	0	0
CHIRONOMINAE								
<i>Chironomus</i> sp.	0	320 (290)	50 (120)	4550 (1210)	0	210 (290)	0	0
<i>Cryptochironomus</i> sp.	0	0	0	0	50 (120)	0	0	0
<i>Microtendipes</i> sp.	0	160 (150)	430 (520)	210 (220)	750 (970)	0	1120 (830)	430 (240)
<i>Polypedilum</i> sp.	0	0	0	0	0	0	210 (350)	0
<i>Tanytarsini</i>	0	0	0	0	0	0	210 (220)	50 (120)
ORTHOCLADIINAE	0	0	0	0	0			110 (240)
TANYPODINAE	160 (150)	750 (830)	370 (300)	860 (510)	430 (520)	480 (510)	1390 (810)	160 (240)
TUBIFICIDAE	6580 (2470)	11700 (10500)	4120 (2010)	22700 (12000)	5990 (2160)	16000 (5040)	14400 (3350)	590 (720)

The benthic invertebrate density of the control and dosed sediment tanks, determined in July (Table 3.7.4) and October (Table 3.7.5), showed no significant difference in the numbers of tubificids and chironomids between the two sets of tanks. It is interesting to note that in October there were considerably more *Pisidium* in one of the iron-dosed tanks than in any of the control tanks. *Pisidium* sp. is generally thought to be very sensitive to iron.

5. DISCUSSION

The results indicate that sediment phosphorus release in the Broads is a very variable phenomenon and there are a number of factors involved.

For significant phosphorus release to occur, the sediment must contain a particulate source of phosphorus which is being continually remobilised, producing a lot of interstitial phosphorus. Although, if the rate of release is very rapid, only relatively low interstitial concentrations will be measured by sampling the pore water profile. The concentration profiles with depth can therefore be misleading as to the ability of the sediment to release phosphorus, since they only show an instant in time. For the interstitial phosphorus to move freely into the overlying water, there must be no ferrous iron present. Hence phosphorus release is more prevalent in sediments which have a high interstitial sulphide concentration, as sulphide will precipitate out the iron as ferrous sulphide.

However, phosphorus release can still occur in sediments with relatively high ferrous iron concentrations in the surface layer if there are significant numbers of large chironomid larvae which burrow beneath the iron-rich layer. The ventilation of the chironomids in their burrows will transport interstitial water, high in phosphorus and sulphide and low in ferrous iron, to the sediment surface, allowing phosphorus release despite the presence of the iron in the surface layer.

Phosphorus release is unlikely in sediments which have high ferrous iron concentrations in the top 10 - 15 cm, even when chironomids are present.

Chironomid larval numbers and the production of sulphide by microbial degradation of organic matter both vary throughout the year and therefore their affect on sediment phosphorus release will also be variable. Hence the variation in release rate and interstitial phosphorus concentration observed in Ranworth and Cockshoot Broads.

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