Institute of
Freshwater
Ecology

Assessment of the potential for phosphorus reduction in river waters

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Report To: Department of the Environment
Contract No: EPG/1/9/09
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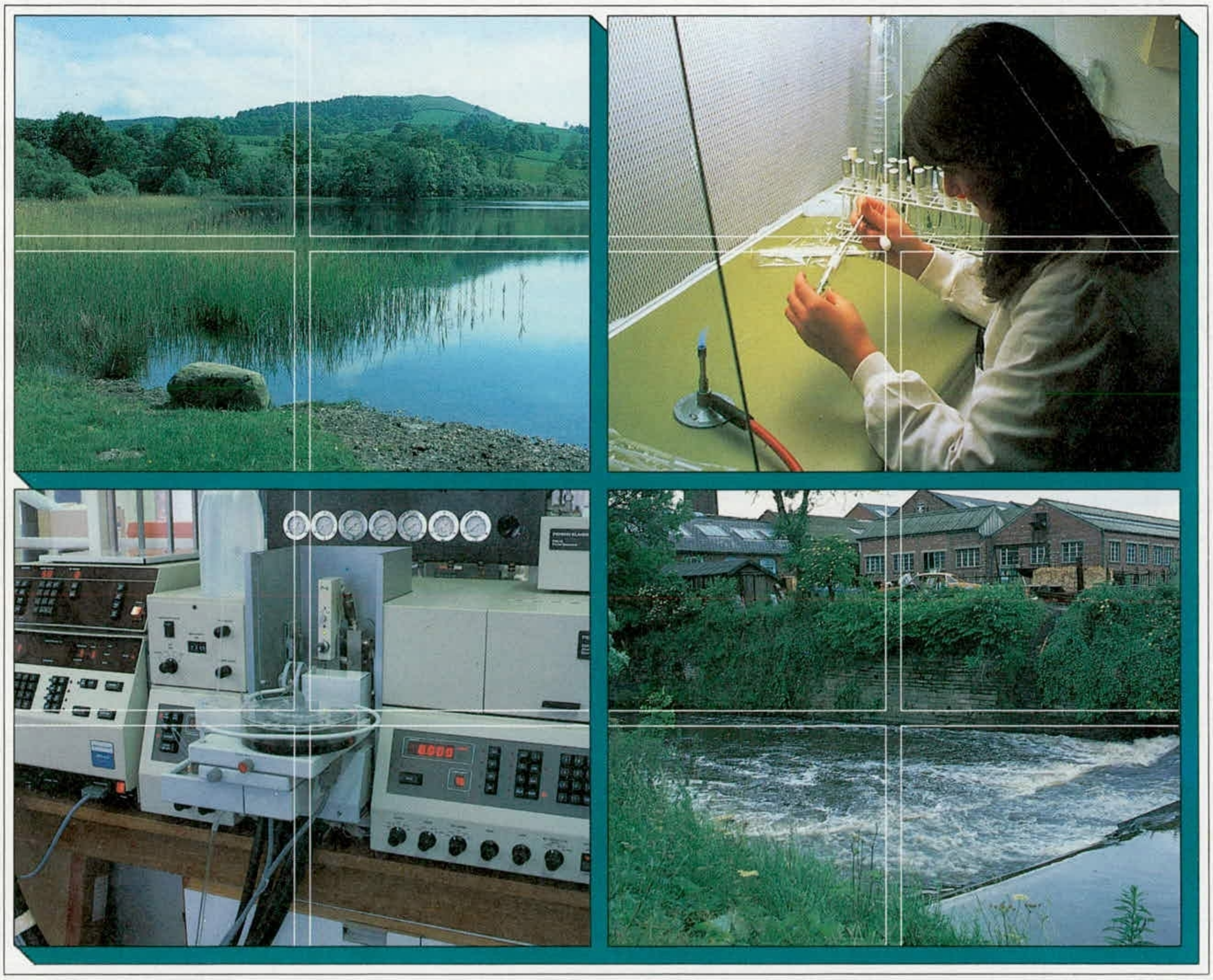

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GLOSSARY OF SYMBOLS

BAP	Bioavailable phosphorus measured here using iron oxide stripping. The concentration of phosphorus which is readily released over 24 h from unfiltered water, suspended sediment or sediment.
C_e	Equivalent to EPC. Normally this is the equilibrium concentration of SRP but because of the slow kinetics involved in the release and uptake of SRP, this is defined here as the concentration after 24 h of contact with suspended solids in well-mixed conditions.
DO	Dissolved oxygen expressed as a % percentage of the aqueous saturation at the field temperature and atmospheric pressure.
EPC	Equilibrium phosphorus concentration. The concentration of SRP in contact with a suspended sediment after 24 h contact in well-mixed conditions. The EPC_0 is the EPC of a sediment containing only native phosphorus ie. when the sediment is in contact with a solution with $SRP=EPC_0$, there is no net flux of SRP.
K_d	Distribution coefficient in units of $dm^3\ kg^{-1}$. The ratio of the concentration of adsorbed SRP to the concentration in the solution after 24 h contact.
Native P	Native phosphorus. That phosphorus in sediments prior to leaching or supplementation in laboratory experiments.
n_i	Initial adsorption amount. The initial concentration of SRP associated with the sediment prior to sorption. n_i is normally < BAP for sediments.
Non-M&R	Non Murphy and Riley phosphorus. Difference between TDP and SRP, ie that phosphorus in organic or polymeric form which is converted to SRP during digestion.
OM	Organic matter content expressed as a percentage of the dry weight measured by combustion at 550 ^{0}C
PP	Particulate phosphorus. Difference between TP and TDP, ie that phosphorus associated with the particulate phase of size > 0.45 μm.
SRP	Soluble reactive phosphorus. Soluble phosphorus measured after filtration through a 0.45 μm membrane filter without acid digestion.
STW	Sewage treatment works.
TDP	Total dissolved phosphorus. Filtered through 0.45 μm membrane filter but subject to acid digestion prior to analysis.

TP	Total phosphorus. Unfiltered and subject to acid digestion prior to analysis.
f_i	Flux in the ith river section; mmol s^{-1}
q_i	Discharge in the ith river section; m^3 s^{-1}
c_i	Concentration of SRP in the ith river section; μmol dm^{-3} or mmol m^{-3}
pc_i, pq_i	Concentration and discharge of point-source in ith section

SUMMARY

The results of the quarterly site visit (spring, 1996) to the R. Blackwater and fluvarium channel results on the release and uptake of inorganic phosphorus are presented. These show the uptake and release of phosphorus in aerated water are in agreement with the results obtained in the spring of 1995 and show little release of phosphorus when the overlying water is subject to low dissolved oxygen concentrations.

Sediment cores were also taken from the R.Blackwater, extruded, sectioned on site and the pore waters analysed for soluble reactive phosphorus, total dissolved phosphorus, silicon, nitrate, nitrite, ammonium, calcium, sulphate, chloride, Mg, Na, K and alkalinity. The sediment sections were also analysed for total phosphorus, total calcium, total iron and organic matter. Tests were also performed to assess changes in pore water chemistry associated with sampling and brief exposure to the atmosphere. The results from the pore waters show very strong concentration gradients from 8 cm depth to the surface in dissolved calcium, alkalinity, phosphorus, nitrite, ammonium, redox, conductivity, sulphate and silicon. The results enable estimates of net chemical fluxes in the sediment and also to or from the water in contact with the river bed-sediment. The influx to the sediment of soluble reactive phosphorus was very similar to total dissolved phosphorus. The equilibrium phosphate concentrations of the core sections were similar (approximately 3-7 μmol dm^{-3}) and were consistent with a net influx of phosphorus to the bed-sediment. Initial estimates of the sediment fluxes of phosphorus, calcium, bicarbonate and ammonium are given in the report.

Trials have also been completed of the determination of several organo-phosphorus compounds by analytical methods routinely used for the measurement of dissolved phosphorus. These methods include that of Murphy & Riley for the determination of soluble reactive phosphorus, a flow-injection method, total dissolved phosphorus by acid oxidation and also soluble phosphorus by ion-exchange chromatography. The results indicate that the majority of the organo-phosphorus compounds are only determined after acid oxidation, i.e. are included in the total dissolved phosphorus fraction but not the soluble reactive phosphorus fraction. Kinetic data also show that some of the organo-phosphorus compounds are converted to SRP after 72 h storage.

The results of the analysis of all the field data from the Gt. Ouse (25.5.94 to 15.11.95) are also examined in more detail. These field data have been submitted in previous reports (RL/T11059J1/(1....4)). The purpose of this work is to summarise the findings of the research on the Gt. Ouse and ascertain as far as possible the role of the sediments in the storage and release of phosphorus compounds. The results show that the total phosphorus content of the surface bed-sediments are not significantly impacted by the STW inputs. It is also evident from the quarterly site visits, that the Gt. Ouse bed-sediments are a sink for soluble reactive phosphorus; only when the concentrations are reduced below the sediment EPC$_0$ can release of soluble phosphorus be expected. The results also indicate the preciptation of calcite and coprecipitation of phosphorus in the bed-sediments during the spring and summer months. This arises from the high dissolved calcium concentrations in the water and low P_{CO_2} (related to the concentration of carbon dioxide) during periods of biological activity. This is an important mechanism controlling the fate of phosphorus in this river.

1. INTRODUCTION

Under the Urban Waste Water Treatment Directive (91/271/EEC), water bodies will be designated as sensitive areas if they fulfil certain criteria. Phosphorus removal will be required at sewage treatment works discharging into these phosphorus limited sensitive areas, the aim being to reduce phosphorus loading to the water body and therefore to reduce the biological symptoms of eutrophication. Member states also have to review and monitor eutrophication in their sensitive areas over the coming years.

There are uncertainties about how water bodies will respond to reductions in phosphorus loading and the time scale for the biological symptoms of eutrophication to be reduced. This project seeks to develop an understanding about how water bodies respond to reductions in phosphorus loading, and in particular how these reductions could be counteracted by phosphorus release from sediments.

The assessment of the effects of phosphorus removal from effluents must involve the development of criteria to establish the release of phosphorus from sediments after reducing phosphorus loading to a river. Sediments vary in their capacity for uptake and release of phosphorus depending on the nature of the binding and occurrence in the sediment. If the sediment has a high loading of exchangeable phosphorus caused by exposure to a diluted sewage effluent, a high release of phosphorus may be expected; this will largely negate the effects of tertiary treatment even in the longer-term. In other sediments, the phosphorus is likely to be fixed by heterogeneous reactions in the sediment. This phosphorus will not be easily released and will contribute a minor component of the phosphorus load in the river subsequent to tertiary treatment.

The objectives of the project are: (a) to develop criteria for predicting whether a sediment will remove/release a substantial flux of phosphorus following a reduction in the river water concentrations of phosphorus and (b) to validate a proposed procedure by prediction using criteria developed above and measured at selected sites.

2. LABORATORY METHODS

The following IFE (River Laboratory) Standard Operating Procedures (SOPs) were used in this work. When other methods are used they are explained or referenced in the text. The SOPs are available to the DoE on request.

SOP: 26/20.7.94 Update none. Particle size analysis of sediment samples.
SOP: 23/18.4.94 Update none. The determination of the organic matter content of a sediment.
SOP: 22/14.3.94 Update none. An ignition method for the determination of the total phosphorus in sediments.
SOP: 21/4.3.94 Update none. Total phosphorus determination by persulphate digestion.
SOP: 20/7.3.94 Update none. The determination of bioavailable phosphorus by iron oxide stripping.
SOP: 19/8.3.94 Update none. The determination of the soluble reactive phosphorus in water by flow-injection analysis.

SOP: 15/12.8.93 Update 5.11.93	Conductivity measurement using Ciba-Corning M90 field meter.
SOP: 14/12.8.93 Update 5.11.93	Oxygen measurement using Ciba-Corning M90 meter
SOP: 13/12.8.93 Update 5.11.93	pH measurement using Ciba-Corning field meter.
SOP: 36/16.5.95 Update none	Determination of total suspended solids in water.
SOP: 37/17.3.95	Determination of Ammonia.
SOP: 32/18.10.94	The determination of Mg, Na, K by atomic absorption spectroscopy.
SOP: 31/18.10.94	The determination of alkalinity using an end-point titration
SOP: 30/18.10.94	The determination of calcium in water by titration using EDTA
SOP: 29/18.10.94	The determination of nitrate in water by flow-injection analysis.
SOP: 28/17.10.94	The determination of silica in water by flow injection analysis.

3.0 QUARTERLY SITE VISITS

Quarterly visits to the R. Blackwater have continued. The results for the visit in the spring 1996 are included in this report. In addition to the normal field work, studies have been completed on sediment cores taken from site B (the site used for the collection of sediment for the fluvarium studies). The sediment cores were extruded and cut on site to produce enough pore water for the analysis of the major nutrients (SRP, TDP, nitrate, nitrite, silicon and ammonium) and major-ions in 0-0.5, 0.5-1.0, 1.0-2.0, 2.0-4.0, 4.0-6.0 6.0-10.0 cm sections. The report also includes measurements of flow related transfer fluxes (FRTF) in the fluvarium channel.

3.1 Fluvarium Channel

The current version of the channel now incorporates the following features:

1. Control of the water velocity over the bed-sediment.
2. The channel is completely enclosed enabling the gas atmosphere to be controlled.
3. The concentration of oxygen in the water can now be controlled by air and nitrogen lines.
4. Measurements of pH, temperature and dissolved oxygen are logged using a Hunter portable computer. Because of electrical interference between conductivity and pH it is necessary to measure conductivity manually at suitable intervals.
5. The flow rate is continually measured using the flow transducer placed downstream of the recirculating pump. The flow rate may be altered by inserting appropriate restrictors in the downstream tank or adjusting the butterfly valve.
6. The filtration and sampling of the water is now fully automated. Samples can be taken at pre-defined intervals, filtered through a 0.45 μm membrane filter and placed in a collection bottle. The system of tubes, filter and syringe are fully flushed prior to each sampling. In addition, the tube connected to the sample collector is flushed with air after each collection. This permits continuous operation over several days or however long is necessary. Normally the system is run for 24 or 48 h periods with sampling at 1 hour intervals.
7. The temperature of the channel is maintained close to the river Frome temperature by flowing water from the fluvarium.

Control experiments without sediment have been done and indicate no contamination of SRP from the equipment. Preliminary experiments have shown satisfactory performance including the ability to reach low oxygen (<2%) in the overlying water. The flow transducer has been calibrated by measuring the time of discharge at various heads of water. The calibration of the transducer was found to be linear with mA loop signal directly proportional to the discharge.

3.2 Field Work

On-site work involved the following:

(a) Sampling the water and on-site filtration for measurements of SRP, TDP, Si, NO_3 and Ca. Sampling the water for suspended solids measurements.
(b) Measurements of pH, T, conductivity and oxygen concentrations.
(c) Assessment of the riverine environment using macrophytes (NRA, 1994).
(d) Sampling the bed-sediment at selected sites for wet chemical analysis, sorption studies and particle size determinations.
(e) Sampling the surface (< 5 cm) bed-sediment at the site downstream of the main STW using stainless steel trays designed for direct insertion into the fluvarium channel.
(f) Measurement of the water velocity across a section of the river to enable the discharge at all the sites to be estimated.
(g) Sampling the water for major-ion and nutrient analysis at additional downstream sites to enable the calculation of discharge from NRA gauging stations. This was necessary for the Gt. Ouse and Blackwater rivers where the gauging station is situated downstream of the confluence with a major tributary.

Samples were filtered using a 0.45 μm cellulose nitrate membrane filter. Samples for total phosphorus measurement were taken on-site and placed in 60 ml HDPE Azlon bottles for direct measurement; this method avoids the loss of suspended solids caused by sub-sampling. All samples were stored in a cold box during transportation. The analyses were done as soon as possible after returning to the main laboratory with SRP, Si and NO_3 all analysed within 1 day of returning.

3.3 Laboratory Measurements

These include:

(a) Nutrient fractions including SRP, total dissolved phosphorus (TDP), total phosphorus (TP), nitrate, silicon as well as major ions such as calcium, magnesium, sodium, potassium and alkalinity.
(b) Measurements on the 2 mm sieved bed-sediment such as the organic matter content (OM), total phosphorus, calcium and iron concentrations after acid digestion.
(c) Measurements of the "biologically available phosphorus", BAP, by the method of iron-oxide stripping.
(d) Measurement of the sorption characteristics of the surface bed-sediment at 10 ^{0}C and calculation of the equilibrium phosphate concentration, EPC_0, initial native phosphorus amount and adsorption affinity, K_d.

The fluvarium channel experiments were conducted as follows:

(a) River bed-sediments were collected from the sites downstream of the major STW input. Surface sediments (<5 cm depth) were collected using the four stainless steel sections. If possible these were forced into the sediment and a horizontal section taken by moving the tray through the sediment. Where this was difficult because of the depth of water, the sediment was taken in shorter sections and placed directly in the tray. No attempt was made to sieve the sediment; the prime purpose was to try and get a representative sediment from the site with a minimum disturbance to the sediment. At sites where the sediment surface was coarse and uneven, this structure was retained as much as possible.

(b) The sections were end-capped and placed in a tray containing about 2-3 cm depth of river water from the site. The tray was then covered with aluminium foil and transported immediately to the fluvarium. The transport time varies between sites from 1.5 to 3 h.

(c) On arrival at the fluvarium, the small amount of fines leached from the sediments were returned to the sections. The sections were then placed in the fluvarium channel in readiness for the phosphorus release experiment. Before adding the background electrolyte (2 mM $CaCl_2$), the pH and dissolved oxygen (DO) sensors were calibrated. The solution was then added and first phosphorus release experiment started. Manual sampling was done at time 0, 15 and 30 mins; thereafter the automatic sampler operated at 1 hour intervals for 24 h.

(d) SRP uptake was investigated by the augmentation of SRP above the expected EPC_0 of the sediment. The kinetics of uptake of SRP was measured over 24 or 48 h.

(e) The release of SRP under anaerobic conditions was evaluated by lowering the DO concentration in the fluvarium channel by the addition of Na_2SO_3 in sufficient amount to just remove all the DO. Subsequently, the solution was purged with high purity nitrogen gas to maintain a DO concentration in the water close to zero percent. The kinetics of the release of SRP was measured over 24 to 48 h.

3.4 Sediment Core Sampling

In addition to the normal field work, several sediment cores were taken during the visit to the river Blackwater in the spring. A total of 14 cores were taken using a Jenkin's sampler with perspex sample tubes (length 50 cm; internal diameter 7 cm) at site B from an area of soft sediment, (approximately 4 m x 6 m), which was relatively clear of macrophytes. Twelve of the cores were sectioned on-site immediately after sampling by mechanical extrusion. The sectioned sediments from each of the 12 cores were mixed in 1 litre polyethylene pots to provide adequate pore water and sediment for chemical analysis. One of the two additional cores was extruded on-site past a redox electrode to measure a redox profile from an undisturbed core, and the final remaining core was left intact, sealed to exclude air contact and transported back to the laboratory. This core was stored overnight in the dark at 6-8 ^{0}C for experiments on the following day.

3.4.1 Laboratory Measurements

a) Sample preparation·

At the end of the sampling day, on return to the laboratory, the mixed sectioned sediments were transferred to centrifuge tubes and spun at 6000 rpm at approximately 10 ^{0}C for 20 minutes to isolate sediment pore water. The supernatant was decanted off and filtered through a 0.45 μm cellulose nitrate membrane. Measurements of the pH and conductivity of the pore water were taken, and the head-space of the bottles purged with CO_2 to minimise the risk of precipitation of calcium carbonate. The pore waters and centrifuged sediments were stored at 4 °C in the dark prior to further chemical analysis.

b) Sample stability study·

The intact core was extruded in a nitrogen atmosphere to minimise changes in the redox potential of the sediment. The extruded sediment was mixed and divided into 3 samples for a comparative study of changes to the dissolved phosphorus, iron and calcium concentrations after different treatments. The first sample was kept sealed at 4 °C in the dark; the second sample was aerated by bubbling with air for 4 h and then left open to the air for a further 5 d at 4 °C in the dark and stirred periodically; the third sample was exposed to air and stirred at frequent intervals for 1 h, before storage at 4 °C in the dark. The redox potentials of the sediments were measured in a nitrogen atmosphere before and after the treatments. After the treatments, the sediments were centrifuged at 6000 rpm for 20 mins, the supernatant decanted, filtered through a 0.45 μm cellulose nitrate membrane and acidified to *ca* pH 2 with spectrosol grade nitric acid. The SRP, calcium and iron concentrations were then determined for each of the 3 samples.

c) Pore water analysis·

The pore waters from the sectioned sediment cores were analysed for nutrient fractions including SRP, TDP, nitrate, nitrite, ammonium, silicon as well as major-ions such as calcium, magnesium, sodium, potassium and alkalinity. The analytical methods are listed in the SOP's (section 2 above).

d) Sediment analysis

Measurements of the centrifuged sediments from the sectioned cores included the organic matter content, total phosphorus, iron and calcium concentrations after acid digestion, biologically available phosphorus by iron-oxide stripping (BAP) and the SRP sorption characteristics at 10 °C. The isotherms were used to calculate the EPC_0, native P, (n_i) and sorption coefficient (K_d) for the sections of sediment. In addition, the water content of the sediments was estimated by mass balance.

3.5 Results

3.5.1 R. Blackwater Quarterly Sampling

The results of the spring 1996 site visit are collected in Appendix A. This is the first quarterly sampling which repeats the previous years work. The previous spring visit was on 10.4.95 (see report RL/T11059J1/3) when the river was in similar flow conditions, i.e. 0.60 $m^3 s^{-1}$ on 18.4.96 compared with 0.5 $m^3 s^{-1}$ on 10.4.95 at the downstream site D. Although the discharge conditions were similar on these visits, the concentration of the P fractions were different. During the latest visit, SRP concentrations were higher and dominated the P fraction whereas during the spring 1995 visit, the organic P and particulate P fractions made a significant contribution to the total amount of P. This variability must reflect the composition of the STW discharges at the time of sampling. The changes in total P concentrations along the study reach were similar in trend to those measured previously and reflect the influences of the STW's on the nutrient chemistry of the river. As during previous visits, the concentrations of both silicon and nitrate were elevated immediately downstream of the Aldershot Town STW.

The sorption data for surface sediments from the sites A to D all produced linear isotherms leading to EPC_0's between 2.5 and 7.4 μmol dm^{-3}. For the sites downstream of the major STW's, the EPC_0's are lower than the SRP concentrations measured in the river indicating a net uptake of SRP by the bed-sediment. At the upstream site A, the SRP concentration in the river was lower than the sediment EPC_0 and so a net release of SRP from the sediment is possible. The sediment from site C is different from the sediments from the other sites as shown by the relatively high iron, P and organic matter contents (Appendix A). This sediment has the highest BAP, K_d and n_i and lowest EPC_0. This indicates that the sediment from site C has a high affinity for P but also contains the highest concentration of bound P and labile P (this is one of the few sediments with n_i > BAP).

3.5.2 Fluvarium Studies.

The results from the fluvarium experiments have not yet been modelled in detail. The experimental results are shown in Appendix B. The bed-sediment released SRP to a concentration close to the EPC_0 of the surface sediment (7.3 μmol dm^{-3}). During the second experiment, the net uptake of SRP was similar to that measured last spring. There was a slight release of SRP from the sediment when the concentration of DO in the water was lowered but over 24 h this amounted to < 2 μmol dm^{-3} change in concentration of SRP in the overlying water.

3.5.3 Particle-Size Distributions.

These are presented in Appendix C and will be combined with the other data on the R. Blackwater sediments at a later stage of the project.

3.5.4 Sediment Cores Results.

All the results from the analysis of the sediment core sections are collected in Appendix D. These are discussed in terms of the six sections: 0-0.5, 0.5-1.0, 1.0-2.0, 2.0-4.0, 4.0-6.0, 6.0-10.0 cm measured from the sediment surface. The Jenkin's corer is particularly suited to producing sections of intact material with a minimum of disturbance to the sediment structure. This is particularly important in sediments with strong redox gradients. Rapid sectioning and analysis of the sediments is also vital in reducing chemical and biological changes in the sediments after sampling. As described in the methods section, special effort was made to ensure the integrity of the cores and that the sectioning of the cores and analysis were done as quickly as possible, i.e. sectioning, filtration of pore waters and some measurements were done on the sampling day and tests with the control sediments on the following day. The control sediment was collected for detailed studies of kinetic changes during sectioning and storage prior to centrifugation and filtration of the pore water.

The detailed analysis of the results is incomplete although several important points are evident:

1. The solute concentrations in the pore waters show large vertical gradients in Ca, ammonium, SRP, TDP, silicon, sulphate and bicarbonate. Small gradients were obtained for K^+ and nitrite and uniform concentrations for Mg, Na, Fe, Cl. The pH values showed little variation between the sections in contrast to conductivity and redox potential. The changes in conductivity are consistent with the measured concentration gradients. A chemical speciation analysis of the pore waters from the sections produced good charge balances and values of the concentration of carbon dioxide in the water. The CO_2 partial pressures increase with depth (to a maximum of 28.8 matm) consistent with microbial respiration in organic sediments. The high CO_2 concentration and low pH of the pore waters is consistent with the extremely high concentrations of calcium and bicarbonate (carbonate alkalinity). The upper sediment section is close to equilibrium with respect to calcite, over saturated with respect to hydroxyapatite but undersaturated with respect to other calcium phosphate minerals such as OCP, DCPD and TCP (see section 5.2 for details of these minerals). The deepest section was more saturated with respect to calcite but not greater than commonly observed in many hardwater rivers and not high enough to expect calcite nucleation in the sediment. This pore water was less saturated with respect to calcium phosphate minerals than the upper surface section.
2. There was a large redox gradient down the cores which is further supported by the absence of nitrate in the cores and concentration profiles of sulphate, ammonium and nitrite (Appendix D). Chemical fluxes through the pore water were estimated by fitting the concentration profiles using an empirical function:
$Ai=a+bz+cz^2+1/(1+z)$, where Ai is the concentration of the solute in the pore water from a section and z the vertical distance from the sediment surface to the centre of the section. In brief, the results for sulphate indicate a net uptake of sulphate by the sediment with the flux at the surface almost two orders of magnitude greater than the flux in the deepest sediment. This is consistent with the reduction of sulphate within the sediment core. The flux for ammonium was calculated from Fick's first law with the porosity and tortuosity taken from de Beer *et. al.*, (1991) from experiments with a similar type of sediment. These parameters will be estimated independently in due course. The results indicate fluxes of a similar magnitude measured by de Beer *et. al.*, (1991) with ammonium microelectrodes. The fluxes varied from 4.8×10^{-8} mol m^{-2} s^{-1} for the upper section to 0.56×10^{-8} mol m^{-2} s^{-1} at 8 cm depth, again indicating the formation of ammonium in the sediment and net efflux of ammonium to the overlying water. No evidence was discovered for the consumption of ammonium in the oxidised surface sediment (probably < 1mm in depth) but this degree of spatial resolution is not possible with the mechanical sectioning method employed here. The results for the distribution of nitrite are more complex with fluxes into the deeper sediment (> 2 cm depth) and efflux from the surface sediment.

3. The fluxes of SRP and TDP were calculated in a similar manner with the diffusion coefficient for HPO_4^{-} taken as 4.7×10^{-10} m^2 s^{-1} at 10 °C. The results of the calculation are shown in Table 1 below:

TABLE 1 Calculated fluxes of SRP and TDP for the sediment sections. The porosity and tortuosity were estimated from the results of de Beer *et.al.*, (1991).

Depth/ cm	Flux of TDP/10^{-8} mmol m^{-2} s^{-1}	Flux of SRP/10^{-8} mmol m^{-2} s^{-1}
0.25	101	97
0.5	70	68
0.75	52	51
1.5	26	26
3	10	11
5	4	5
8	2	2

This shows that the two fluxes are very similar, i.e. organo-phosphorus and other hydrolysable phosphorus compounds do not contribute significantly to the influx of phosphorus to the sediment (see section 4.0 for a discussion of the groups of compounds determined by SRP and TDP measurements). The results also support the conclusion (previously ascertained from measurement of EPC_0 of the surface sediment) that there is a net influx of P to the sediment. They also indicate that this flux decreases with depth, suggesting the consumption of SRP by sorption, chemical reaction and biological assimilation in the sediment. The fluxes calculated above are very much smaller than those measured in the fluvarium channel experiments using the R. Blackwater sediments. This may be caused by differences in the composition of the core sediments compared with surface sediments used in the fluvarium channel but also suggests the importance of surface processes, i.e. in the top millimetre of sediment, in controlling the net uptake. The results indicate the largest chemical gradients in SRP (and TDP) in the upper 5 mm layer and a discontinuity with the higher concentration of SRP in the bulk water (93 μmol dm^{-3} compared with 37.2 μmol dm^{-3} in the pore water of the upper section). *These results for SRP and TDP fluxes are the first reported in detail for river sediments and open a number of questions about the processes operating in deeper sediments and fate of the P in these conditions.*

4. The large calcium and alkalinity gradients measured in these sediments were unexpected. The chemical speciation programme (written in Mathcad for phosphorus speciation), indicated good charge-balances and the measured conductivity values for the pore waters are consistent with the increasing water hardness with depth in the sediment. The pore water was superaturated with respect to calcite formation but not to such a high degree that heterogeneous nucleation and precipitation could be expected. The high concentrations of SRP in the upper sediment will inhibit calcite growth. The chemical gradient of calcium and bicarbonate (from alkalinity), indicate an efflux of both from the sediment. Table 2 shows the calculated fluxes of calcium and bicarbonate together with the ratio of the fluxes. The increases in flux of calcium and alkalinity with approach to the surface, means that calcium and alkalinity are generated in the sediment. The mechanism for the reaction(s) which lead to this profile is as yet unknown. Further analysis of the results from these cores will be continued because of the possible implications for P chemistry in sediments.

TABLE 2. Comparison of the calcium and bicarbonate fluxes in the sediment at different depths. The fluxes were estimated using the porosity and tortuosity data of de Beer (1991). The diffusion coefficients were calculated from limiting conductivity data at 10 °C (Cassford *et.al.*, 1983) by the Nernst equation.

Distance, z/ cm	$[HCO_3^-]$ /10^{-8} mol m^{-2} s^{-1}	$[Ca^{2+}]$/10^{-8} mol m^{-2} s^{-1}	Ratio of fluxes: $[Ca^{2+}]/[HCO_3^-]$ as %
0.25	20.9	3.7	17.6
0.50	16.4	3.2	19.3
0.75	13.7	2.9	20.9
1.5	10.0	2.4	24.2
3.0	7.8	2.1	27.0
5.0	7.1	1.9	27.1
8.0	6.9	1.8	25.2

5.0 The results for silicon are particularly interesting in view of the very low concentrations of dissolved silicon often observed in both large, e.g. R. Trent, and small rivers during diatom growth. During such periods the supply of silicon from either bed or suspended sediments is likely to be important in controlling diatom growth when SRP and nitrate are abundant. The pore water concentrations indicate a linear increase in the silicon flux through the length of the cores, consistent with the generation of dissolved silicon.

4.0 MEASURMENT OF ORGANOPHOSPHORUS COMPOUNDS

The project has been concerned with both SRP and TDP phosphorus fractions in the filtrate. The difference between the two has been ascribed to the amounts of hydrolysable organo-phosphorus and polyphosphate compounds in samples. Because of the low concentrations of polyphosphates in most natural waters, the difference: TDP-SRP is often equated with dissolved organo-phosphorus compounds (OP). A study to assess the contribution that selected organophosphorus and inorganic polyphosphate compounds make to the phosphorus determined as SRP and TDP has been performed. For the past 40 years there has been a considerable amount of experimental work that suggests that SRP determinations overestimate dissolved inorganic monophosphate. Hydrolysis of organo-phosphorus and inorganic polyphosphate compounds during the analytical procedure has been suspected as a possible source of error caused either by acid or molybdate catalysed hydrolysis.

Solutions were prepared of a range of synthetic compounds (listed below) with equal concentrations of phosphorus (12 μmol dm^{-3}), and the phosphorus determined by three different methods commonly used to measure SRP in natural water samples. The SRP measurements were done within 4 h of preparing the solutions of the synthetic compounds to minimise errors caused by hydrolysis during storage. The stability of the solution composition was assessed by repeating the determinations by one of the SRP methods after 3 days. The TDP and dissolved organic carbon concentrations in the solutions were also measured.

No significant ($p>0.95$) amount of P was measured by the three SRP methods in any of the solutions containing the synthetic compounds. The mean values of 5 replicate determinations were below the limit of determination except for myo-inositol 2-

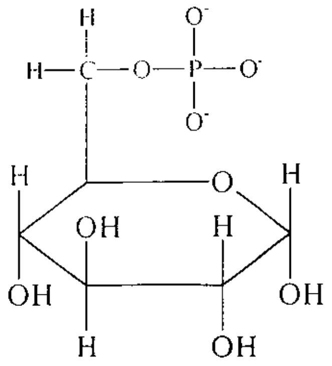
monophosphate which was determined as 0.26 and 0.36 μmol dm^{-3} by the Murphy & Riley and flow-injection analysis methods respectively, and tripolyphosphate which was measured as 0.32 μmol dm^{-3} by flow- injection analysis. The maximum phosphorus measured by the SRP methods (at a 95 % Confidence Level , CL) was calculated using the data from the 5 replicates and is given in Table 3 expressed as a percentage of the mean TDP concentration..

The concentrations of TDP were generally in close agreement with the formulated values, with recoveries within 5 % of the expected concentration for all the compounds except for inositol hexaphosphate (85.6 % recovery). The results from the DOC analysis of the organic compounds were also close to the formulated values, with recoveries within 10 % of the expected concentration for all the compounds except for 2-aminoethylphosphonic acid (84 % recovery). The data for TDP and DOC determinations are given in Table 4.

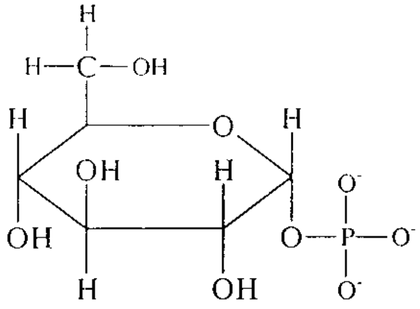
There was evidence that hydrolysis of phosphate occurred during storage in six of the synthetic compounds, as the FIA-P increased significantly after 72 hours ($p < 0.05$). The data for the model compounds showing an increase in P are given in Table 5.

List of synthetic compounds used:

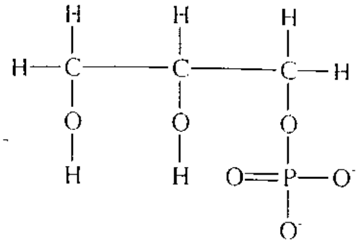
α-D-Glucose 1-phosphate di-sodium salt (G1P)
D-Glucose 6-phosphate di-sodium salt (G6P)
Adenosine 5' triphosphate di-sodium salt (ATP)
p-Nitrophenyl phosphate di-sodium salt (NPP)
Adenosine 3',5'-cyclic monophosphate (AMP)
Glycerophosphate di-sodium salt (GYP)
myo-Inositol 2-monophosphate Di(cyclohexylammonium) salt (IMP)
Inositol hexaphosphate dodecasodium salt (IHP)
2-Aminoethylphosphonic acid (AEP)
Tetra sodium pyrophosphate (PYP)
Pentasodium tripolyphosphate (TPP)
Trisodium trimetaphosphate (TMP)



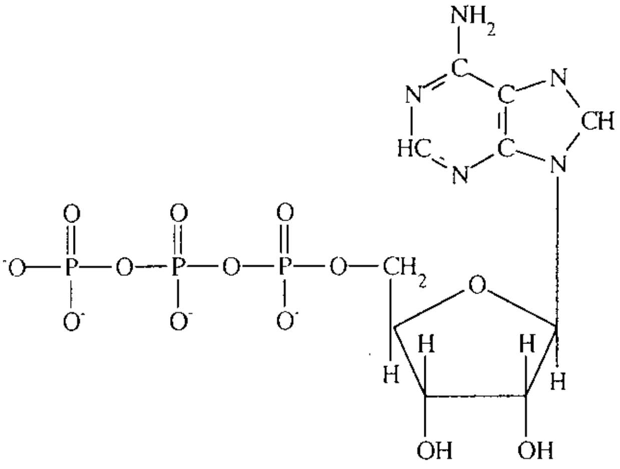
α–D-Glucose 6-phosphate (G6P)



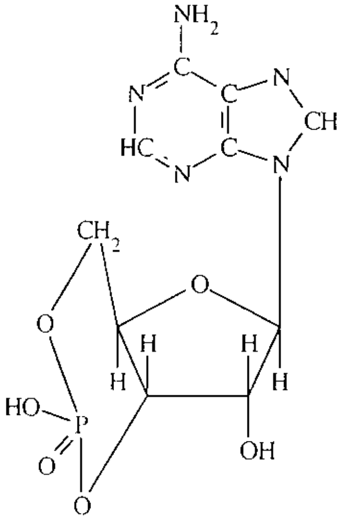
α–D-Glucose 1-phosphate (G1P)



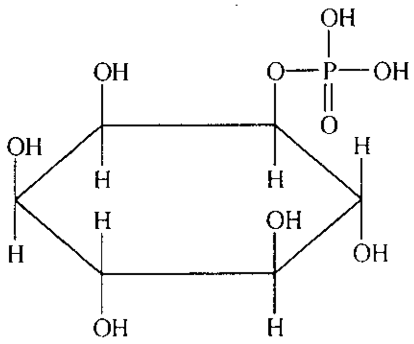
Glycerophosphate (GYP)



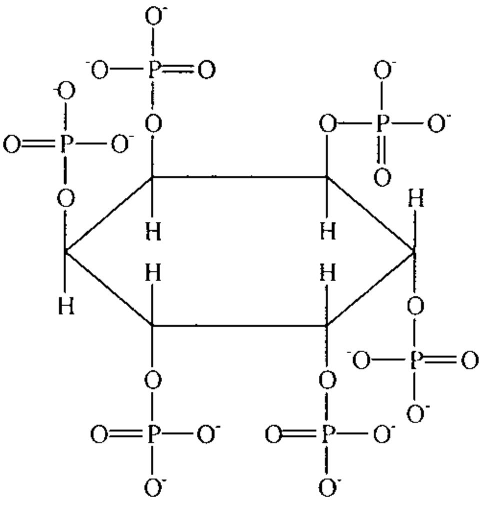
Adenosine 5' triphosphate (ATP)



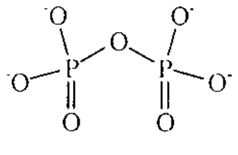
Adenosine 3':5'-cyclic monophosphate (AMP)



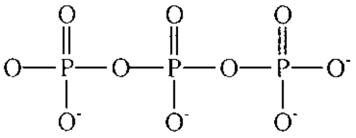
myo-Inositol monophosphate (IMP)



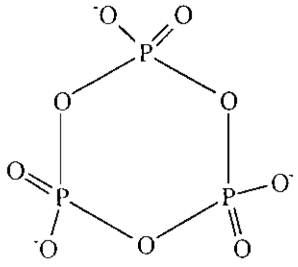
Inositol hexaphosphate (IHP)



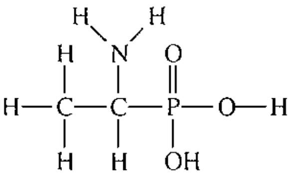
Pyrophosphate (PYP)



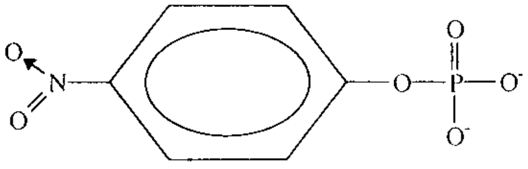
Tripolyphosphate (TPP)



Trimetaphosphate (TMP)



2-Aminoethylphosphonic acid (AEP)



p-Nitrophenol phosphate (NPP)

TABLE 3. The maximum P determined by the three Soluble Reactive Phosphorus methods (at a 95 % CL) expressed as a % of the Total Dissolved Phosphorus determined for the compounds.

Compound	Murphy &Riley maximum P determined/ % of TDP	Flow-Injection Analysis (FIA) maximum P determined/ % of TDP	Anion Exchange Chromatography maximum P determined/ % of TDP
G1P	1.2	7.1	2.2
G6P	0.6	4.6	1.0
ATP	0.3	3.5	0.2
NPP	1.2	5.5	5.7
AMP	0.4	3.4	1.9
GYP	0.2	3.1	0.6
IMP	2.9	7.8	2.6
IHP	0.2	8.2	1.0
AEP	0.6	1.4	1.0
PYP	0.4	2.6	0.4
TPP	1.1	5.6	1.0
TMP	0.2	4.3	0.7

TABLE 4. Recoveries from the synthetic compounds by the measurement of Total Dissolved Phosphorus (TDP) and Dissolved Organic Carbon. The standard deviations are shown in brackets. Standard Error values are given at a 95 % confidence limit.

Compound	DOC/ mg dm^{-3}	Recovery of DOC (%)	TDP/ µmol dm^{-3}	Recovery of TDP (%)
G1P	0.83	95.9	12.12 (0.02)	101.0 ± 0.5
G6P	0.87	100.2	12.37 (0.11)	103.1 ± 2.6
ATP	0.53	110.1	12.19 (0.23)	101.6 ± 5.3
NPP	0.88	101.3	12.23 (0.09)	101.9 ± 2.1
AMP	1.43	99.2	12.21 (0.06)	101.8 ± 1.4
GYP	0.41	94.2	12.28 (0.02)	102.3 ± 0.5
IMP	2.43	93.7	11.69 (0.33)	97.4 ± 7.6
IHP	0.15	100.9	10.27 (0.02)	85.6 ± 0.5
AEP	0.24	84.0	11.91 (0.27)	99.2 ± 6.3
PYP			20.03 (0.04)	99.5 ± 0.5
TPP			11.72 (0.03)	97.7 ± 0.8
TMP			11.85 (0.10)	98.8 ± 2.2

TABLE 5. Sample stability. The SRP determined by flow injection analysis after 72 h storage at ambient temperature. The standard deviations are shown in brackets. Standard Error values are given at a 95 % confidence limit. The mean value of 5 replicate determinations within 4 h of sample preparation was < 0.32 μmol dm^{-3}.

Compound	FIA-P/ μmol dm^{-3}	FIA-P/ % of TDP
G6P	0.41 (0.04)	3.3 ± 1.4
NPP	1.82 (0.09)	14.9 ± 3.1
GLP	1.72 (0.14)	13.9 ± 4.8
PYP	2.02 (0.06)	10.2 ± 1.3
TPP	0.83 (0.03)	6.9 ± 1.2
TMP	0.85 (0.05)	7.2 ± 1.8

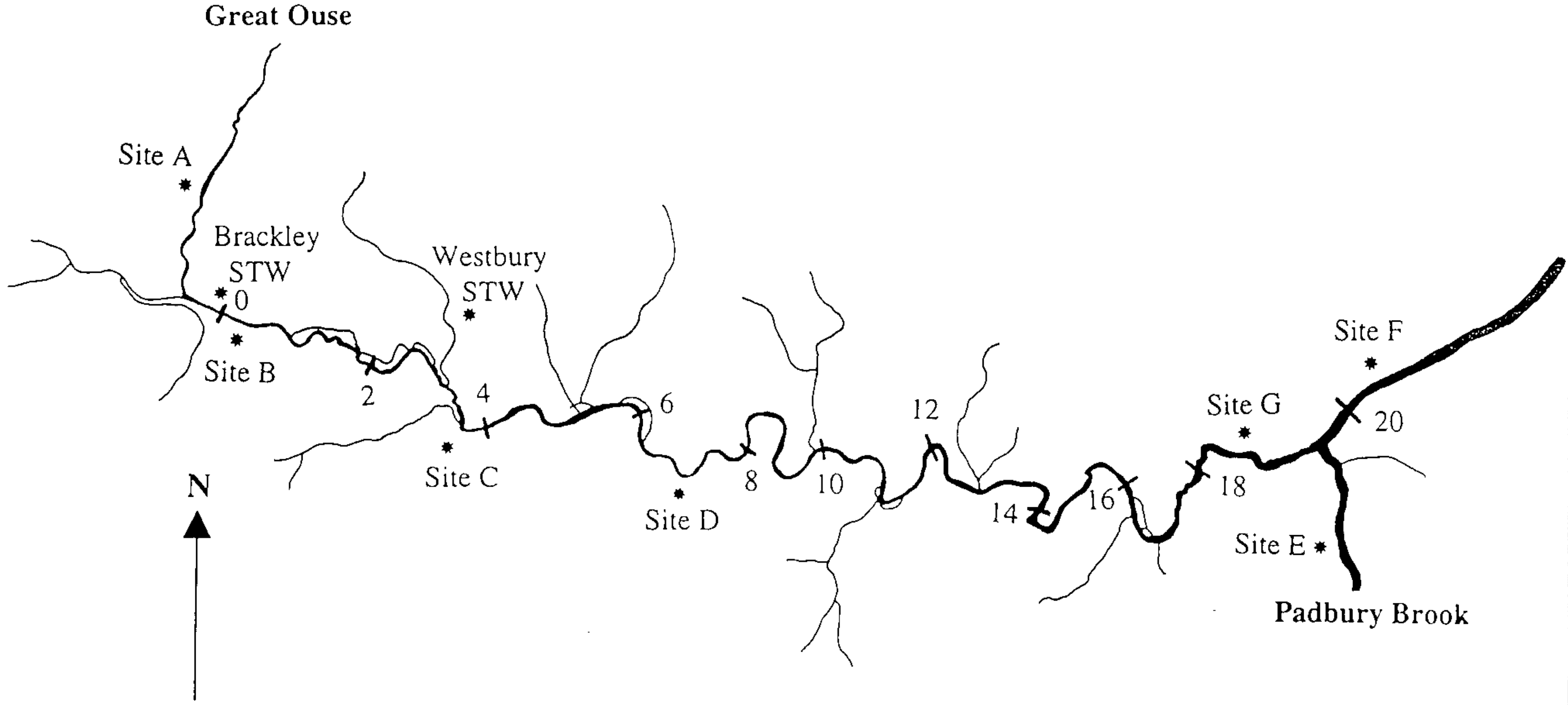
5.0 REVIEW OF RESEARCH ON THE GT. OUSE

5.1 Nutrient Water Chemistry

The field visits involved the chemical measurements that are listed in section 3.2. These results were used in a chemical speciation program developed in Mathcad to calculate the importance of ion-pairs in solution, the ionic strength, partial pressure of CO_2, pCO_2, cation and anion sum and thus charge-balance as well as the supersaturation with respect to various calcium containing minerals such as calcite, hydroxyapatite, HAP, octacalcium phosphate, OCP, dicalcium phosphate dihydrate, DCPD and tricalcium phosphate, TCP (Fig.1). The charge-balance gives an estimate of the reliability of the chemical data as agreement between the cation and anion sums are expected to be better than 5 % unless important determinands have been omitted, the solution contains high concentrations of polyelectrolytes such fulvic acids or there is an error in the chemical analysis.

The results of the chemical analysis are shown in Table 6 for sites A-D shown on the attached map, together with information collected during the field visits, e.g. pH, temperature, conductivity, dissolved oxygen and water discharge. In addition, the concentration of phosphorus in the suspended matter (μmol g^{-1}) is calculated from the concentration of suspended solids and particulate phosphorus concentration (TP-TDP). The results are summarised as follows:

1. The water discharge on the winter sampling date was highest, with the spring sampling slightly lower but well above the discharge measured in the summer and autumn visits of 1995. As shown during the summer and autumn sampling, the discharge remained approximately constant between sites B and D indicating negligible inputs from minor tributaries in this section. During the winter visit, the discharge did increase from 0.99 to 1.44 m^3 s^{-1} between sites B and D. The increase observed during all visits between the flows at A and B is caused by a tributary entering in the section upstream of the STW.


Great Ouse
Site A
Brackley
STW
0
Site B
2
Westbury
STW
4
Site C
6
Site D
8
10
12
14
16
Site G
18
Site F
20
Site E
Padbury Brook
N

2. Calcium and nitrate concentrations varied little, either temporally or spatially, indicating the lack of impact of the Brackley STW discharge on these chemicals. The dissolved calcium concentrations are particularly high and well above concentrations of 2-2.5 mmol dm^{-3} often measured in chalk streams in the south of England.

3. The STW had no noticeable impact on the dissolved oxygen concentrations. The carbon dioxide concentrations (Table 7) calculated by the speciation program, are lower during the spring sampling in comparison to the other visits. This is consistent with photosynthetic activity and the depression in silicon concentrations (see below).

4. The dissolved silicon concentrations were found to be similar in the autumn and winter but depressed in the spring and slightly elevated in the summer. The low concentrations measured in the spring show a trend of decreasing concentration downstream which is consistent with the uptake of silicon by benthic diatoms. It is not clear why the concentrations are higher in the summer, although the results are consistent with a low dilution of a point input near site B and uptake by the bed-sediment between site B and C. One of the other rivers in this study also shows similar behaviour throughout the year with an increase dissolved silicon immediately downstream of the main STW inflow and decrease in concentration at downstream sites.

5. The main impact of the STW located just upstream of site B is on the phosphorus fractions, in particular the SRP concentration. The change in SRP concentration downstream of the Brackley STW is greatest during the summer and autumn visits when the river flow was relatively low. The partition of each of the P fractions: SRP, dissolved hydrolysable P (TDP-SRP, mainly organophosphorus compounds) and particulate P (TP-TDP), was similar at each of the sites during each visit. The percentage of SRP was slightly lower and organophosphorus slightly higher at the upstream site A in comparison with the other sites. However, the major differences in the P fractionation were seasonal with a higher percentage of SRP in the river at lower flows, when the effluent inputs were less diluted. In such conditions, the percentage of the particulate P fraction was lower than during the autumn and winter visits. The concentration of P in the particulates, decreased on passage downstream during the winter and spring visits but no systematic trends were noted for the other visits.

6. The suspended solid concentration of all the samples were low (<12.5 mg dm^{-3}) and showed no systematic trend along the study reach. The concentrations found in autumn sampling were lower than the concentrations measured in the summer in similar low flow conditions.

7. The charge-balances (Table 7) are excellent with only two above 5 %. The results from the chemical speciation program show that the river waters are supersaturated with respect to calcite and calcium phosphates at certain times of the year (Fig. 1). This means that it is thermodynamically possible for these minerals to form in the river when the appropriate saturation index, SI>0. The lowest supersaturations with respect to calcite were measured in the winter when the P_{CO_2} was relatively high and the water temperature low. The greatest supersaturations with respect to calcite were found in the spring. At site B, SI=1.47 at this time which is high enough to promote heterogeneous precipitation (House and Tutton, 1982). If calcite does precipitate, inorganic P will be coprecipitated and included in the mineral lattice of calcite, i.e. this P is unavailable to plants and

algae (House, 1990; Hartley *et al.*, 1995). The process is effectively a self-cleaning mechanism reducing biological available P in water. Generally, two factors determine the importance of coprecipitation in streams:

a). The concentration of SRP; this influences the inhibition of crystal growth of calcite. As the SRP concentration increases, the pH needed to initiate precipitation increases, i.e. the initial supersaturation with respect to calcite increases.

b). The abundance and activity of algal biofilms associated with gravel, stones and macrophytes in the river. Hartley *et al.*, (1995; 1996) have shown the importance of algae and algal biofilms in promoting calcite precipitation in the presence of SRP.

8. It is also possible that other calcium P minerals will form such as octacalcium phosphate (OCP), tricalcium phosphate (TCP) and hydroxyapatite (HAP). In fact the formation of HAP has been suggested as a major control on the concentration of SRP in rivers. The Gt. Ouse is supersaturated with respect to all of these minerals at some of the sampling times. However, the high supersaturations with respect to HAP are unlikely to lead to its formation because precursor mineral phases such as OCP and TCP are more soluble and grow faster than HAP. It is possible that either OCP or TCP form, particularly in the summer and autumn, when the supersaturations are highest (see Table 7, where positive values of SI indicate supersaturation with respect to the mineral phase).

TABLE 6. Summary of the nutrient and major-ion concentrations in the Gt. Ouse obtained during the quarterly field visits. Sites are: A: upstream of the main STW inflow at NGR SP595368, B: immediately downstream of the main STW inflow at NGR SP602358. Sites C and D are downstream at approximately 5 and 8 km from the main STW inflow at NGR's SP627346 and SP652341 respectively. SS is the suspended solids concentration (mg dm^{-3}) and PP the concentration of phosphorus associated with the suspended solids (μmol dm^{-3}). The ratio of PP/SS is the concentration of phosphorus in the suspended material normalised with respect to the suspended mass, i.e. μmol g^{-1} (dry wt.). Symbol M means mol dm^{-3}.

Date: 9.10.95			**WINTER**		
SITE	A	B	C	D	Mean
T/ ^{0}C	6.8	7.1	6.4	7.0	6.8
pH	7.24	7.46	7.71	7.79	7.55
Conductivity/ μS cm^{-1}	756.0	1345.0	620.0	773.0	873.5
DO/ %	99.0	98.0	93.0	88.0	94.5
Ca/ mM	3.66	3.59	3.54	3.58	3.59
nitrate/mM	0.79	0.81	0.79	0.82	0.80
silicon/μM	139	128	125	120	128
SRP/μM	2.08	2.67	4.68	2.35	2.95
TDP/μM	2.82	3.12	6.72	3.27	3.98
TP/μM	3.18	3.82	7.05	3.53	4.40
TDP-SRP/μM	0.74	0.45	2.04	0.92	1.04
PP/μM	0.36	0.70	0.33	0.26	0.41
SS/mg dm^{-3}	4.6	5.6	4.0	6.4	5.2
PP/SS/μmol g^{-1}	78.26	125.00	82.50	40.63	81.60
discharge/ m^{3}s^{-1}	0.62	0.99	1.13	1.44	-
Date: 27.3.95			**SPRING**		
SITE	A	B	C	D	Mean
T/ ^{0}C	7.5	4.4	4.4	7.6	6.0
pH	8.49	8.23	8.26	8.61	8.40
Conductivity / μS cm^{-1}	835	893	845	820	848
DO/ %	113	94	93	116	104
Ca/ mM	3.82	3.77	3.79	3.62	3.75
nitrate/mM	0.84	0.99	0.93	0.94	0.93
silicon/μM	93	83	62	62	75
SRP/μM	3.1	8.4	3.8	4.5	5.0
TDP/μM	3.2	11.3	5.1	6.0	6.4
TP/μM	1.9	13.1	5.8	7.0	6.9
TDP-SRP/μM	0.0	2.9	1.2	1.5	1.4
PP/μM	ND	1.8	0.8	1.1	1.2
SS/mg dm^{-3}	6.3	5.7	4.0	7.2	5.8
PP/SS/μmol g^{-1}	ND	310.5	187.5	145.8	214.6
discharge/m^{3}s^{-1}	0.2	0.8	0.8	1.1	-

TABLE 6. Continued for the summer and autumn field visits. Legend as on previous page.

Date: 10.7.95			**SUMMER**		
SITE	A	B	C	D	Mean
T/ ^{0}C	19.6	20.3	20.8	21.3	20.5
pH	8.06	7.70	8.20	7.87	7.96
Conductivity / μS cm^{-1}	811	981	871	882	886
DO/ %	106	93	138	101	110
Ca/ mM	3.8	3.7	3.6	3.7	3.7
nitrate/mM	0.5	1.2	0.8	0.9	0.8
silicon/μM	147.8	206.2	167.7	170.2	173.0
SRP/μM	5.3	72.2	33.4	31.6	35.6
TDP/μM	6.4	82.5	38.0	36.0	40.7
TP/μM	7.0	84.5	39.0	37.0	41.9
TDP-SRP/μM	1.0	10.3	4.6	4.4	5.1
PP/μM	0.7	2.0	1.0	1.0	1.2
SS/mg dm^{-3}	4.1	12.5	4.9	6.6	7.0
PP/SS/μmol g^{-1}	158.5	160.0	204.1	151.5	168.5
discharge/ m^{3}s^{-1}	0.05	0.16	0.14	0.15	-
Date: 15.11.95			**AUTUMN**		
SITE	A	B	C	D	Mean
T/ ^{0}C	11.0	11.9	11.1	11.1	11.3
pH	8.09	8.19	8.26	8.19	8.18
Conductivity/ μS cm^{-1}	877	909	830	922	885
DO/ %	76	79	81	87	81
Ca/ mM	4.1	3.6	3.6	3.7	3.7
nitrate/mM	0.8	0.6	0.7	0.7	0.7
silicon/μM	154	140	141	140	144
SRP/μM	3.2	12.3	12.6	16.5	11.2
TDP/μM	2.9	16.1	15.5	19.2	13.4
TP/μM	5.0	16.3	16.0	19.4	14.2
TDP-SRP/μM	ND	3.8	2.9	2.7	3.1
PP/μM	2.1	0.2	0.5	0.2	0.7
SS/mg dm^{-3}	2.1	1.6	1.4	2.3	1.9
PP/SS/μmol g^{-1}	1000.0	106.2	385.7	69.6	390.4
discharge/ m^{3}s^{-1}	0.1	0.2	0.3	0.3	-

FIGURE 1. Frequency of occurrence of saturation index values for samples from the Gt. Ouse for calcite and calcium phosphate minerals: hydroxyapatite, HAP, octacalcium phosphate, OCP, and tricalcium phosphate, TCP. Positive values indicate that the water is supersaturated with respect to the mineral phase whilst negative values indicate undersaturation. Key: Saturation index, SI=log(IAP/K_{sp}) where IAP is the ion-activity product and K_{sp} the thermodynamic solubility product for the mineral.

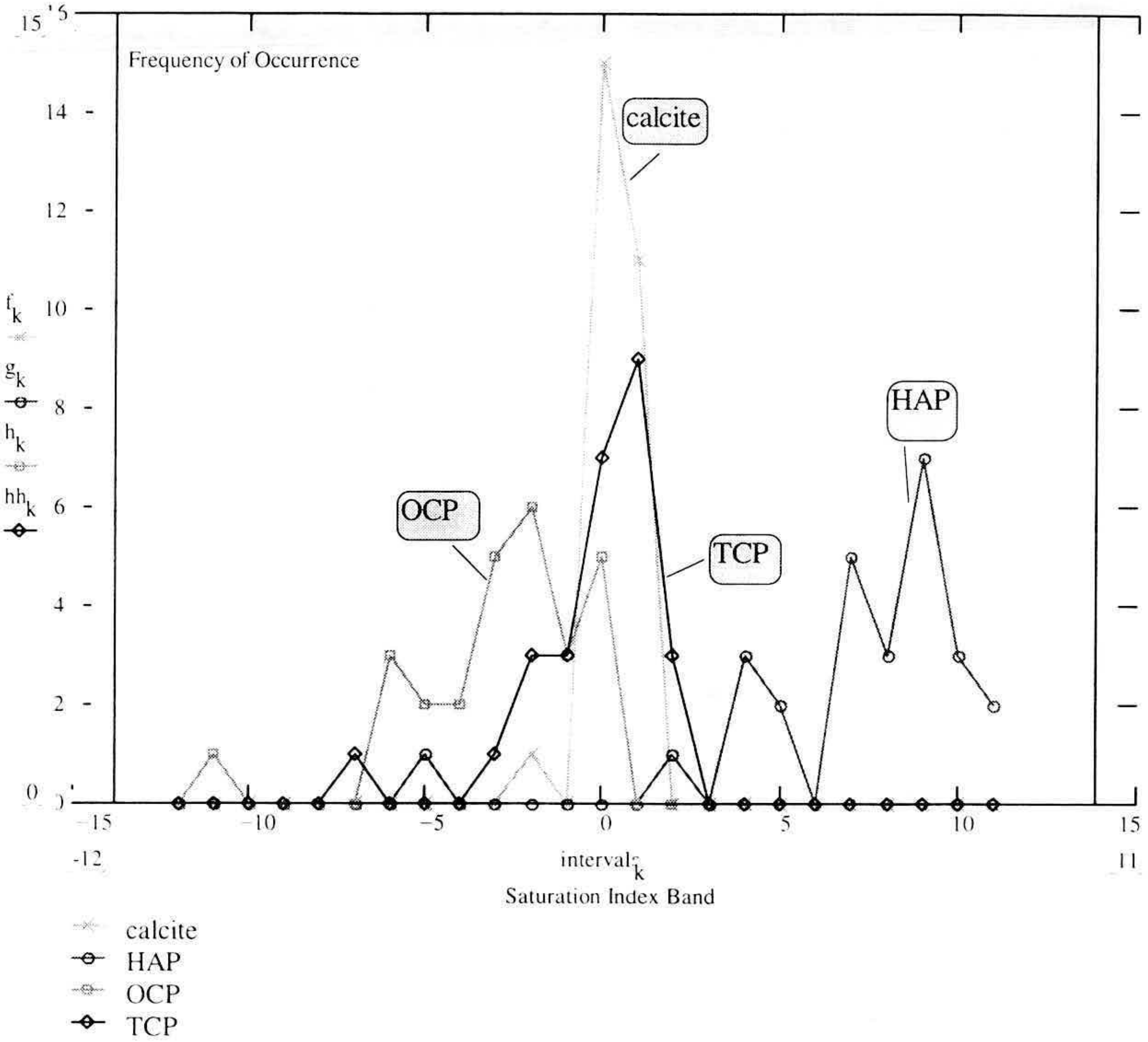


TABLE 7. Saturation of the Gt, Ouse river water with respect to calcite and calcium phosphate minerals together with the calculated ionic strength and partial pressure of carbon dioxide (pCO2). The charge balance, expressed as a %, is calculated from the major-ion analysis and chemical speciation calculations and is given by: $100*(\Sigma_+ - \Sigma_-)/0.5*(\Sigma_+ + \Sigma_-)$ where Σ_+ and Σ_- are the sum of the cations and anions respectively.

Date	9.1.95							
Site	SI (calcite)	SI(HAP)	SI(DCPD)	SI(OCP)	SI(TCP)	I/ M	pCO2/ matm	charge balance
A	0.09	2.84	-2.33	-5.79	-2.36	0.013	12.6	0.3
B	0.31	4.19	-2.17	-4.87	-1.61	0.013	7.8	1.2
C	0.56	5.93	-1.90	-3.61	-0.60	0.013	4.4	1.0
D	0.60	5.46	-2.19	-4.26	-0.98	0.013	3.3	0.6
E	0.89	8.30	-1.63	-2.01	0.72	0.014	1.7	2.1
F	0.99	7.97	-1.84	-2.49	0.46	0.014	1.4	0.7
Date	27.3.95							
Site	SI (calcite)	SI(HAP)	SI(DCPD)	SI(OCP)	SI(TCP)	I/ M	pCO2/ matm	charge balance
A	1.08	8.62	-1.65	-1.90	0.89	0.014	1.33	3.5
B	1.13	7.75	-1.98	-2.84	0.29	0.013	1.3	2.0
C	1.47	9.51	-1.94	-1.86	1.17	0.013	0.55	3.4
D	1.20	9.70	-1.61	-1.25	1.41	0.013	0.91	0.5
E	1.10	7.23	-2.25	-3.43	-0.14	0.014	1.36	3.1
F	0.19	4.37	-2.36	-5.01	-1.63	0.008	3.34	1.7
Date	10.7.95							
Site	SI (calcite)	SI(HAP)	SI(DCPD)	SI(OCP)	SI(TCP)	I/ M	pCO2/ matm	charge balance
A	0.67	10.73	-0.69	0.73	2.28	0.015	4.4	1.9
B	1.21	11.66	-1.05	0.66	2.57	0.015	1.57	5.4
C	0.91	10.44	-1.04	0.06	1.96	0.014	3.38	1.3
D	1.21	11.55	-1.12	0.51	2.45	0.014	1.63	0.3
E	0.80	10.17	-0.99	0.00	1.85	0.014	4.31	1.6
F	0.73	8.71	-1.33	-1.25	0.96	0.014	5.21	2.2
Date	15.11.95							
Site	SI (calcite)	SI(HAP)	SI(DCPD)	SI(OCP)	SI(TCP)	I/ M	pCO2/ matm	charge balance
A	1.08	9.66	-1.46	-1.02	1.45	0.015	1.41	2.7
B	1.17	9.87	-1.46	-0.91	1.56	0.014	1.32	0.4
C	1.10	9.93	-1.34	-0.71	1.65	0.016	1.54	2.3
D	0.80	9.03	-1.38	-1.22	1.18	0.016	1.94	0.7
E	0.82	9.30	-1.27	-0.92	1.37	0.017	2.11	6.2
F	0.81	7.65	-1.76	-2.48	0.31	0.014	2.56	0.2

TABLE 8. Comparison of the bed-sediment properties for the main sites on the Gt. Ouse. TP: total phosphorus content, TCa: total calcium content, TFe: total iron content, BAP: biologically available phosphorus by iron oxide stripping, OM: organic matter content by combustion, EPC$_0$: equilibrium phosphorus concentration after 24 h, K$_d$: distribution coefficient or adsorption constant, ni: native phosphorus concentration determined from the sorption isotherm.

Date: 9.1.95			**WINTER**		
	A	B	C	D	MEAN
OM/%	3.62	3.73	4.08	2.55	3.50
TP/μmol g^{-1}	13.95	17.57	13.94	9.12	13.65
TCa/μmol g^{-1}	2163	2361	3152	2299	2493
TFe/μmol g^{-1}	469.3	481	423.8	649	506
BAP/μmol g^{-1}	0.92	1.83	1.51	1.11	1.34
EPC$_0$/μM	1.1	2.46	4.51	2.6	2.7
Kd/dm^3 kg^{-1}	ND	151.1	79.5	182.0	137.5
ni/μmol g^{-1}	ND	0.37	0.36	0.47	0.40
Date: 27.3.95			**SPRING**		
	A	B	C	D	MEAN
OM/%	2.56	2.97	1.96	2.37	2.47
TP/μmol g^{-1}	2.84	4.31	4.98	3.87	4.0
TCa/μmol g^{-1}	1320	2407	2756	1336	1955
TFe/μmol g^{-1}	480.5	485.8	785.5	212.6	491.1
BAP/μmol g^{-1}	1.49	2.51	1.65	2.23	1.97
EPC$_0$/μM	0.85	2.29	3.7	2.78	2.41
Kd /dm^3 kg^{-1}	193.5	240.5	55.5	96.3	146.5
ni/μmol g^{-1}	0.17	0.55	0.21	0.27	0.30
Date: 10.7.95			**SUMMER**		
	A	B	C	D	MEAN
OM/%	3.77	2.78	2.61	2.05	2.80
TP/μmol g^{-1}	43.5	26.91	22.45	25.87	29.68
TCa/μmol g^{-1}	3014	4098	4580	4605	4074
TFe/μmol g^{-1}	286	456	437	465	411
BAP/μmol g^{-1}	0.65	1.25	1.85	1.11	1.22
EPC$_0$/μM	0.33	1.92	5.67	3.4	2.83
Kd / dm^3 kg^{-1}	524.6	203	103.2	90.6	230.4
ni/μmol g^{-1}	0.17	0.39	0.59	0.31	0.36

Date: 15.11.95			AUTUMN		
	A	B	C	D	MEAN
OM/%	7.31	10.22	6.96	7.59	8.02
TP/μmol g^{-1}	15.37	33.75	29.27	49.33	31.93
TCa/μmol g^{-1}	4123	2976	3883	3346	3582
TFe/μmol g^{-1}	490.4	460.2	827.5	674.7	613.2
BAP/μmol g^{-1}	0.76	1.83	1.17	1.15	1.23
EPC$_0$/μM	1.65	1.07	9.88	3.79	4.10
Kd/dm^3 kg^{-1}	241.8	610.6	60.5	122.2	258.8
ni/μmol g^{-1}	0.40	0.65	0.60	0.46	0.53
			SPRING 1994		
	A	B	C	D	MEAN
OM/%	2.36	2.1	2.09	2.57	2.28
TP/μmol g^{-1}	19.43	39.38	17.07	23.56	24.86
TCa/μmol g^{-1}	ND	ND	ND	ND	ND
TFe/μmol g^{-1}	ND	ND	ND	ND	ND
BAP/μmol g^{-1}	0.62	1.43	1.13	1.2	1.10
EPC$_0$/μM	0.41	3.53	4.78	2.93	2.91
Kd/dm^3 kg^{-1}	312.4	924.4	736.9	832.9	701.7
ni/μmol g^{-1}	0.13	0.33	0.35	0.24	0.26

5.2 Sediment Chemistry

The results of the analysis of the bed-sediments for organic matter (OM), total P, Ca and Fe after digestion, BAP by iron oxide stripping and EPC$_0$, K$_d$ and n$_i$ from sorption measurements, are collected in Table 8. The results are summarised as follows:

1. The amount of organic matter is low (< 5 %) apart from the values measured during the autumn sampling when a result of >10 % was obtained for the sediment from site B. There is no discernible trend along the river or noticeable increase at site B caused by effluent discharge.

2. The total phosphorus concentrations in the sediment (TP) measured after combustion and acid digestion are generally much lower than the values calculated for suspended solids (PP in μmol g^{-1} in Table 6). The highest values recorded were in the autumn with a mean for all sites of 31.9 μmol g^{-1} which compares with a mean of 390.4 μmol g^{-1} measured in the suspended sediments at the same time (Table 6). The TP concentrations in the spring 1995 are very low, i.e. a mean of 4.0 (SD) μmol g^{-1} for all the sites compared with 13.6 (SD) measured in the previous winter sampling. The results for the spring 1994 do not exhibit this depression in concentration (mean of 24.9 (SD) μmol g^{-1}). There is a lot of variability in the TP concentrations but little difference between site A (upstream of the STW) and sites C and D downstream. Site B has sediment with a slightly higher TP, i.e. mean of 24.4 (12.9) μmol g^{-1} at B compared with 19.0(15.) μmol g^{-1} at site A, although the difference is not significant (independent t-test, 95 % CL). *The results therefore show that the TP content of the surface sediments are not significantly impacted by the STW inputs.* The sediment

from site A, upstream of the STW, contains similar concentrations of TP to the other sites indicating that P from the STW is not accumulating in the surface sediments (<5 cm).

3. The total calcium concentrations are much greater than the phosphorus or iron with values as high as 4600 μmol g^{-1}, i.e. 46 % by weight expressed as $CaCO_3$ solid. This is confirmed by x-ray diffraction analysis of sediment from site B on 27.8.95 where the calcite content was estimated as 51 % by mass (report RL/T11059J1/4, p 17). At each sampling visit, the highest concentration of calcium was measured at site C (see Table 8 and Fig. 3a). It is also evident from the seasonal data that the highest concentrations of calcium at each site were measured in the summer sampling. This suggests that mineralisation reactions involving calcium occur in the sediments during the early spring to summer period, e.g. the formation of calcite and/or TCP/OCP (see Table 8). The formation of calcite will lead to a precipitate which incorporates P into the crystal lattice such that the molar ratio of [Ca]/[P] in the solid is between 200 and 2500 depending on the concentration of SRP in solution (House *et al.*, 1986). At high SRP concentrations in the Gt. Ouse, the molar ratio is expected to be close to 200 (House *et al.*, 1986; Kleiner, 1988). This leads to a concentration in the precipitate of approximately 50 μmol g^{-1}. If calcium phosphate, TCP, is formed as a pure mineral, the concentration of P will be approximately 6600 μmol g^{-1}.

As shown in Table 9, if the difference in the calcium content of the sediment between the early spring and summer sampling is the result of the *in-situ* precipitation of calcite, either abiotically or in conjunction with biofilms, the change in the TP content of the sediment may be predicted if it is assumed that no other processes contribute. The results of such a calculation are shown in Table 9. The predicted change in TP is less than measured in the surface sediments but of the correct order of magnitude. The agreement between the predicted and measured TP concentrations improve downstream from site A (see Table 9). Sites B to D have similar supersaturations with respect to calcite growth and it is possible that the higher concentrations of SRP at sites B and C affect the amount of precipitate (because of the inhibiting effect of SRP on calcite growth). Another possibility is that settling of suspended material containing a relatively high concentration of P occurs at sites B and to a lesser extent at site C and D thus causing an increase in the P content of the sediment relative to the calcium content. There is some evidence for this from samples of suspended solids collected in the summer survey when the concentrations increased from 4.1 to 12.5 mg dm^{-3} between sites A and B and then dropped to 4.9, 6.6 mg dm^{-3} at sites C and D respectively. The concentrations of calcium in the sediment decreased between the summer and autumn sampling, possibly as a result of spates flushing the surface sediment or through the dissolution of calcite during periods of high P_{CO_2} at night. The latter appears more likely because the TP values remain high, indicating that P is retained in the sediment rather than transported with suspended sediments.

4. The total iron concentrations are also variable but are much lower than the calcium concentrations. There is evidence for the loss of iron from the sediments between the spring and summer at site A and C, possibly as a result of reducing conditions developing in the top 5 cm layer. Site B shows less seasonal variability than the other sites (CV =3.2 % in contrast to site D with a CV of 43%). The decreases in iron content are not accompanied by losses of TP from the sediments collected in the spring and summer

TABLE 9. Comparison of the changes in total calcium and P in the sediments sampled in the spring and summer of 1995 at the four Gt. Ouse sites. ΔP(coppt.) is the predicted amount of P

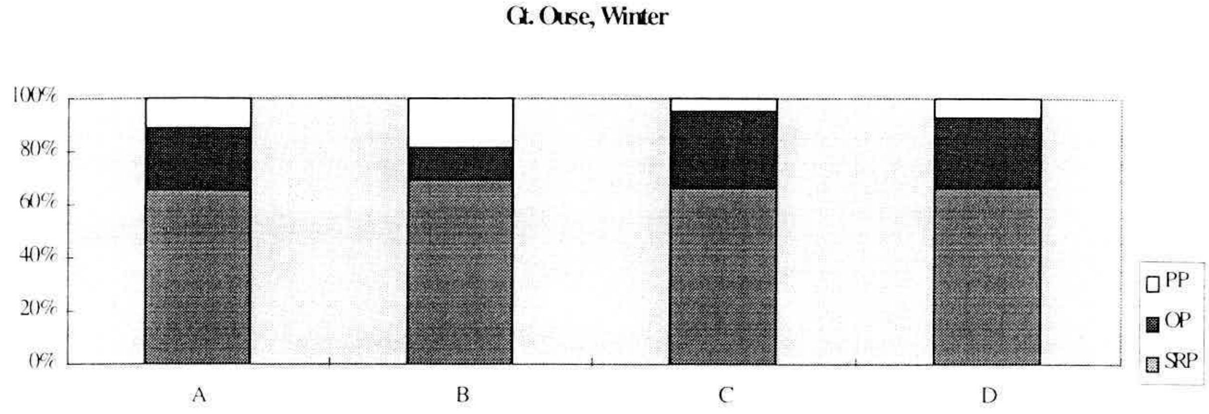
coprecipitated with calcite assuming a mole ratio of Ca:P of 1:200 (House *et al.*, 1986) in the precipitate and Δ TP is the measured change in the P content of the sediments between the spring and summer sampling. The percentage: ΔP/ Δ TP, gives the agreement between the predicted increase in P content of the solid and the measured value. The best agreement is at the downstream site D.

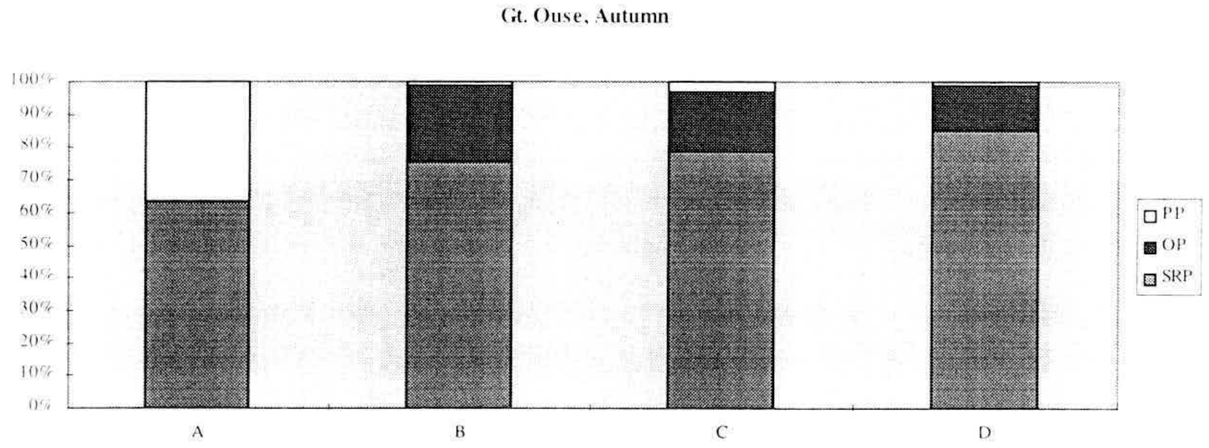
Site	A	B	C	D
TCa (spring)/ μmol g^{-1}	1320	2407	2756	1336
TCa(summer)/ μmol g^{-1}	3014	4098	4580	4605
change in TCa/ μmol g^{-1}	1694	1691	1824	3269
ΔP(coppt.)/ μmol g^{-1}	8.5	8.5	9.1	16.3
Δ TP/ μmol g^{-1}	40.7	22.6	17.5	22.0
ΔP/ Δ TP/ %	21	37	52	74

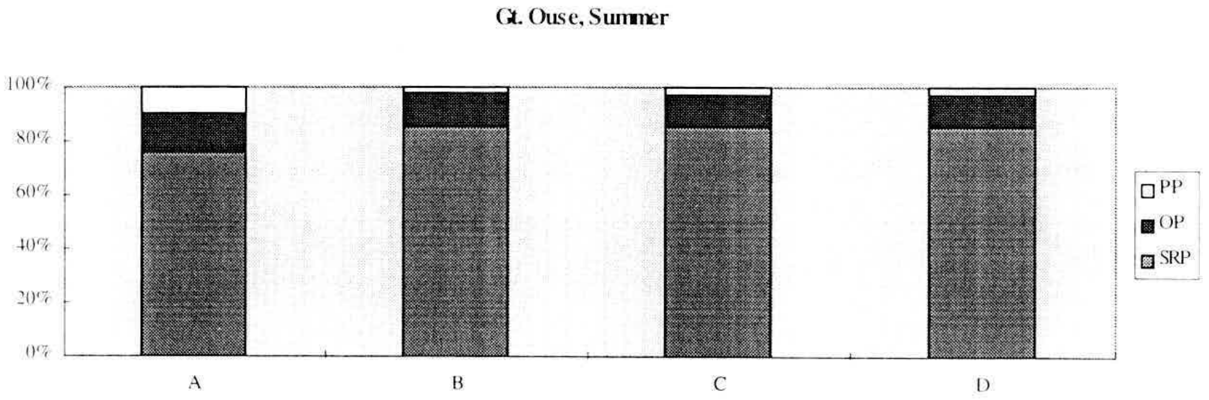
5.0 There is a difference between the mean EPC_0's (independent t-test, 5% confidence limit) of: (a) sites A and B, C, D; (b) site B and C; (c) site C and D but not between sites B and D. Site A, which is upstream of the Brackley STW, has sediments with the lowest EPC_0 on all occasions apart from 15.11.95 when the EPC_0 for site B is slightly lower. This is consistent with the lower SRP concentrations measured at this site. The sediment from site C has the highest EPC_0 on all occasions and also shows a poor correlation with the SRP concentration in the overlying water at the time of sampling. The high EPC_0 is not accounted for by differences in the particle size distributions.

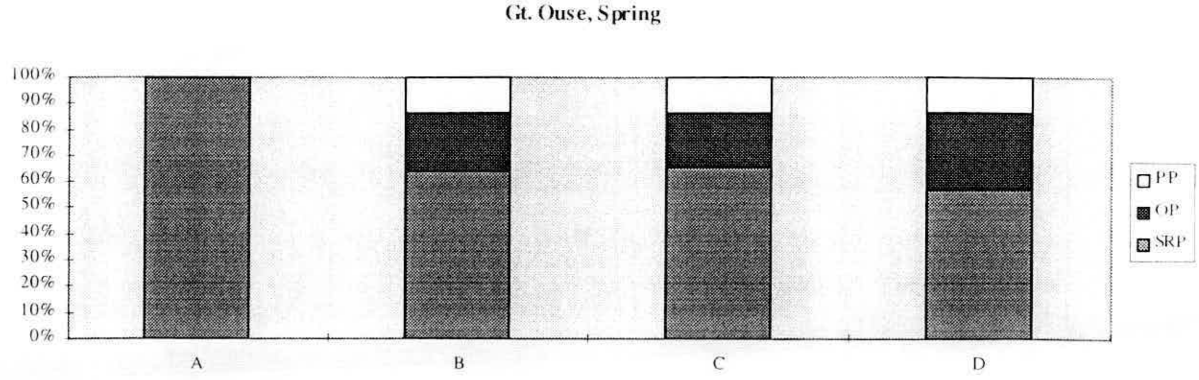
6.0 The relationship between EPC_0 and SRP for the site visits is demonstrated in Fig. 4. The results show a general trend of increasing EPC_0 with increasing SRP concentration but the correlation is relatively poor (R^2=0.18). If data points with SRP> 5.0 μmol dm^{-3} are excluded, the correlation is better R^2=0.58) as shown in Fig.5. The data for the winter sampling on 9.1.95 illustrate the best agreement between SRP and EPC_0 (regression slope of 0.79 and R^2=0.88). This suggests that the sediment section sampled (< 5 cm depth) does not respond quickly to transient changes in SRP in the water. It is probable that the top surface layer of sediment, e.g. 1-10 mm, does respond quickly and reach an EPC_0=SRP. Subsequent changes in SRP in the deeper sediments depend on diffusion and generation of SRP in the deeper sediment.

FIGURE 2. Comparison of the seasonal distribution of phosphorus fractions in the Gt. Ouse. PP: particulate P, OP: organo-phosphorus compounds and SRP: soluble reactive phosphorus.


Gt. Ouse, Winter


Gt. Ouse, Autumn


Gt. Ouse, Summer


Gt. Ouse, Spring
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
A
B
C
D
PP
OP
SRP

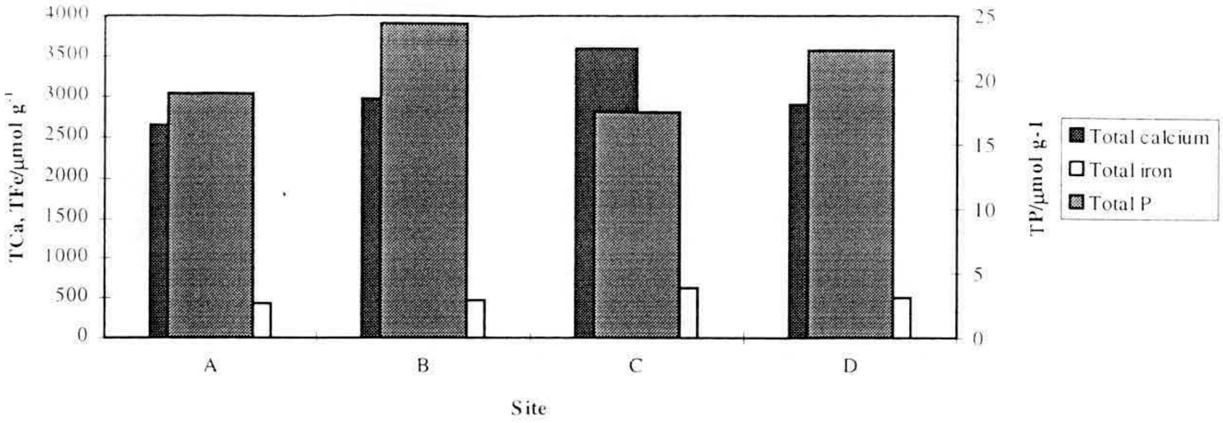


FIGURE 3a Comparison of the total P, calcium and iron obtained for digested river bed-sediments from the four Gt. Ouse sites. Values are the means from the quarterly sampling.

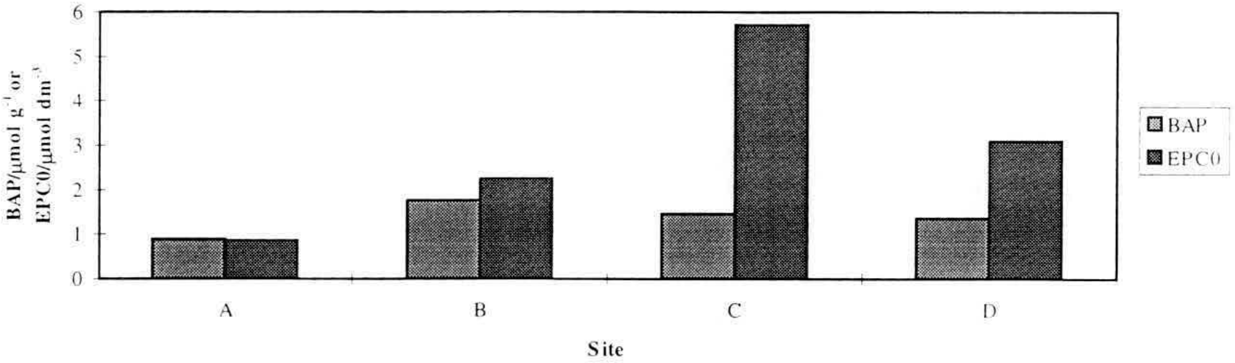


FIGURE 3b Comparison of mean EPC_0 and BAP results for the four sites on the Gt. Ouse. The EPC_0 was determined from sorption experiments and BAP using the iron oxide stripping method.

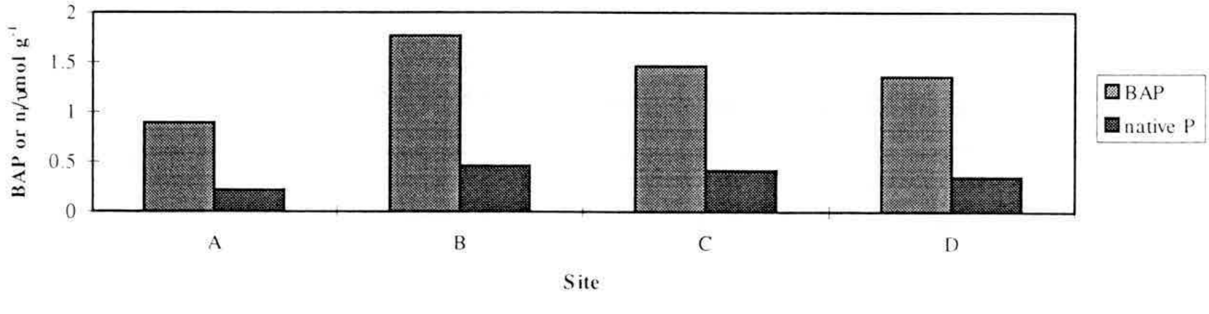


FIGURE 3c Comparison of the mean BAP and native P (n_i) results for the four Gt. Ouse sites.

FIGURE 4 . Comparison of the EPC_0 of the bed sediments with the SRP concentration in the river water at the time of sampling. When the EPC_0 of the sediment < SRP concentration, there will be a net uptake of P. In contrast, when the EPC_0 > SRP, the net flux is from the sediment to the overlying water. One point from sampling site B on 10.7.95 is omitted because of the exceptionally high SRP concentration.

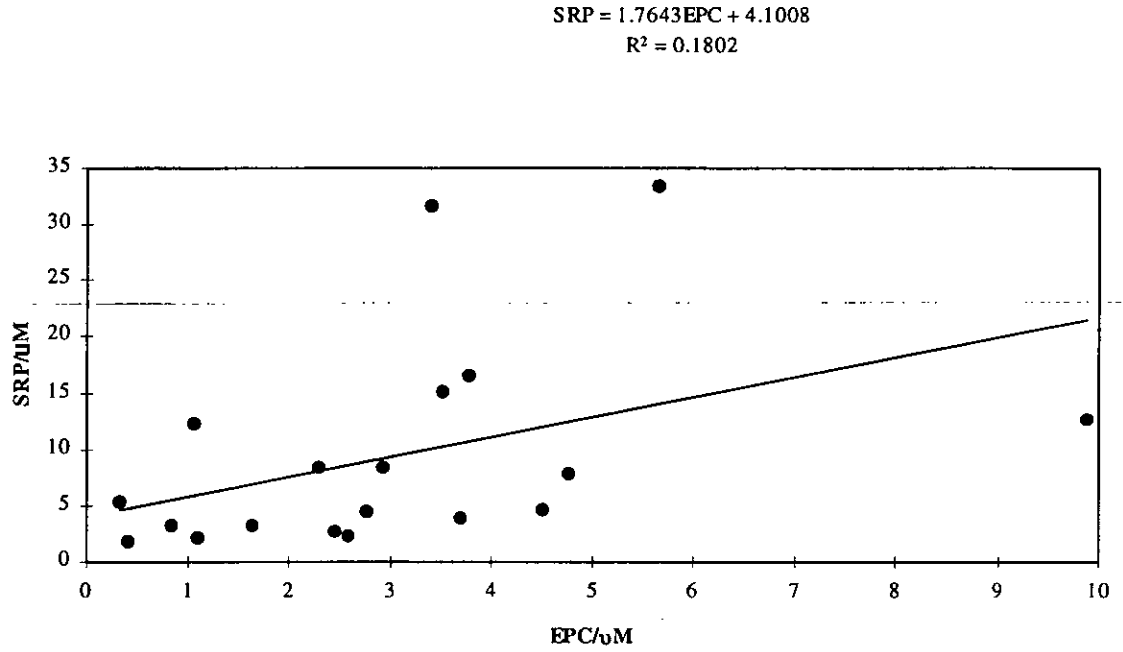
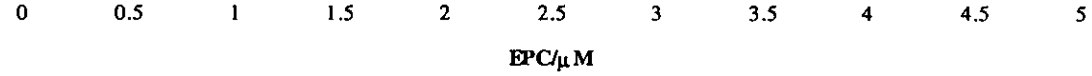


FIGURE 5. Relationship between SRP and EPC_0 for all data where the SRP concentration < 5 μmol dm^{-3}. There is a general trend of increasing EPC_0 with increasing SRP.



7.0 The values of the native P (n_i) and bioavailable P (BAP) by iron oxide stripping are also shown in Table 8. The values of n_i and BAP relate to the amount of sorbed P associated with the sediment at the time of sampling, as determined through the sorption experiments, and the amount of P that can be desorbed by the sediment to an infinite sink in the solution, respectively. They are expected to be equivalent if the BAP is entirely composed of SRP. However, the BAP method also determines organo-phosphorus compounds which are hydrolysed during the reaction with the immobolised iron oxide phase. The iron oxide catalyses the hydrolysis reaction and leads to a determination of P associated with the sediment which is a combination of SRP and organo-phosphorus compounds. As illustrated in Fig. 3c , BAP > n_i for all the results. There are generally poor correlation between ni and BAP when all data are compared on a site to site basis (R^2<0.34). However, the spring and summer seasonal data at all sites give good correlation (R^2=0.78 and 0.99 respectively) as does the regression of the mean values at each site taken over all seasonal data (Fig. 6). The regression indicates that native P is approximately 29 % of BAP. Similar proportions were calculated for the spring and summer data taken at all sites; i.e. 32 and 35 % respectively. The autumn and winter results at all sites, show very poor correlation between n_i and BAP.

FIGURE 6. Relationship between the mean values of the native P and bioavailable P (iron oxide stripping) measured at each site.

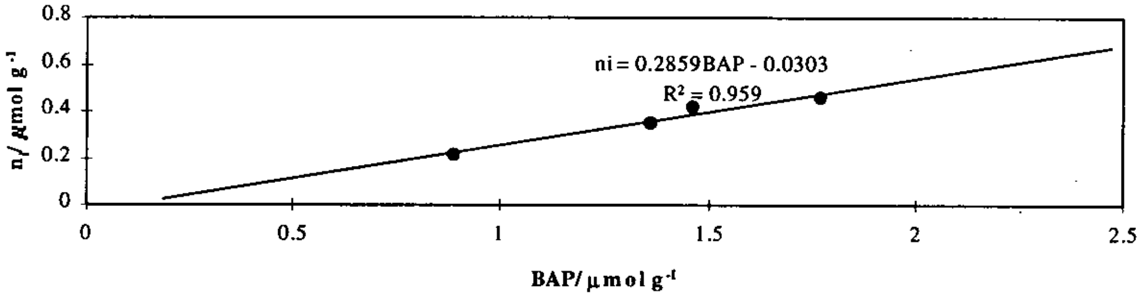
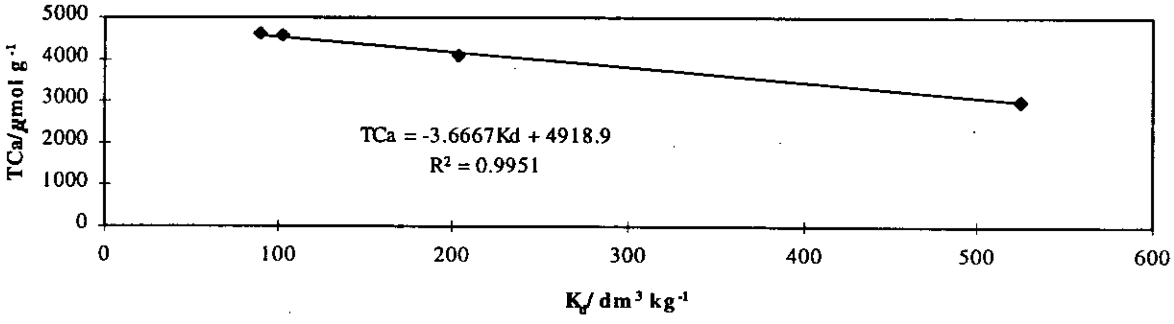


FIGURE 7 Illustration of the relationship between the total calcium concentration and the sorption constant for the sediments collected on the summer 1995 site visits.



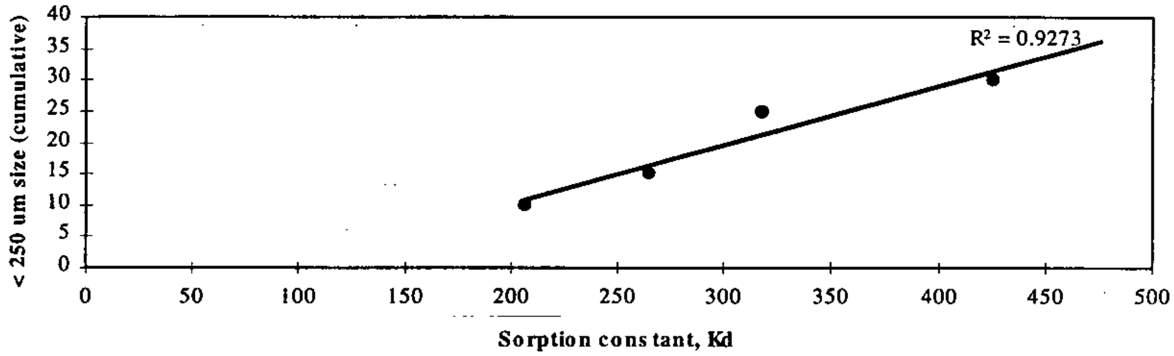
8.0 The overall mean of the sorption constants, K_d, (including all site specific and seasonal data) is 304 dm^{-3} kg^{-1} with the highest mean value from site B sediments and the lowest from site C, (see Table 10).

TABLE 10. Comparison of the mean sorption constants at each site together with the standard deviations (SD) and the coefficients of variation. K_d's in units of dm^{-3} kg^{-1}

Site	A	B	C	D
mean	381	426	207	265
SD	146	323	297	320
CV/%	46	78	143	121

The sorption constant is a measure of the affinity of SRP to the sediment and is related to the buffering capacity of the sediment. The higher the value of K_d, the greater the ability of the sediment to reduce the SRP concentration in the water. The sorption constant is expected to increase with decreasing particle size (Fig. 8), i.e. as the specific surface area of the sediment increases. The K_d for calcite is typically 110 dm^{-3} kg^{-1} (at 10 ^{0}C and pH=8, specific surface area of approximately 1 m^2 g^{-1}, House and Donaldson, 1986).

FIGURE 8. Illustration of the increase in the mean sorption constant, K_d (dm^3 kg^{-1}) with decreasing particle size (mean cumulative % recovered) measured at each site.



5.3 Results from fluvarium channel experiments

The uptake of SRP by the bed-sediments was modelled using a combination of the Elovich and parabolic equations with the parabolic rate constant adjusted to take account of the varying flow along the river section (House *et al.,* 1995). The flow rate dependence and flux of P in each river section, i, may be described by the equations:

$$kpv_i := kp \cdot \left(0.714 v_i + 1\right) \qquad [1]$$

$$f_{i+1} := f_i + cq_{(i+1)} - \frac{\ln\left[1 + b \cdot t_i \cdot \left[kpv_i \cdot \left[\left(\frac{f_i + cq_i}{q_i}\right) - epc_i\right]^2\right]\right] \cdot q_i}{b \cdot depth_i} \qquad [2]$$

where kpv is the parabolic rate constant at water velocity, v, kp is the rate constant at zero velocity, f is the flux of P (in mmol s^{-1}), cq is th point source inputs, b is the Elovich constant and epc the EPC_0 of the sediment in the section. The fluvarium channel experiments were designed to investigate the parameters kpv and b by measuring the net flux of SRP to or from the sediment in different conditions. The field studies showed that at the times of sampling there was a net loss of SRP to the sediments, i.e. SRP> EPC_0.

The results from the fluvarium experiments are shown in Table 11. These have been presented in previous reports but have been further checked and are collected together here for convenience. The parameters "a" and "b" relate to the Elovich equation and K_p to the parabolic equation (House *et.al.,* 1995).

TABLE 11. Results from the kinetic experiments in the fluvarium channel. K_p is in m^4 $mmol^{-1}$ s^{-1}, a in μmol m^{-2} h^{-1} and b in m^2 $μmol^{-1}$. Values in brackets are standard deviations or EPC_0's as appropriate.

Date	Kp/ 10^{-6}	Elovich, a	Elovich, b/10^{-3}	Final SRP/ μM
Release:				
9.1.95	1.65(0.04)	17.51(3.0)	11.20(2.1)	1.9(2.5)
28.3.95	no release	no release	no release	0.3-0.4(2.3)
10.7.95	not parabolic	1.92	-10.19(1.02)	2.1(1.9)
15.11.95	0.14(0.04)	12.03(1.02)	6.46(0.75)	2.2(1.07)
Uptake				
9.1.95	0.041(0.002)	542.1(100.2)	0.934(0.095)	15.8
28.3.95	0.053(0.003)	415.0(106.8)	0.799(0.133)	12.3
10.7.95	0.030(0.001)	493.3(74.5)	0.869(0.073)	17.2
15.11.95	0.014(0.001)	36.8(4.2)	-0.207(0.150)	20.24

The release experiment in the spring produced no release of SRP with the final SRP concentration in the overlying water of 0.3-0.4 μmol dm^{-3}. This is lower than the EPC_0 of the sediment and suggests uptake of SRP by benthic diatoms. This is confirmed by the downstream reduction in dissolved silicon measured during this site visit. The release experiment in the summer produced unexpected results which did not conform to the parabolic equation. Instead, the intial release of SRP was very slow but increased rapidly to the measured EPC_0 towards the end of the experiment. This behaviour has been observed for other sediments and has not been explained. The results for the winter 1995 show a slow release of SRP to a concentration close to the EPC_0 of the surface sediment. However, the results from the sediment collected in the autumn show a slower release than the winter, and the final concentration of SRP in the overlying sediment was greater than the surface sediment EPC_0 , i.e. 2.2 compared to 1.07 μmol dm^{-3}. This may reflect the decomposition of organic matter which had accumulated in the sediment during the summer.

The uptake of SRP (Table 11) was similar for the sediments collected in the spring, summer and winter. The results for the sediment collected in the autumn produced a lower K_p , a and b (Elovich) than at other sampling times. The flux of SRP was almost constant with time and did not show the typical initial increase and then decrease with time as the SRP concentration in the overlying water decreased. Again, this is a result of the balance between the efflux and influx of SRP and possible role of the decomposition of organic matter in the autumn.

5.4 Developments in the Modelling of Riverine Processes

The PNFILE program has been modified as follows:

a. The velocity dependence of the parabolic rate constant has been included according to the form of equation (1) above. Hence the rate constant extrapolated to zero velocity is used in the optimisation.

b. The optimised solutions are checked using a contour plot of the optimised parameters (Kp and b) and the root-mean-squared deviation between the computed profile of SRP along the river section with the measured profile.

c. The loss or gain of SRP is calculated along the river section and expressed normalised with respect to the bed-sediment area. This does not imply the assumption that all changes in SRP are associated with processes in the sediment.

The water velocity in the fluvarium channel experiments and at the river sites (estimated from the velocity profile 5 cm above the sediment surface) are collected in Table 12. As shown, the water velocity in the fluvarium channel is closest to that measured at site B.

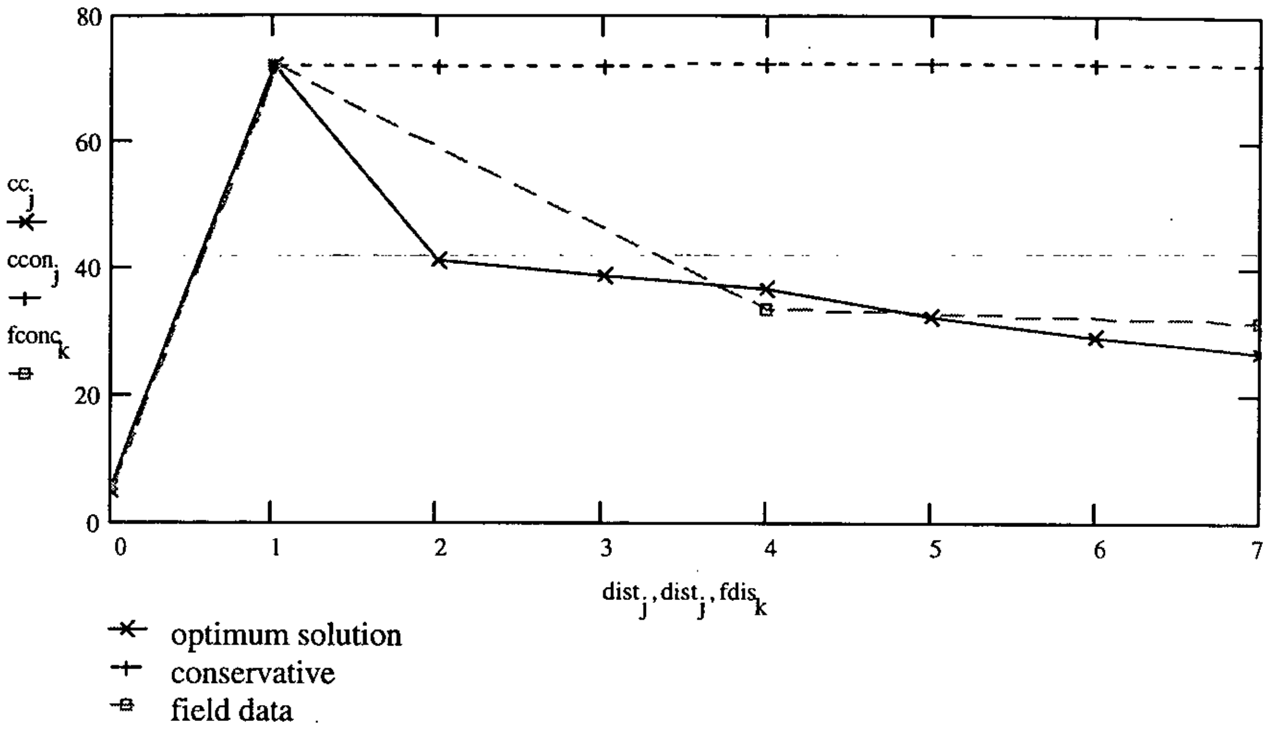
TABLE 12. Comparisons of the flow rate (cm s^{-1}) estimated at a distance of 5 cm above the bed-sediment and the velocity calculated for the fluvarium channel from flow rate and depth measurements.

Site	A	B	C	D	fluvarium
10.1.95	12.6	8.5	20.4	39.3	11.8
17.3.95	4.6	20.6	27.7	24.2	11.8
10.7.95	2.8	8.8	23.8	28.9	11.8
15.11.95	6.4	9.9	24.0	20.0	11.8
25.5.94	7.0	18.9	26.8	25.7	-

The PNFILE program was operated in the following manner:

a. A 7 km section was selected between Brackley and site D. The quarterly sampling results for SRP, river width, depth and water velocity were used in the computation together with the EPC_0's for each section. It was assummed that the parameters measured at the four sites could be applied in the sections immediately downstream.

FIGURE 9. Modelling SRP uptake from the summer 1995 data. Optimum parameters are shown in Table 13.



b. Data on discharges and dissolved phosphorus concentration associated with effluents from the STW's was sought from Anglian Water plc. Single measurements were available for Brackley STW and Westbury. Soluble phosphorus data were selected for each of the seasons, e.g. in the summer of 1995 this amounted to 6 measurements at Brackley and 3 at Westbury. No discharge data was available at Westbury but daily records were available for the new Brackley STW.

c. For small streams not routinely monitored, the concentration of SRP was equated with that measured at site A. These streams were in the 6 th and 7 th kilometre sections. The dilution factor was set at 0.001 unless the measured river discharge necessitated an increase to maintain the water balance. Groundwater inputs/losses and rainfall/evaporation were ignored in the water balance.

d. A mass balance at site B (immediately downstream of Brackley STW) was made to determine the SRP concentration in the STW effluent. This concentration was used in PNFILE and also compared with the concentrations measured in the effluent. The program was then used to examine the water balance and adjust this to match the field measurements as necessary.

e. When the water balance was satisfactory, the program was run to determine the parameters, K_p and b to produce the best agreement with measured SRP concentration profile. This theoretical profile was then compared with the measured profile and the SRP profile expected for a conservative system.

The results for the summer and spring sampling visits are shown in Figs. 9 and 11. Figure 10 compares the field and theoretical profiles with K_p and b taken from the fluvarium channel results rather than optimised using PNFILE. The results of the optimisation are summarised in Table 13.

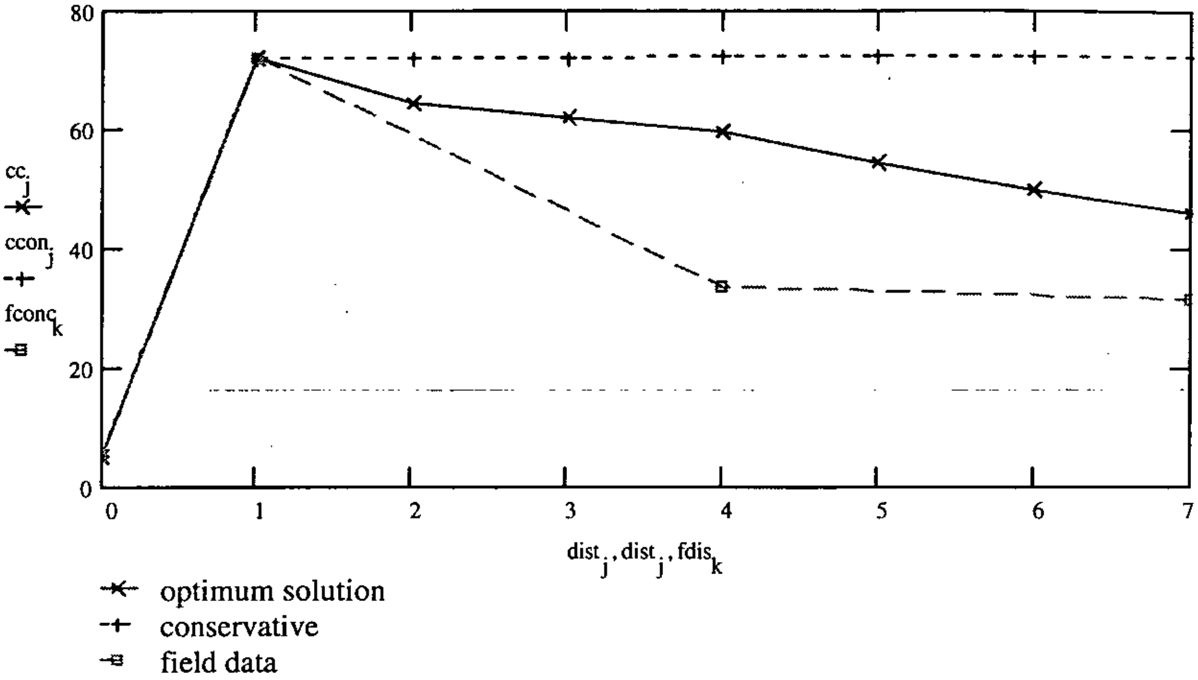


FIGURE 10. Comparison of the expected uptake by the bed-sediment if the fluvarium channel results for K_p and b are used in the PNFILE program incorporating corrections for the velocity dependence of K_p.

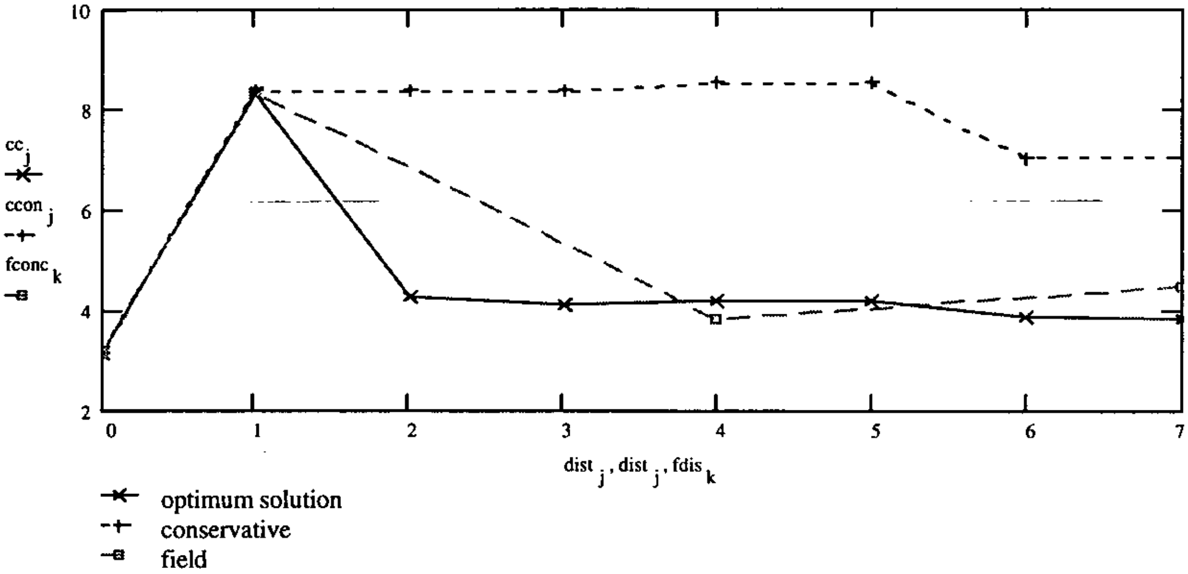


FIGURE 11. Modelling SRP uptake from the spring 1995 data.

The data from the winter and autumn sampling show no systematic decrease in SRP downstream and was not analysed using PNFILE because of the lack of information on STW inputs and the contribution of minor tributaries during high flows in the winter sampling .

TABLE 13. Comparison of the values of K_p (v=0) and b obtained from the fluvarium channel experiments and analysis of the field data using PNFILE.

	$Kp/10^{-6}$ m^4 mmol s^{-1}		b/m^2 $mmol^{-1}$	
	spring	summer	spring	summer
Field: PNFILE	0.315	0.006	0.090	$0.2x10^{-5}$
Fluvarium channel	0.006	0.003	0.799	0.869

As shown in Fig. 10 and Table 13, if the parameters determined from the fluvarium channel experiments are used to estimate the uptake in the river section, the removal of SRP is lower than measured in the field. This is particularly marked for the spring results and probably reflects the importance of biological uptake at this time. Further work is now necessary with this data to examine these effects in more detail .

Calculated losses of SRP as high as 70 mmol m^{-2} d^{-1} are noted in the summer with the downstream sites showing losses of between 5-10 mmol m^{-2} d^{-1} . During the spring sampling, the concentration of SRP in the river was lower and the maximum loss was estimated as 52 mmol m^{-2} d^{-1} with downstream losses between 0.1 and 1.3 mmol m^{-2} d^{-1}.

6.0 MACROPHYTE SURVEYS

During the 1995 spring and summer site visits to the rivers selected for intensive study, macrophytes were surveyed at the sites chosen for sediment sampling. A 100 m length of river was surveyed at each site, 50 m above and below the sampling point, macrophytes were surveyed to provide a taxa list, percentage cover data for each taxon and total macrophyte cover as a percentage of the river bed area. Diversity indicies were calculated for each site using Pielou's modification of Simpson's diversity index, which relates the contribution made by each species to the total number of individuals present. It is calculated using the formula given below:

$$DiversityIndex(\%) = \left(1 - \sum_{i=1}^{X} \frac{n_i(n_i - 1)}{N(N-1)}\right) \times 100$$

n_i = % cover by the ith species
X = number of species present
N = total macrophyte cover (%)

Value increases with diversity.
These data have not been examined and related to the results from PNFILE. This will be attempted in the next stage of the modelling.

TABLE 14. Results of macrophyte surveys: Gt, Ouse, 1995.

River Great Ouse: Macrophyte survey results							
Sample date	27-28/3/95			10-11/7/95			
Site Code	A	B	D	A	B	C	D
NGR	SP 595 368	SP 602 358	SP 652 341	SP 595 368	SP 602 358	SP 627 346	SP 652 341
Species Cover %							
Enteromorpha sp.				2			1
Stigeoclonium sp.				5			
Cladophora sp.	20	50	20		50	60	40
Hygrohypnum luridum	1			1	0.1	8	
Apium nodiflorum	5			2		1	
Callitriche obtusangula	2			5		1	2
Callitriche stagnalis				5		2	
Epilobium hirsutum	2	2	1				
Myosotis sp.				10			2
Nuphar lutea						1	1
Ranunculus fluitans				2		2	
Veronica anagalis-aquatica				2		1	
Carex riparia					1		
Elodea nuttallii						1	
Glyceria maxima	2		2	2			
Lemna sp.				1	0.1		
Phalaris arundinacea	5	5	4	10	2	2	2
Potamogeton crispus	4			3			
Scirpus lacustris			1			5	5
Sparganium emersum				5	5	5	5
Sparganium erectum	4	4	5	25	2	1	2
Total cover %	45	61	33	80	60	90	60
Diversity index (%)	77	32	61	86	30	55	55

TABLE 15. Result of macrophyte surveys, R. Wey, 1995.

River Wey: Macrophyte survey results

Sample date	05/05/95				04/08/95			
Site Code	A	C	D	E	A	C	D	E
NGR	SU 724 396	SU 733 403	SU 745 412	SU 756 417	SU 724 396	SU 733 403	SU 745 412	SU 756 417
Species Cover %								
Vaucheria sp.	2.5							
Enteromorphia sp.	5							2
Cladophora sp.		70	50	50	2	50	30	15
Apium nodiflorum	22	2.5	1	1	75	2	10	5
Berula erecta	5	2			2			1
Callitriche obtusangula	1							
Callitriche platycarpa	2.5	2	10		1	1	1	
Callitriche stagnalis	1				1	1	2	5
Epilobium hirsutum	5		1	1	1			
Mentha aquatica	5	1		1	10	1	1	1
Myosotis scorpioides				1				
Polygonium amphibium		1						
Ranunculus penicillatus		2.5	2.5	25	1	1	2	40
Rorippa nasturtium -aquatica		1	1	1		1		
Solanum dulcamara			1					
Veronica anagalis-aquatica	1							
Alisma plantago-aquatica				1				
Elodea canadensis						2	2	2
Glyceria maxime			1	1			1	1
Lemna sp.		1				1	1	1
Phalaris arundinacea	10	10	2.5	1	2	2	2	1
Phragmites australis						5		
Potamogeton crispus			25			2	5	
Sparganium emersum		1	1	2			1	1
Sparganium erectum		1	4			1	2	
Total cover %	60	95	100	85	95	70	60	75
Diversity index (%)	82	45	68	57	37	49	72	67

TABLE 16. Result of macrophyte surveys, R. Blackwater, 1995.

River Blackwater: Macrophyte survey results

Sample date	10/04/95				21/07/95			
Site Code	A	B	C	D	A	B	C	D
NGR	SU 882 499	SU 885 538	SU 880 559	SU 859 594	SU 882 499	SU 885 538	SU 880 559	SU 859 594
Species Cover %								
Cladophora sp.	60		2		75	45	50	20
Apium nodiflorum	5	2		4	10	1	2	1
Callitriche sp.		5	2			2	10	
Epilobium hirsutum	2	1	1	1		2	1	
Mentha aquatica	1				1		1	
Nuphar lutea								1
Oenanthe crocata	1							
Ranunculus sp.							2	
Rorippa nasturtium-aquatica						1	1	
Veronica anagalis-aquatica				1				
Alisma plantago -aquatica					1			
Carex sp.						1		
Elodea nuttallii	2	5			5	5	5	
Glyceria maxime				2	2			
Iris pseudacorus		1						
Juncus sp.		1	5					
Lemna sp.						5		
Phalaris arundinacea	2		10	5			5	5
Potamogeton natans		20		10		2	2	2
Scirpus lacustris						1	1	
Sparganium emersum		5	5	5		10	5	25
Sparganium erectum		10				10	2	35
Typha latifolia				1				
Total cover %	73	50	25	29	94	85	87	89
Diversity index(%)	32	78	78	82	35	69	65	72

7.0 FUTURE RESEARCH

The quarterly sampling and fluvarium studies on the R. Blackwater will continue in the hope that the implementation of the improvement to the STW at Aldershot will occur in the lifetime of the project. The best estimate for implementing the tertiary treatment plant is in the spring of 1997.

Experiments are planned to examine the stability of the R. Blackwater with respect to the precipitation of calcium phosphate minerals. The information obtained on the sediment cores (as partly reported in section 3.5.4) will also be examined further.

It is planned to complete the data analysis of the Gt. Ouse and complete any further work as a result of these studies with a view to publish the results in an international journal. A preliminary manuscript will be submitted to DoE in due course.

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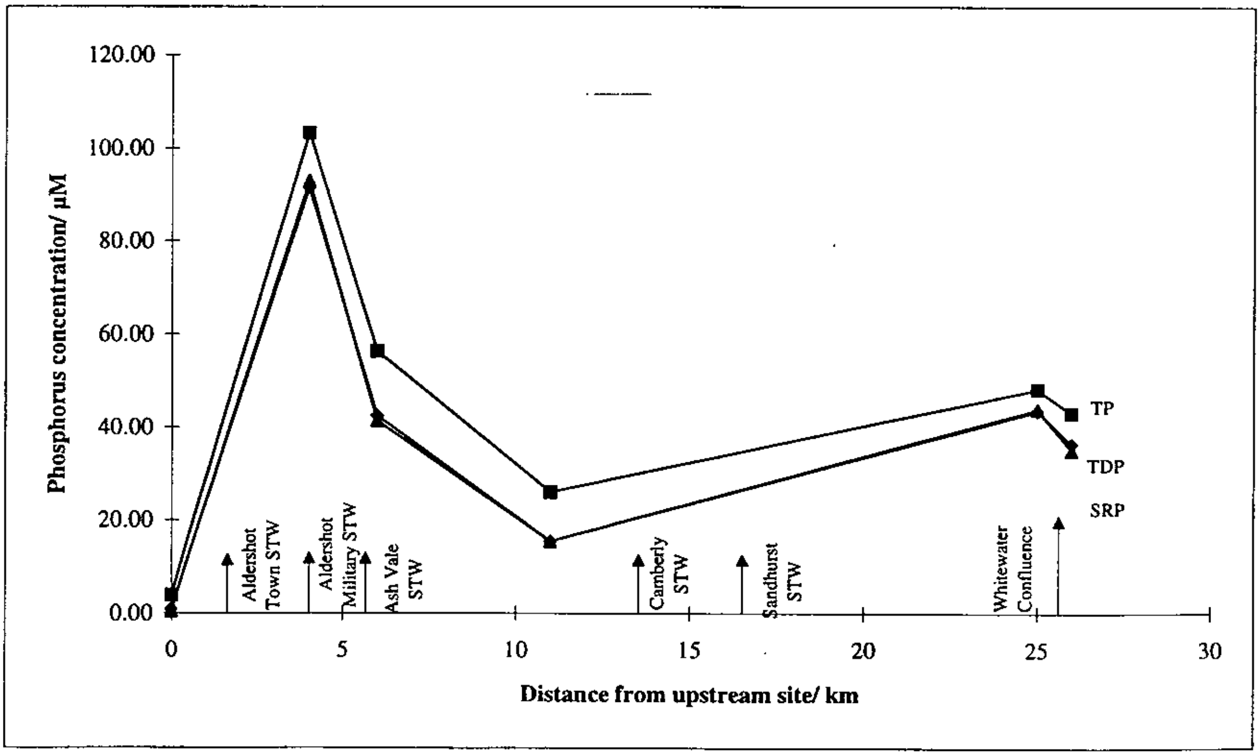
APPENDIX A

SITE VISIT TO RIVER BLACKWATER
18/04/96

SITE	A	B	C	D	E	G (Whitewater)	F
NGR of site	SU 882 499	SU 885 538	SU 880 559	SU 859 594	SU 742 634	SU 742 635	SU 740 638
Distance from upstream site/ km	0	4	6	11	25		26
pH	6.91	7.50	8.25	8.13	8.40	8.48	8.51
Conductivity (µS/cm)	560	879	735	591	667	571	650
Dissolved Oxygen (%)	63	82	109	136	114	111	109
Temperature	9.9	11.3	11.9	11.6	12.1	11.6	11.9
Flow (m^3/s)	0.02	0.19	0.27	0.50			
Filtered water (0.45 µm)							
Ca++ (mmol/ l)	1.75	2.23	2.26	1.80	1.88	2.20	2.08
Mg++ (mmol/ l)	0.34	0.37	0.36	0.30	0.31	0.24	0.28
Na+ (mmol/ l)	1.21	2.77	2.39	1.64	2.03	1.22	1.72
K+ (mmol/ l)	0.06	0.30	0.25	0.18	0.22	0.09	0.17
Alkalinity (mEq)	2.36	3.8	3.23	2.41	2.36	2.64	2.64
NO3- (mmol/ l)	0.30	0.54	0.45	0.31	0.51	0.45	0.49
Silicon (µmol/ l)	77	279	239	189	348	102	152
Soluble Reactive Phosphorus (µmol/ l)	0.41	92.98	41.32	15.53	43.91	45.20	35.19
Total Dissolved Phosphorus (µmol/ l)	0.87	91.41	42.49	15.54	43.58	57.18	36.51
Non - MR Reactive fraction (µmol/ l)	0.46	-1.57	1.16	0.01	-0.33	11.98	1.32
Unfiltered water							
Total Phosphorus (µmol/ l)	3.79	103.30	56.33	26.12	48.19	72.23	43.12
Particulate Phosphorus (µmol/ l)	2.91	11.90	13.84	10.59	4.61	15.05	6.60
Suspended Solids (mg/l)	13.6	7.2	10.6	9.2	9	9.8	8.8
Sediment sieved 2mm							
% water	23.49	22.55	49.73	19.11			
Organic Matter (% of dry wt)	2.54	1.61	5.56	0.88			
Total Phosphorus (µmol/g)	18.5	33.2	280	51.8			
Total Calcium (µmol/g)	337	99	168	21.4			
Total Iron (µmol/g)	512	132	738	218.6			
Bioavailable Phosphorus (µmol/g)	0.65	1.64	4.28	2.67			
Equilibrium Phosphorus Concentration (µmol/ l)	2.84	7.3	2.5	7.41			
Kd (dm^3/kg)	336	144	2143	107			
ni (µmol/g)	0.95	1.1	5.5	0.8			

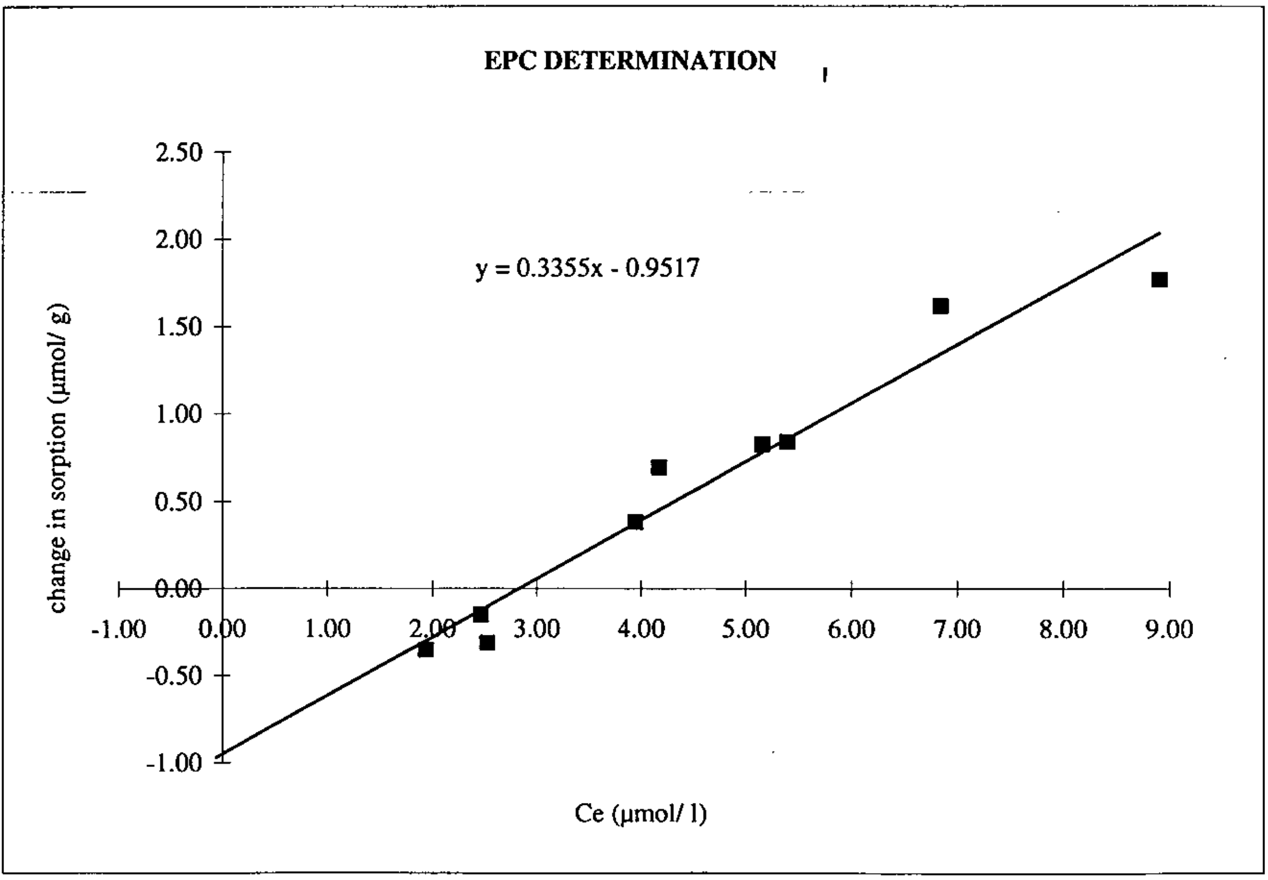


SITE A BLACKWATER. SEDIMENT & WATER COLLECTED 18/4/96

EPCo DETERMINATION				
weight of wet sediment/ g	weight of dry sediment/ g	initial [P] (µmol/ l)	[P] at 24 h (µmol/ l)	dN (µmol/ g dry wt)
1.4375	1.10	0	1.94	-0.35
1.5364	1.18	10	5.16	0.82
1.6394	1.25	20	8.90	1.77
2.0935	1.60	0	2.52	-0.31
2.1960	1.68	10	4.17	0.69
2.1268	1.63	20	6.84	1.62
4.2595	3.26	0	2.46	-0.15
4.1548	3.18	10	3.95	0.38
4.5517	3.48	20	5.39	0.84

% water of sediment = 23.49
Organic matter of sediment as % of dry weight = 2.54
Total phosphorus of sediment = 18.5 µmol/ g
Total calcium of sediment = 337 µmol/ g
Total iron of sediment = 512 µmol/ g

SRP of river water = 0.4 µmol/ l
TDP of river water = 0.9 µmol/ l
TP of river water = 3.8 µmol/ l
EPCo = 2.84 µmol/ l
Kd = 336 l/kg
ni = 0.95 µmol/g

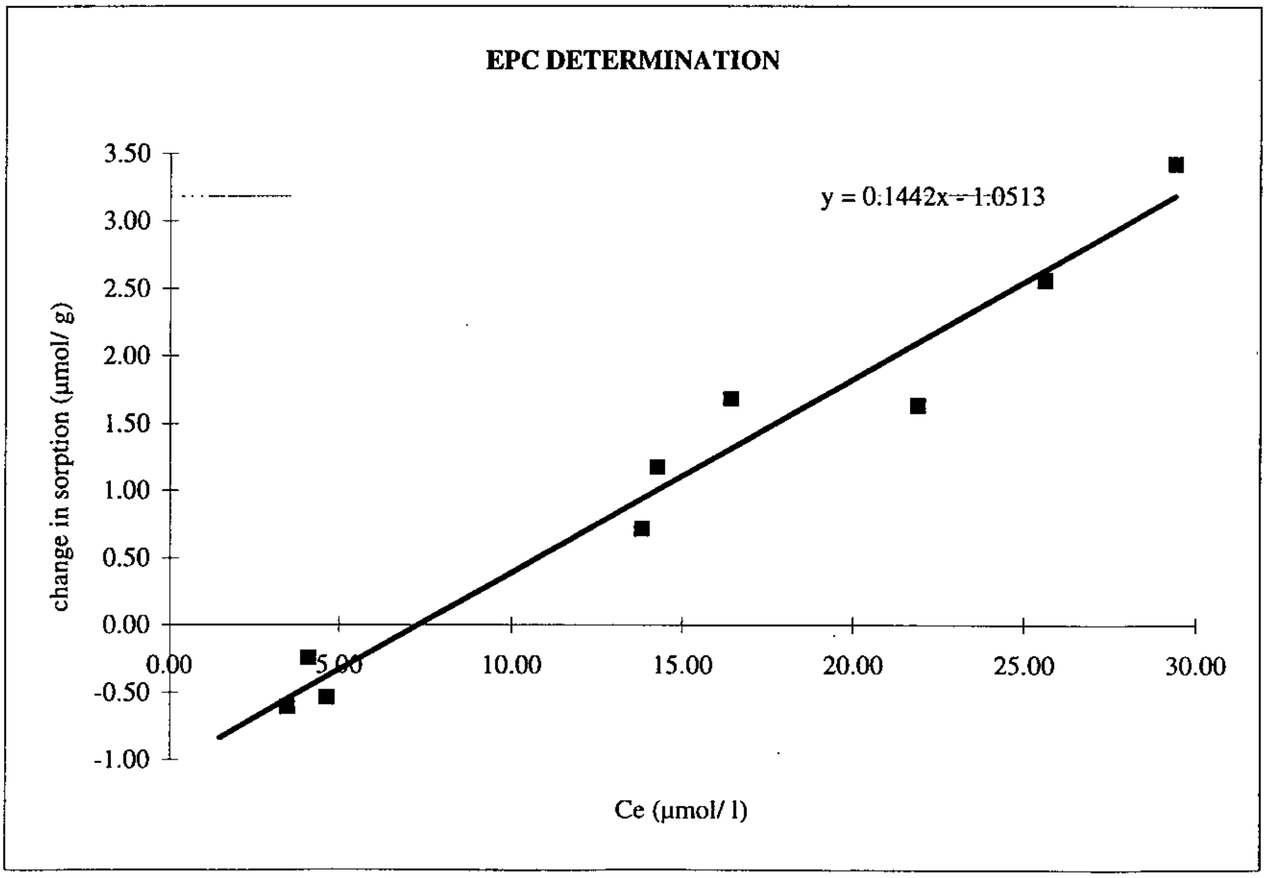


SITE B BLACKWATER. SEDIMENT & WATER COLLECTED 18/4/96

EPCo DETERMINATION				
weight of wet sediment/ g	weight of dry sediment/ g	initial [P] (µmol/ l)	[P] at 24 h (µmol/ l)	dN (µmol/ g dry wt)
1.4718	1.14	0	3.49	-0.61
1.3158	1.02	25	16.41	1.69
1.5547	1.20	50	29.40	3.42
2.2145	1.72	0	4.64	-0.54
2.3547	1.82	25	14.27	1.18
2.4565	1.90	50	25.61	2.56
4.3351	3.36	0	4.10	-0.24
4.0145	3.11	25	13.83	0.72
4.4327	3.43	50	21.90	1.64

% water of sediment = 22.55
Organic matter of sediment as % of dry weight = 1.61
Total phosphorus of sediment = 33.2 µmol/ g
Total calcium of sediment = 99 µmol/ g
Total iron of sediment = 132 µmol/ g

SRP of river water = 93.0 µmol/ l
TDP of river water = 91.4 µmol/ l
TP of river water = 103.3 µmol/ l
EPCo = 7.3 µmol/ l
Kd = 144 l/kg
ni = 1.1 µmol/g

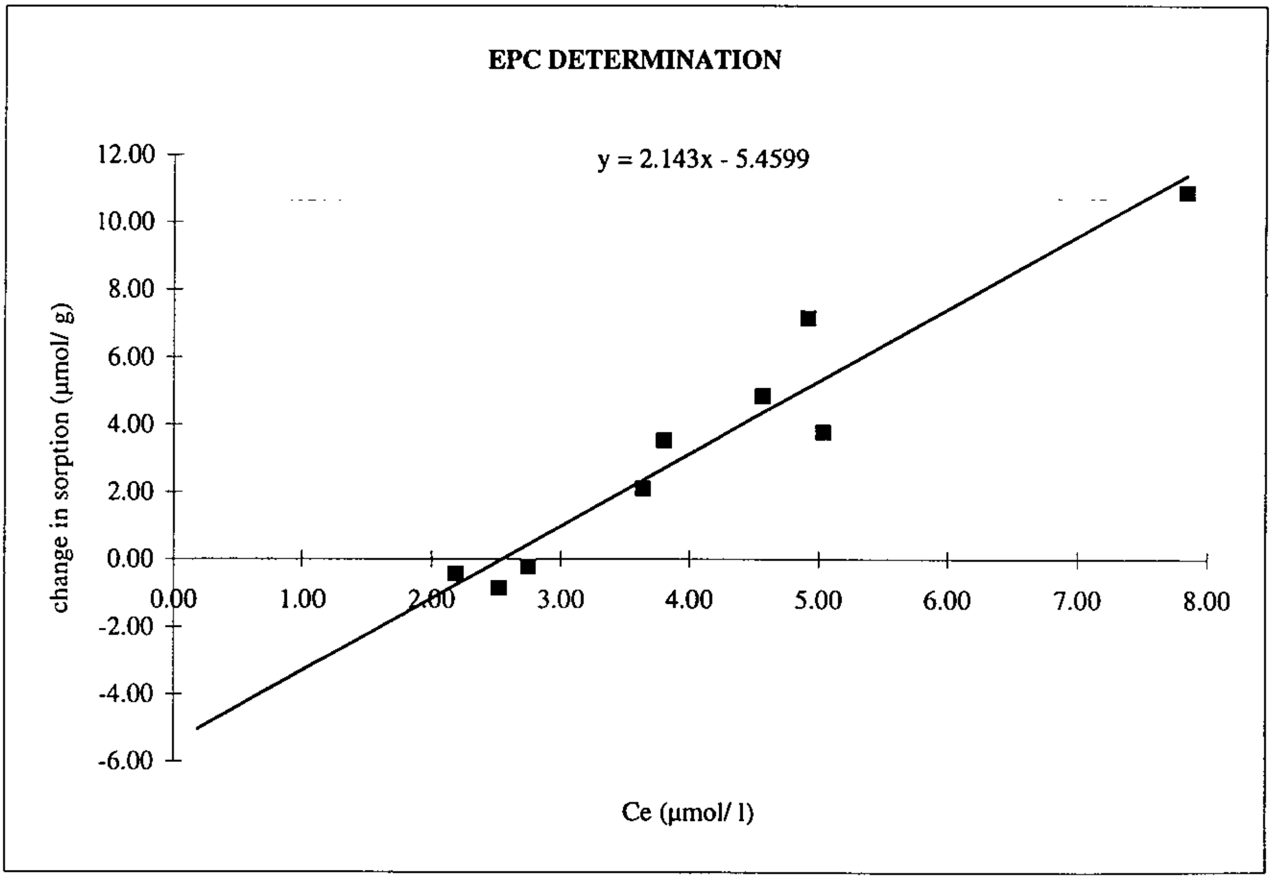


SITE C BLACKWATER. SEDIMENT & WATER COLLECTED 18/4/96

EPCo DETERMINATION				
weight of wet sediment/ g	weight of dry sediment/ g	initial [P] (µmol/ l)	[P] at 24 h (µmol/ l)	dN (µmol/ g dry wt)
1.1757	0.59	0	2.52	-0.85
1.6823	0.85	25	4.57	4.83
1.5441	0.78	50	7.84	10.86
2.0418	1.03	0	2.19	-0.43
2.3950	1.20	25	3.80	3.52
2.5058	1.26	50	4.92	7.16
4.7896	2.41	0	2.75	-0.23
4.0417	2.03	25	3.64	2.10
4.7548	2.39	50	5.04	3.76

% water of sediment = 49.73
Organic matter of sediment as % of dry weight = 5.56
Total phosphorus of sediment = 280 µmol/ g
Total calcium of sediment = 168 µmol/ g
Total iron of sediment = 738 µmol/ g

SRP of river water = 41.3 µmol/ l
TDP of river water = 42.5 µmol/ l
TP of river water = 56.3 µmol/ l
EPCo = 2.5 µmol/ l
Kd = 2143 l/kg
ni = 5.5 µmol/g

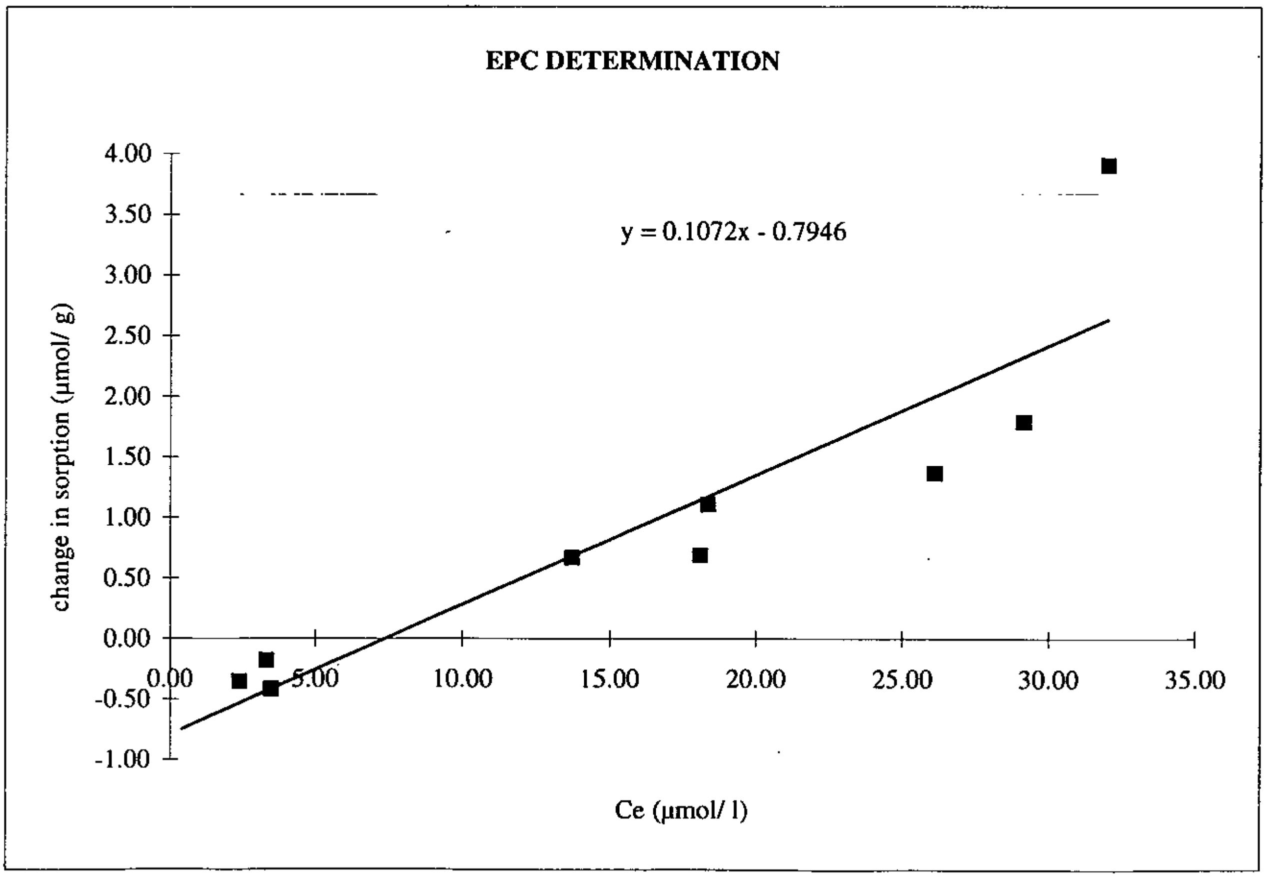


SITE D BLACKWATER. SEDIMENT & WATER COLLECTED 18/4/96

EPCo DETERMINATION				
weight of wet sediment/ g	weight of dry sediment/ g	initial [P] (µmol/ l)	[P] at 24 h (µmol/ l)	dN (µmol/ g dry wt)
1.7032	1.38	0	2.42	-0.35
1.4826	1.20	25	18.35	1.11
1.1388	0.92	50	32.02	3.90
2.0786	1.68	0	3.51	-0.42
2.4692	2.00	25	18.09	0.69
2.8713	2.32	50	29.14	1.80
4.5715	3.70	0	3.35	-0.18
4.1743	3.38	25	13.75	0.67
4.3188	3.49	50	26.11	1.37

% water of sediment =19.11
Organic matter as % of dry weight = 0.88
Total phosphorus of sediment = 51.8 µmol/ g
Total calcium of sediment = 21.4 µmol/ g
Total iron of sediment = 218.6 µmol/ g

SRP of river water = 15.5 µmol/ l
TDP of river water = 15.5 µmol/ l
TP of river water = 26.1 µmol/ l
EPCo = 7.41 µmol/ l
Kd = 107 l/kg
ni = 0.8 µmol/g



APPENDIX B

Fluvarium experiments with River Blackwater sediment Spring 1996

Sediment collected 18/4/96

River water chemistry at time of sampling:

Ca++ = 2.23 mmol/ l
Mg++ = 0.37 mmol/ l
Na+ = 2.77 mmol/ l
K+ = 0.30 mmol/ l
Alkalinity = 3.8 mEq

NO3- = 0.54 mmol/ l
Silicon = 279 µmol/ l
SRP = 93.0 µmol/ l
TDP = 91.4 µmol/ l
TP = 103.3 µmol/ l

Channel experiment conditions:

Volume of solution = 21 litres
Flow rate = 13.2 litres/min
Velocity over sediment = 9.76 cm/s

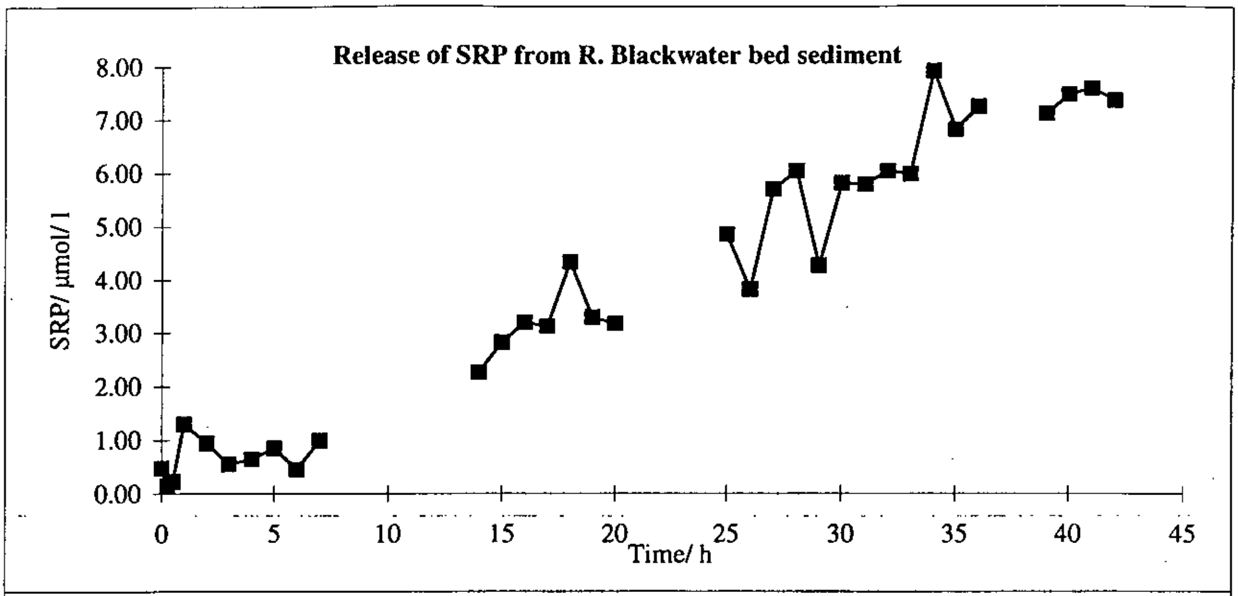
Experiment 1 - release experiment. 2 mM CaCl2 solution put into channel and sampling started 5 minutes after circulation started.

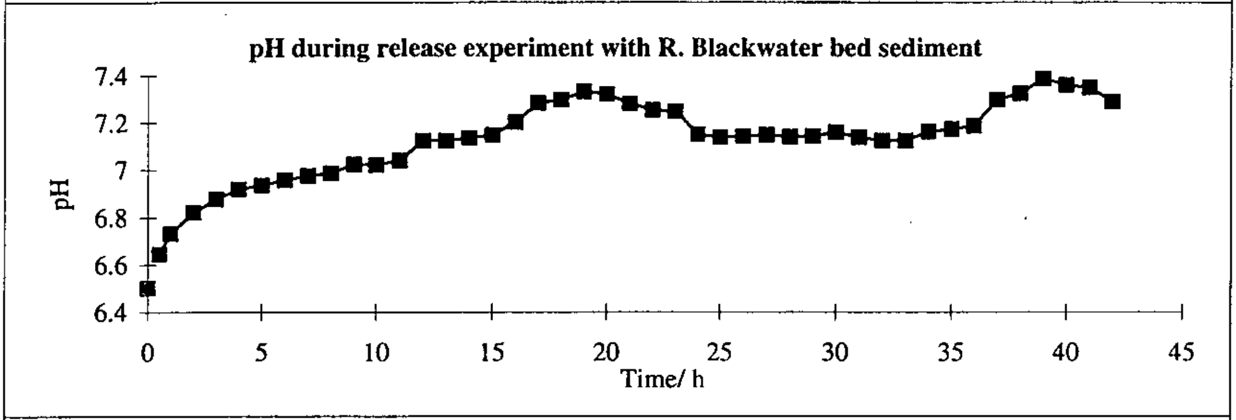
Experiment 2 - uptake experiment. 42 ml of 20 mM KH2PO4 added and sampling started after 5 minutes.

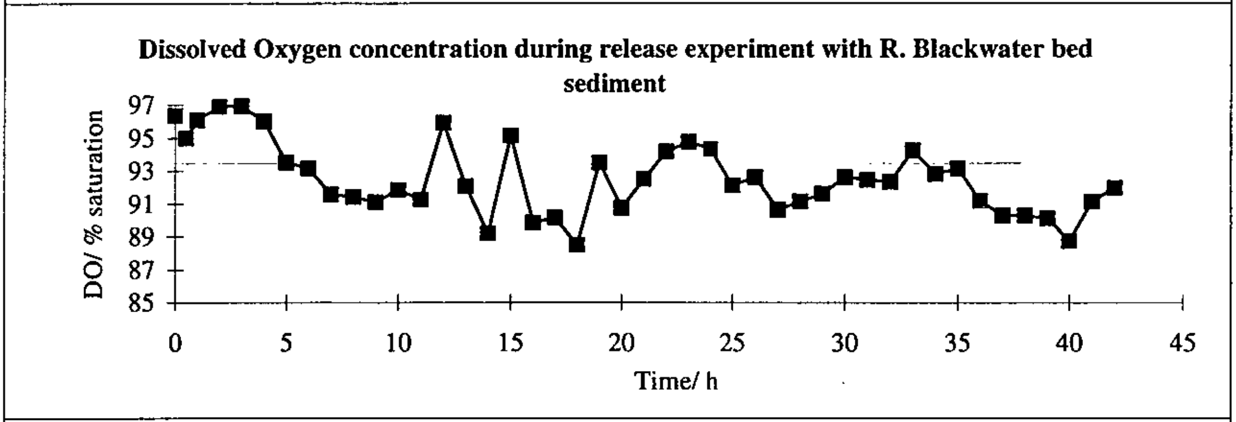
Experiment 3 - Anaerobic experiment. 6.7g sodium sulphite added, and nitrogen supply switched on. 1st sample after 5 minutes.

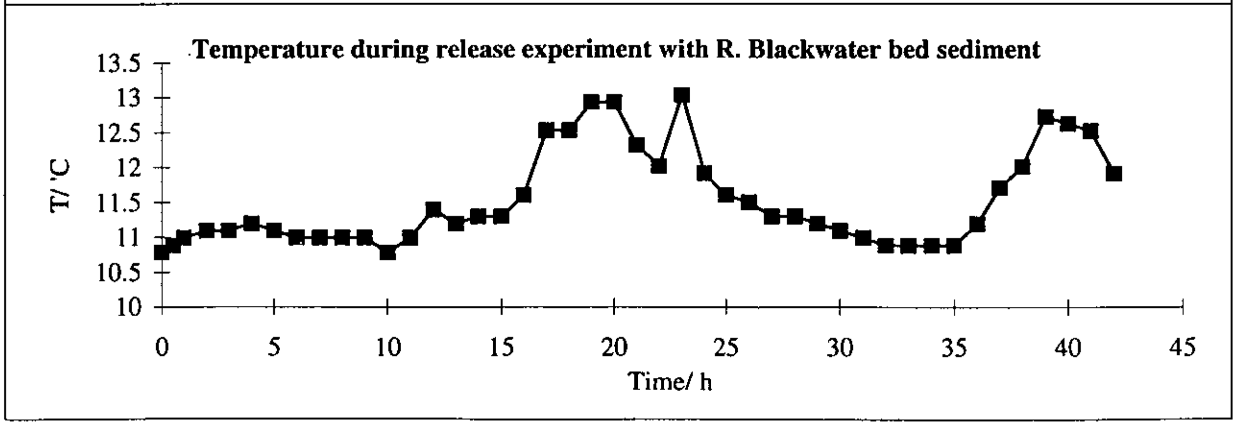
Sediment: EPCo = 7.3 µM; Kd = 144 dm^3/kg; ni = 1.1 µmol/g

Blackwater (18/4/96)

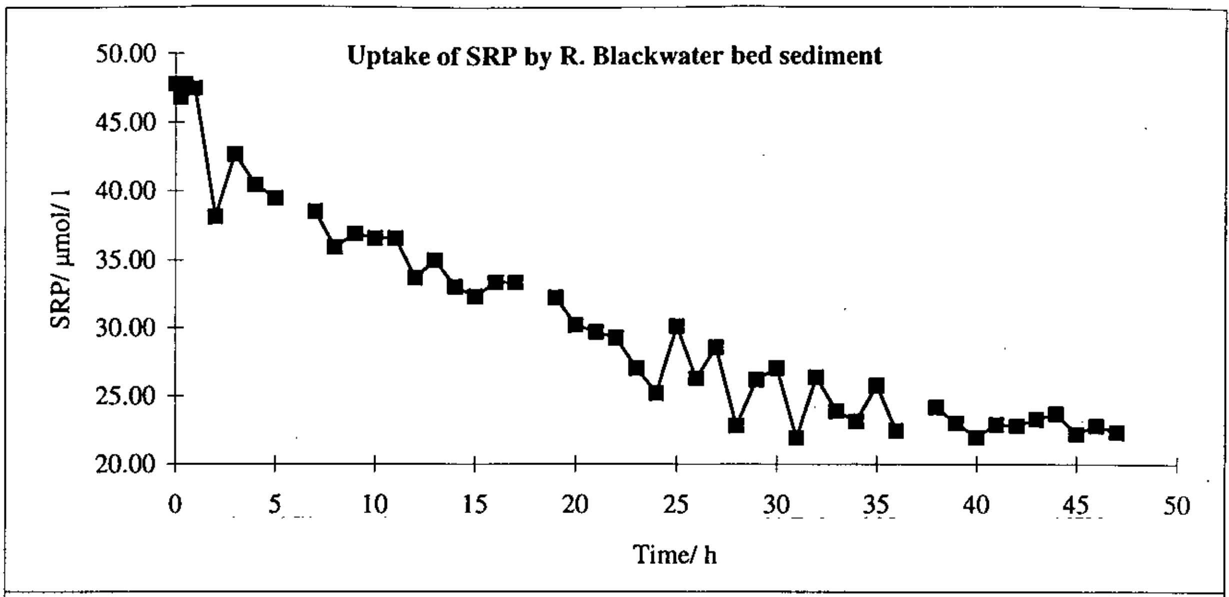

Release of SRP from R. Blackwater bed sediment

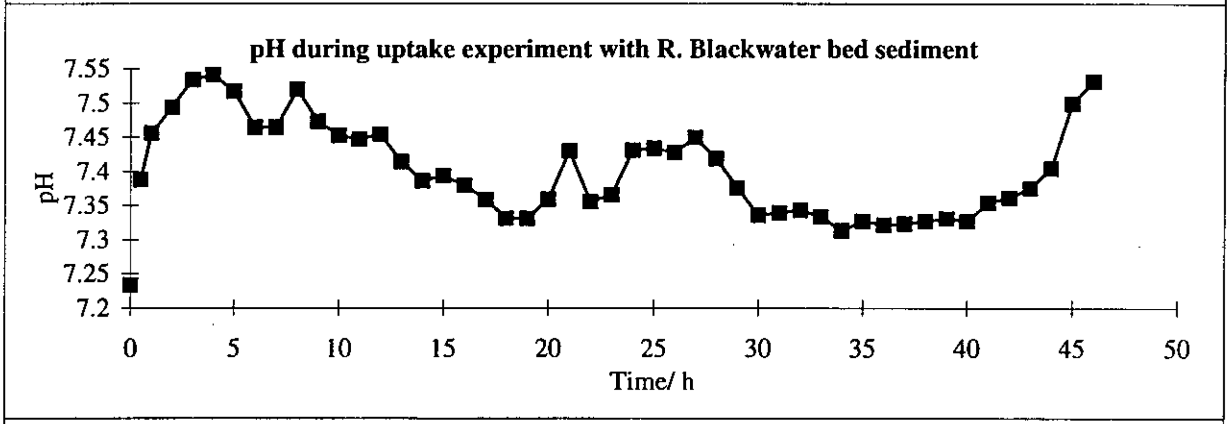

pH during release experiment with R. Blackwater bed sediment

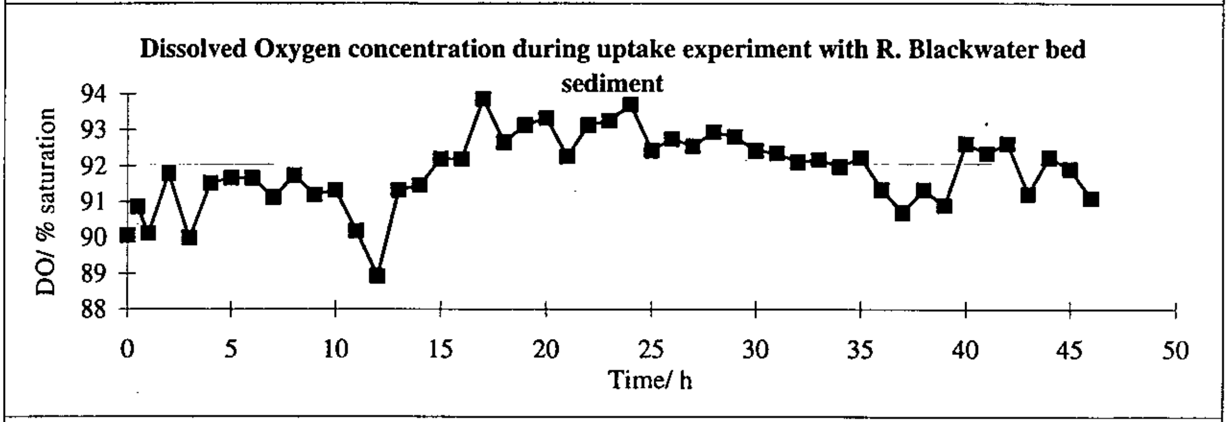

Dissolved Oxygen concentration during release experiment with R. Blackwater bed sediment

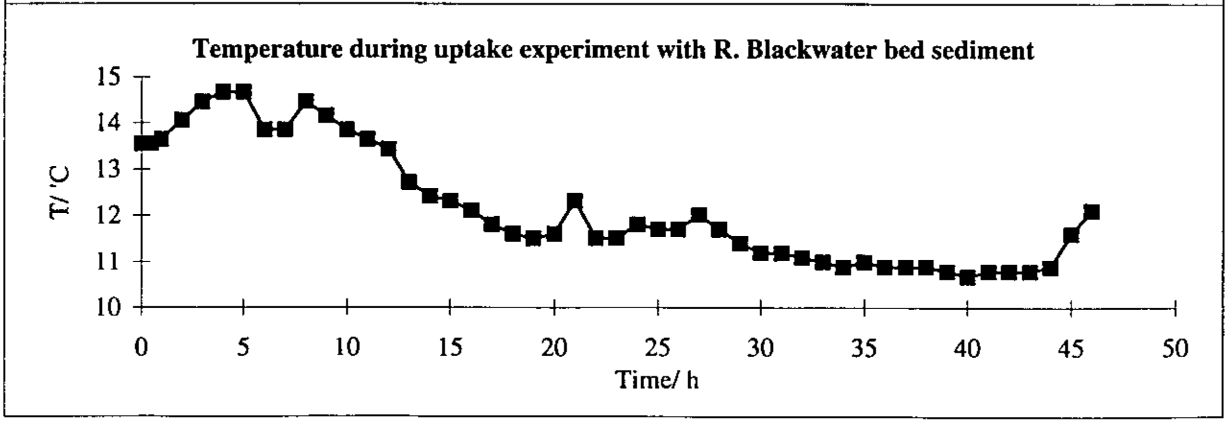

Temperature during release experiment with R. Blackwater bed sediment

Blackwater (18/4/96)

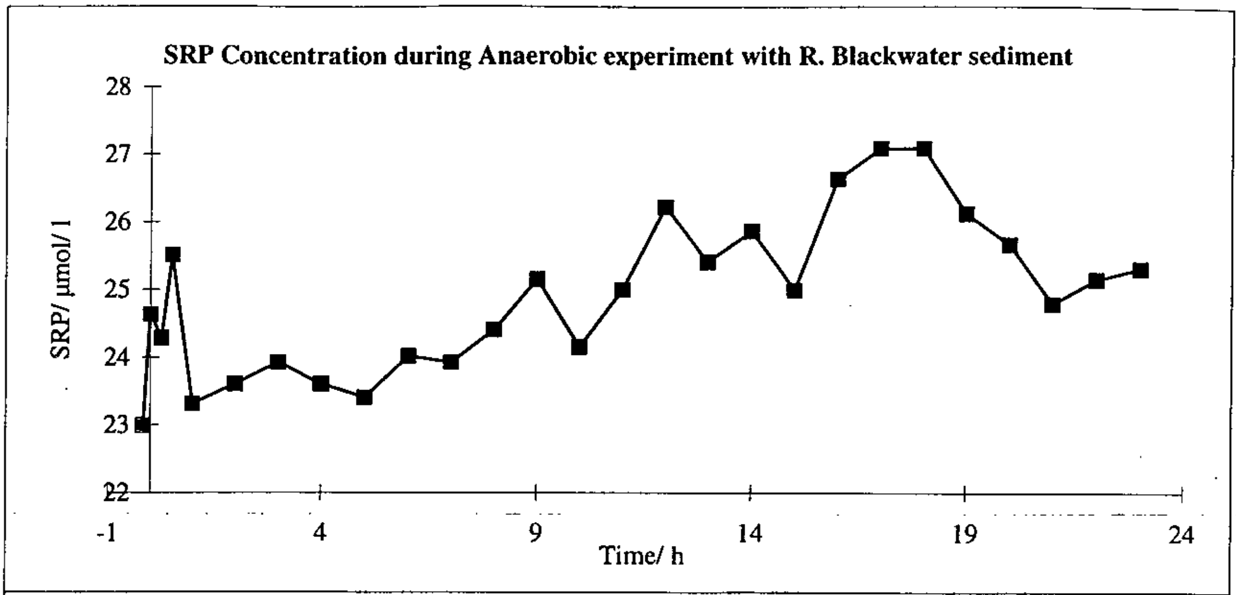




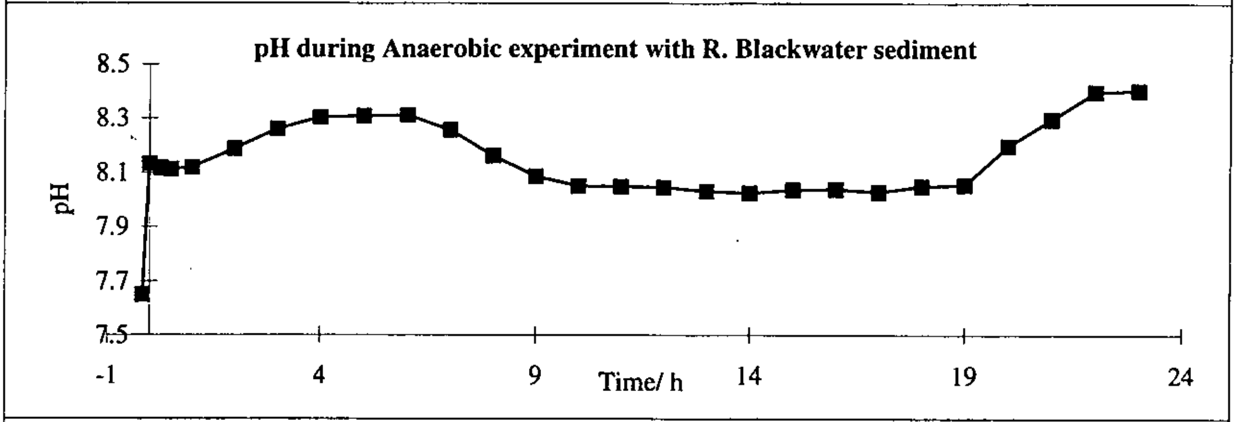




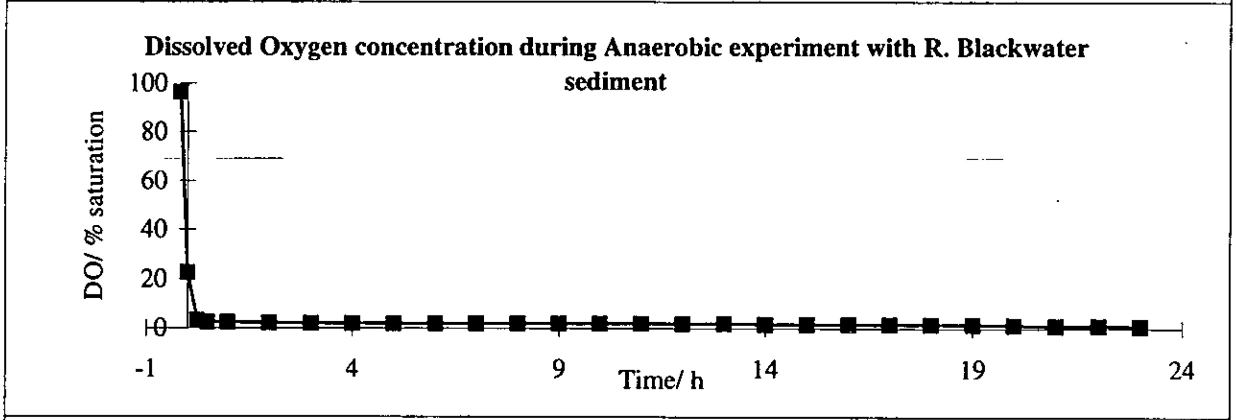
Blackwater (18/4/96)



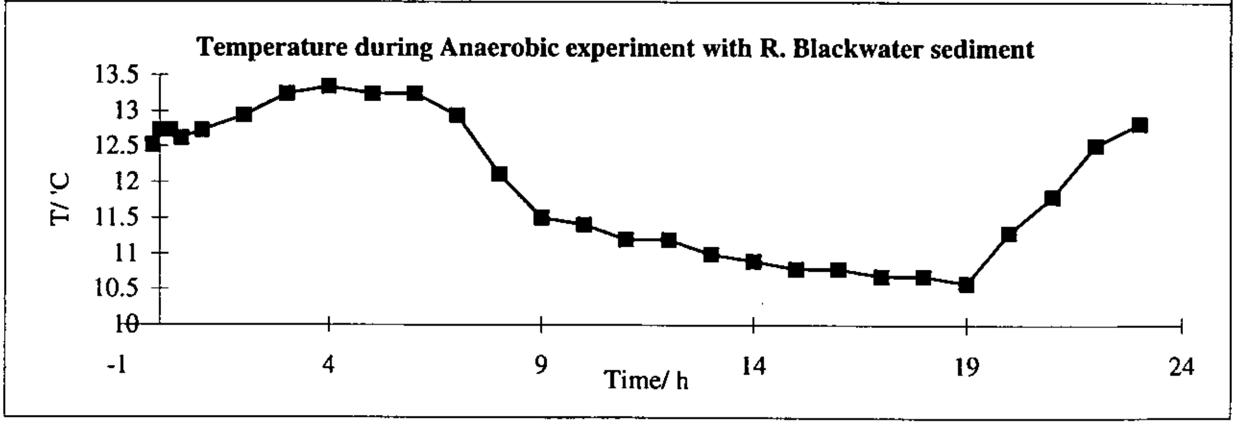
SRP Concentration during Anaerobic experiment with R. Blackwater sediment



pH during Anaerobic experiment with R. Blackwater sediment

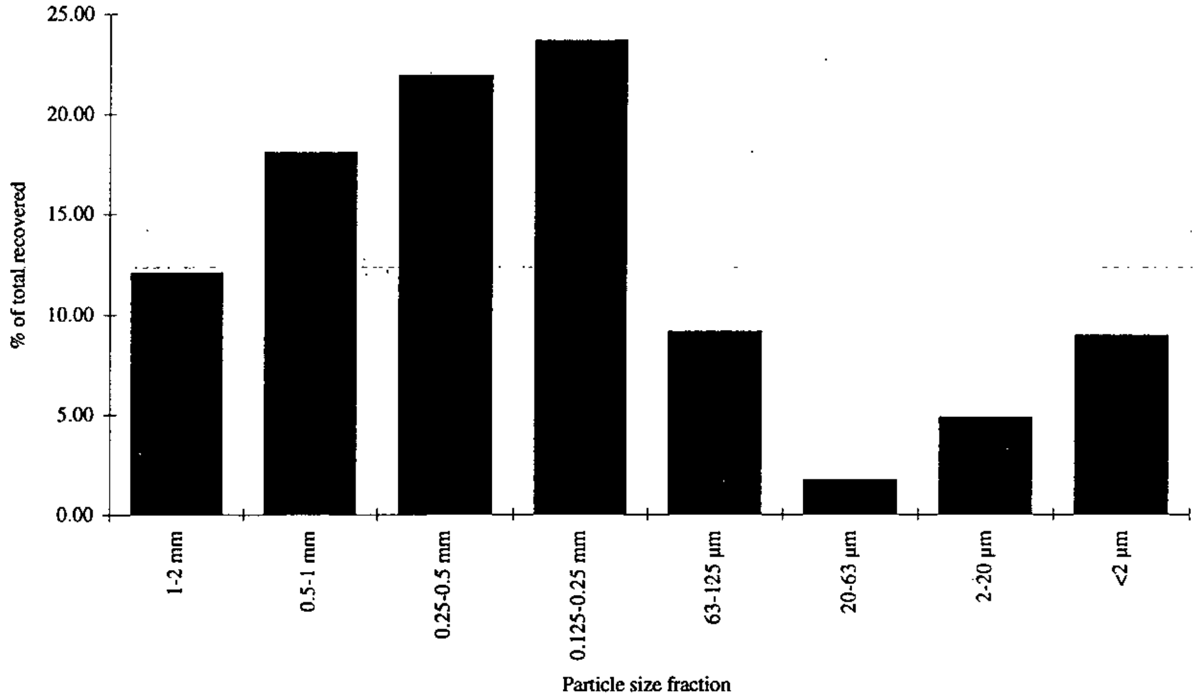


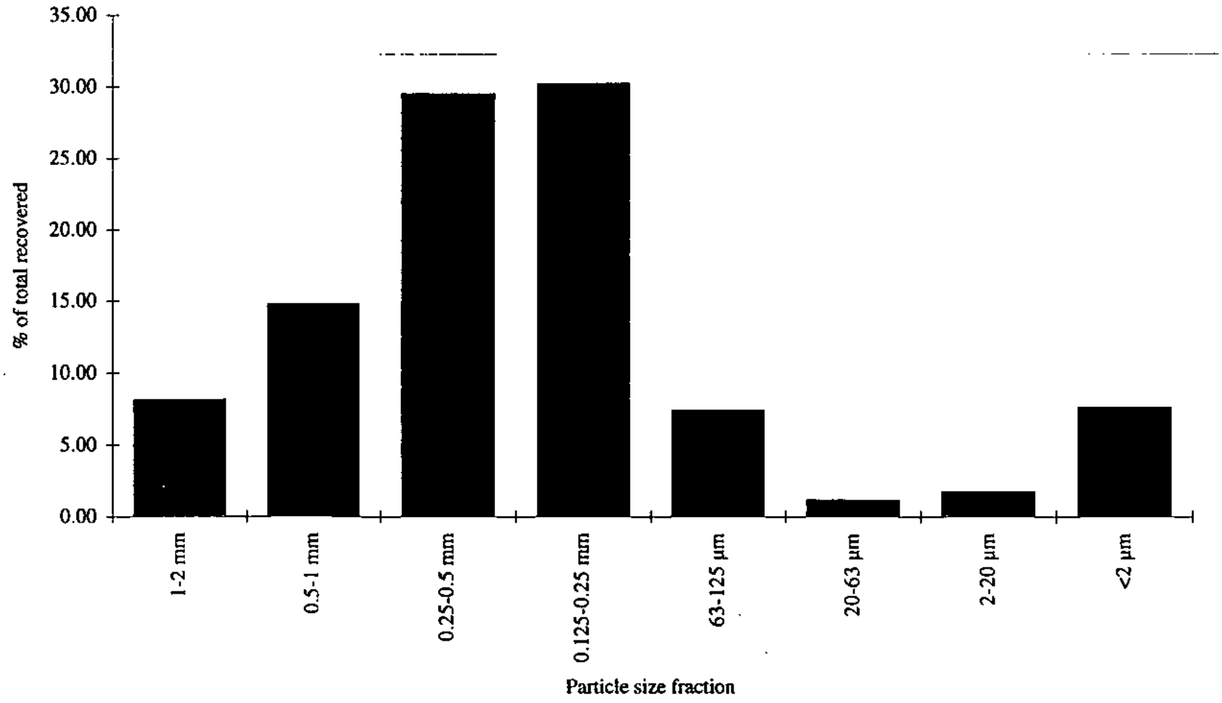
Dissolved Oxygen concentration during Anaerobic experiment with R. Blackwater sediment



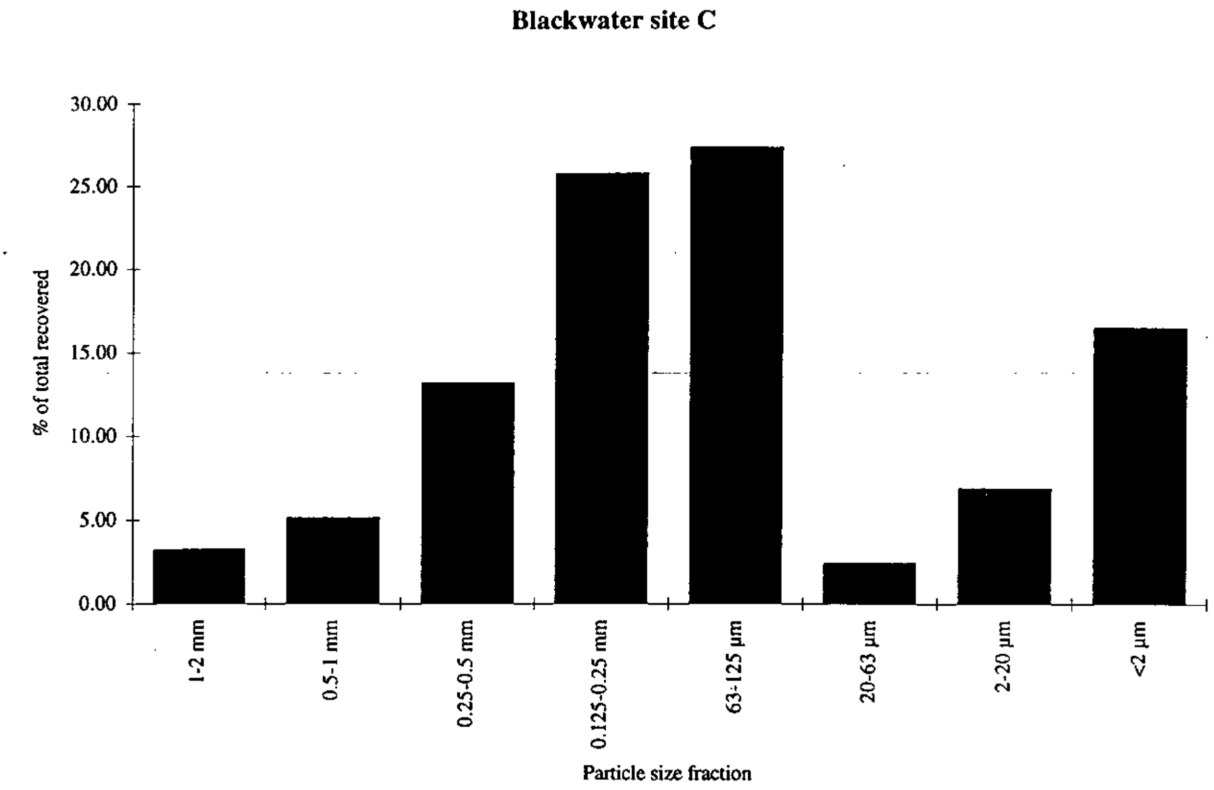
Temperature during Anaerobic experiment with R. Blackwater sediment

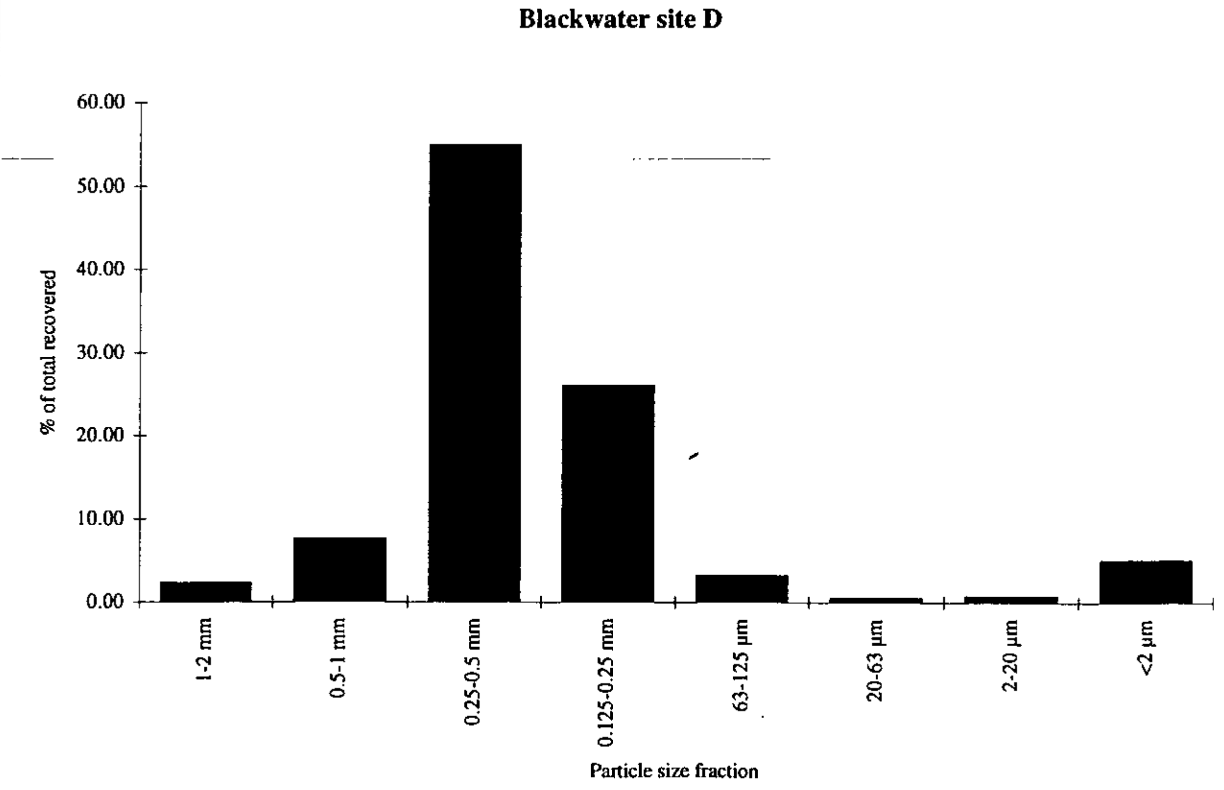
PARTICLE SIZE DISTRIBUTION OF RIVER BLACKWATER SEDIMENTS
SAMPLE DATE 18/4/96


Blackwater site A


Blackwater site B

PARTICLE SIZE DISTRIBUTION OF RIVER BLACKWATER SEDIMENTS
SAMPLE DATE 18/4/96





APPENDIX D

RESULTS FROM ANALYSIS OF SEDIMENT CORE SECTIONS
Sediment collected 18/4/96

Sample	P1	P2	P3	P4	P5	P6
Section (cm from sediment surface)	0 - 0.5	0.5 - 1	1 - 2	2 - 4	4 - 6	6 - 10
% water	82.3	74.2	77.0	84.5	81.5	62.4
% water of centrifuged sediment	57.9	49.4	54.2	61.8	57.1	40.2
pH	7.5	7.47	7.59	7.57	7.6	7.48
Conductivity (µS/ cm @ 25 'C)	832	913	1025	1275	1393	1697
Temperature ('C)	12.1	12.1	12.1	12	12	12
Redox potential (mV)	207	159	116	94	81	67
Calcium (mmol/ l)	2.4	2.7	3.3	4.7	5.4	7.3
Magnesium (mmol/ l)	0.3	0.3	0.3	0.3	0.2	0.4
Potassium (mmol/ l)	0.4	0.4	0.5	0.5	0.6	0.6
Sodium (mmol/ l)	2.6	2.7	2.8	2.7	2.4	3.0
Iron (µmol/ l)	3.6	3.6	3.6	3.6	3.6	7.2
Ammonium (mmol/ l)	0.4	0.6	0.9	1.4	1.6	1.9
SRP (µmol/ l)	37.2	29.4	17.2	7.7	6.4	1.0
TDP (µmol/ l)	38.5	30.6	18.6	8.2	8.9	3.4
Nitrate	ND	ND	ND	ND	ND	ND
Nitrite (µmol/ l)	0.7	1.0	2.4	1.6	1.6	0.9
Silicon (µmol/ l)	278	313	354	438	484	513
Chloride (mmol/ l)	2.1	2.0	2.0	2.0	2.0	2.2
Bromide (µmol/ l)	ND	ND	ND	6.8	5.3	10.3
Sulphate (µmol/ l)	791	645	437	250	146	83
Bicarbonate (mmol/ l)	5.2	6.3	8.2	11.8	13.4	18.3
Organic matter (% of dry weight)	15.7	12.42	15.9	20.17	16.34	9.53
Total Phosphorus (µmol/ g)	423	317	350	481	452	167
Total Calcium (µmol/ g)	531	512	460	399	602	313
Total Iron (µmol/ g)	1001	831	1017	1165	1065	524
Bioavailable Phosphorus (µmol/ g)	6.3	4.7	4.7	7.1	5.85	3.1
Equilibrium Phosphorus Concentration (µmol/ l)	6.8	5.4	4.6	5.3	5.2	2.9
Adsorption affinity, Kd (l/ kg)	2293	1790	2488	2430	1734	1364
Initial native phosphorus, ni (µmol/ g)	15.5	9.6	11.4	12.9	9	4

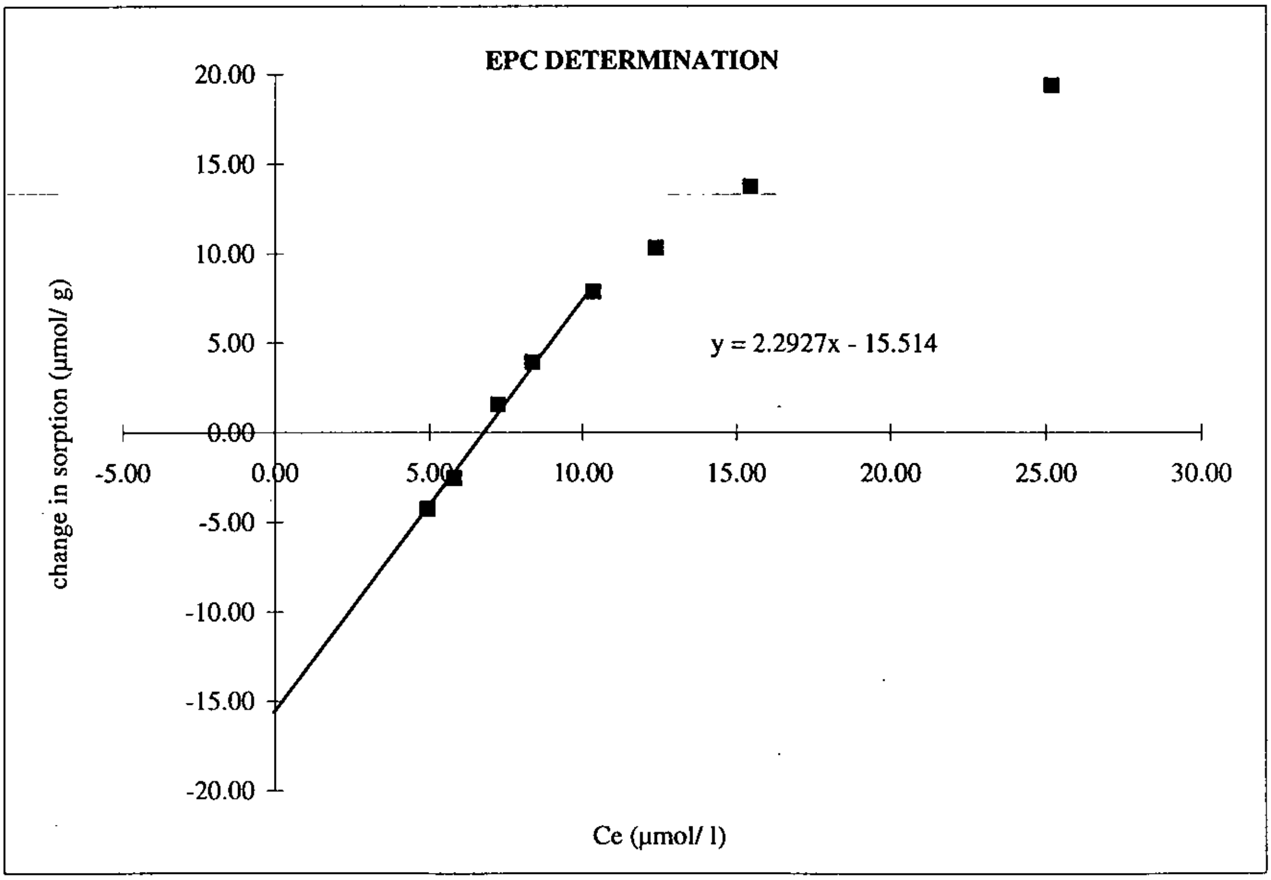
Sample	S1	S2	S3
Treatment	Left sealed under nitrogen until centrifugation	Aerated for 4 hours, then left exposed to air for 5 days at 4 'C	Exposed to air and stirred periodically for 1 hour
Redox potential before treatment (mV)	-16	-11	-23
Redox potential after treatment (mV)	35	408	60
[SRP] in supernatant (µmol/ l)	19.3	3.9	19.4
[Ca] in supernatant (mmol/ l)	5.4	4.8	5.6
[Fe] in supernatant (µmol/ l)	149	11	154

EPC determination of sediment from vertical cores taken from river Blackwater site B
Sample P1 (0 - 0.5 cm depth from sediment surface)

EPCo DETERMINATION: ANALYSIS 29/4/96				
weight of wet sediment/ g	weight of dry sediment/ g	initial [P] (µmol/ l)	[P] at 24 h (µmol/ l)	dN (µmol/ g dry wt)
1.08	0.46	0	5.80	-2.55
0.55	0.23	0	4.95	-4.27
2.34	0.99	15	7.23	1.57
2.61	1.10	30	8.36	3.93
2.09	0.88	45	10.35	7.88
2.19	0.92	60	12.40	10.31
2.06	0.87	75	15.47	13.73
1.22	0.51	75	25.20	19.37

% water of sediment = 57.86
Organic matter as % of dry weight = 15.70
Total phosphorus of sediment = 423 µmol/ g
Total Calcium of sediment = 531 µmol/ g
Total Iron of sediment = 1001 µmol/ g

SRP of river water = 93.0 µmol/ l
SRP of sediment pore water = 37.2 µmol/ l
TDP of sediment pore water = 38.5 µmol/ l
EPCo = 6.8 µmol/ l
Kd = 2293 l/ kg
ni = 15.5 µmol/ g

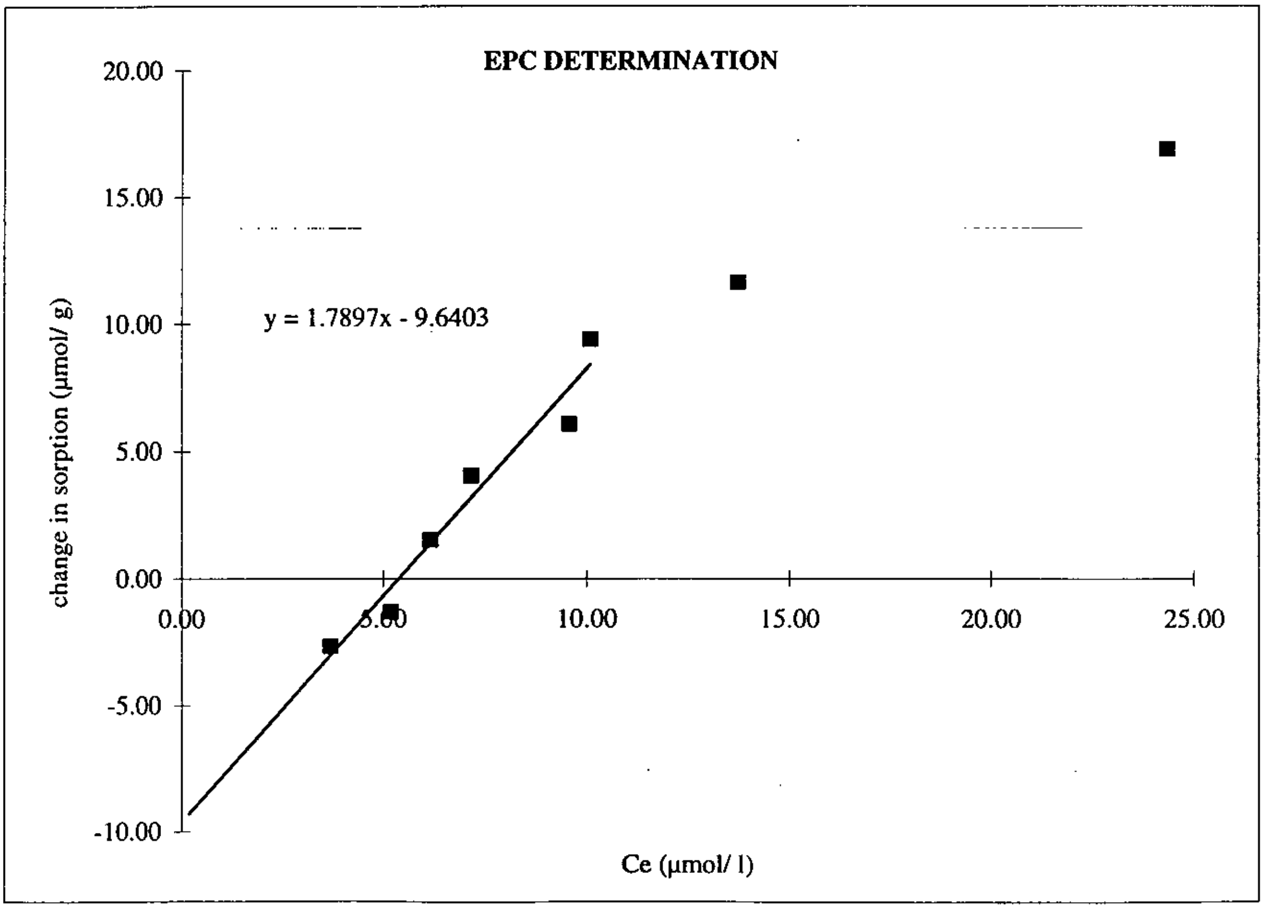


EPC determination of sediment from vertical cores taken from river Blackwater site B
Sample P2 (0.5 - 1 cm depth from sediment surface)

EPCo DETERMINATION: ANALYSIS 29/4/96				
weight of wet sediment/ g	weight of dry sediment/ g	initial [P] (μmol/ l)	[P] at 24 h (μmol/ l)	dN (μmol/ g dry wt)
1.56	0.79	0	5.20	-1.31
0.55	0.28	0	3.70	-2.67
2.26	1.14	15	6.16	1.54
2.22	1.13	30	7.16	4.06
2.30	1.17	45	9.57	6.07
2.10	1.06	60	10.09	9.41
2.08	1.05	75	13.71	11.62
1.18	0.60	75	24.34	16.90

% water of sediment = 49.35
Organic matter as % of dry weight = 12.42
Total phosphorus of sediment = 317 μmol/ g
Total Calcium of sediment = 512 μmol/ g
Total Iron of sediment = 831 μmol/ g

SRP of river water = 93.0 μmol/ l
SRP of sediment pore water = 29.4 μmol/ l
TDP of sediment pore water = 30.7 μmol/ l
EPCo = 5.4 μmol/ l
Kd = 1790 l/ kg
ni = 9.6 μmol/ g

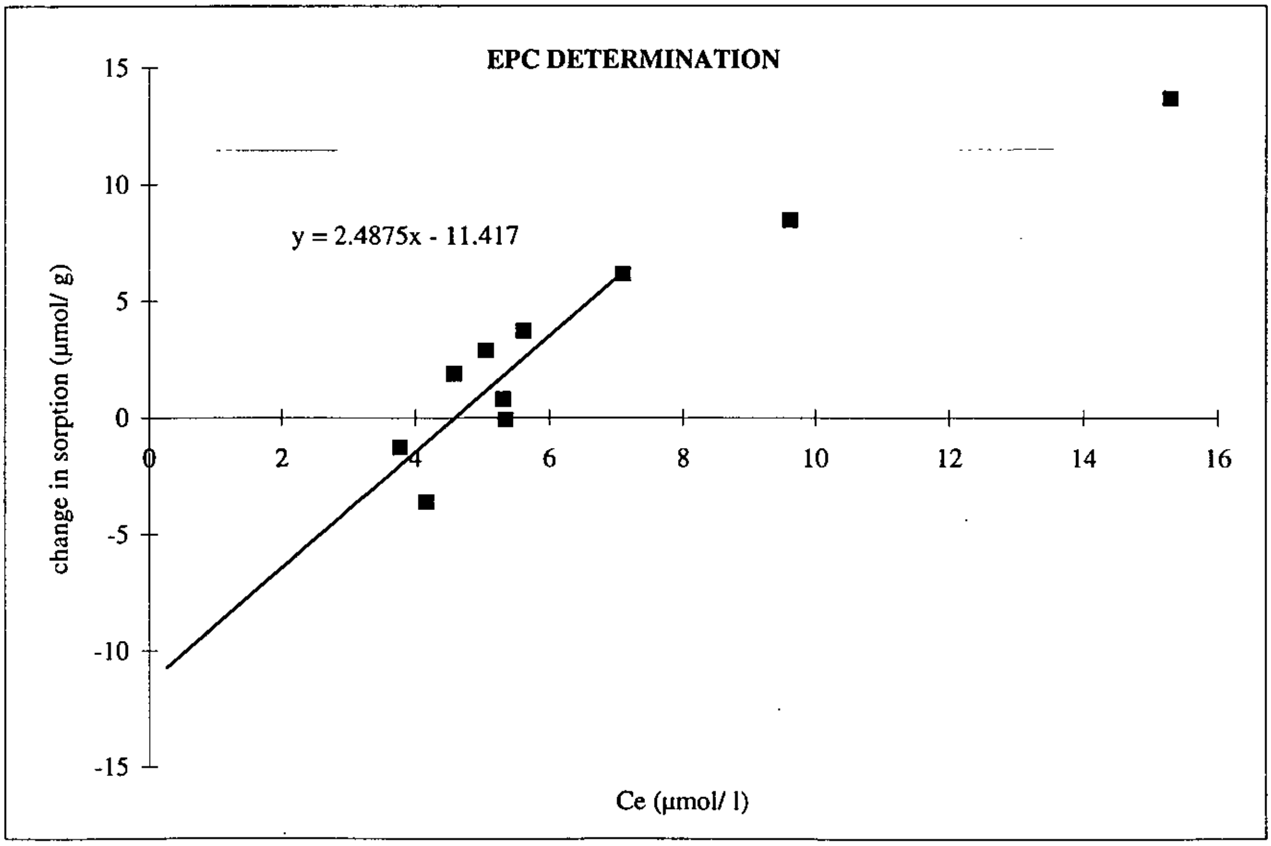


EPC determination of sediment from vertical cores taken from river Blackwater site B
Sample P3 (1 - 2 cm depth from sediment surface)

EPCo DETERMINATION: ANALYSIS 29/4/96				
weight of wet sediment/ g	weight of dry sediment/ g	initial [P] (µmol/ l)	[P] at 24 h (µmol/ l)	dN (µmol/ g dry wt)
1.30	0.59	0	3.77	-1.27
0.51	0.23	0	4.16	-3.60
2.17	0.99	5	5.35	-0.07
2.58	1.18	10	5.31	0.80
2.42	1.11	15	4.58	1.89
2.27	1.04	20	5.05	2.87
2.28	1.04	25	5.61	3.71
1.63	0.74	30	7.10	6.15
1.11	0.51	50	15.30	13.65
2.08	0.95	50	9.63	8.47

% water of sediment = 54.24
Organic matter as % of dry weight = 15.89
Total phosphorus of sediment = 350 µmol/ g
Total Calcium of sediment = 460 µmol/ g
Total Iron of sediment = 1017 µmol/ g

SRP of river water = 93.0 µmol/ l
SRP of sediment pore water = 17.2 µmol/ l
TDP of sediment pore water = 18.6 µmol/ l
EPCo = 4.6 µmol/ l
Kd = 2488 l/ kg
ni = 11.4 µmol/ g

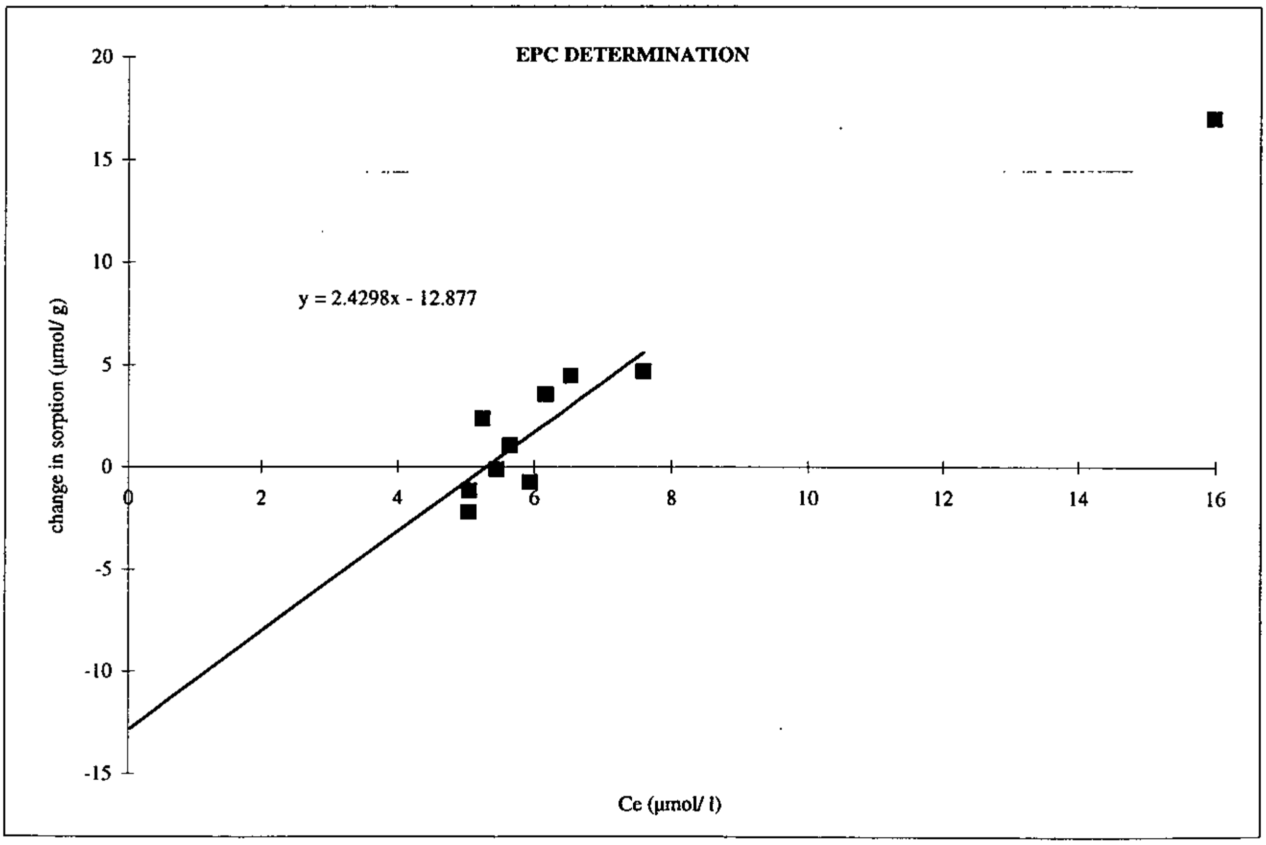


EPC determination of sediment from vertical cores taken from river Blackwater site B
Sample P4 (2 - 4 cm depth from sediment surface)

EPCo DETERMINATION: ANALYSIS 29/4/96				
weight of wet sediment/ g	weight of dry sediment/ g	initial [P] (µmol/ l)	[P] at 24 h (µmol/ l)	dN (µmol/ g dry wt)
4.13	1.58	0	5.93	-0.75
2.28	0.87	0	5.04	-1.16
1.20	0.46	0	5.03	-2.20
2.18	0.83	5	5.45	-0.11
2.17	0.83	10	5.64	1.05
2.15	0.82	15	5.24	2.38
2.04	0.78	20	6.16	3.55
2.17	0.83	25	6.52	4.46
1.05	0.40	50	15.98	16.99
4.73	1.81	50	7.59	4.69

% water of sediment = 61.77
Organic matter as % of dry weight = 20.17
Total phosphorus of sediment = 481 µmol/ g
Total Calcium of sediment = 399 µmol/ g
Total Iron of sediment = 1165 µmol/ g

SRP of river water = 93.0 µmol/ l
SRP of sediment pore water = 7.7 µmol/ l
TDP of sediment pore water = 8.2 µmol/ l
EPCo = 5.3 µmol/ l
Kd = 2430 l/ kg
ni = 12.9 µmol/ g

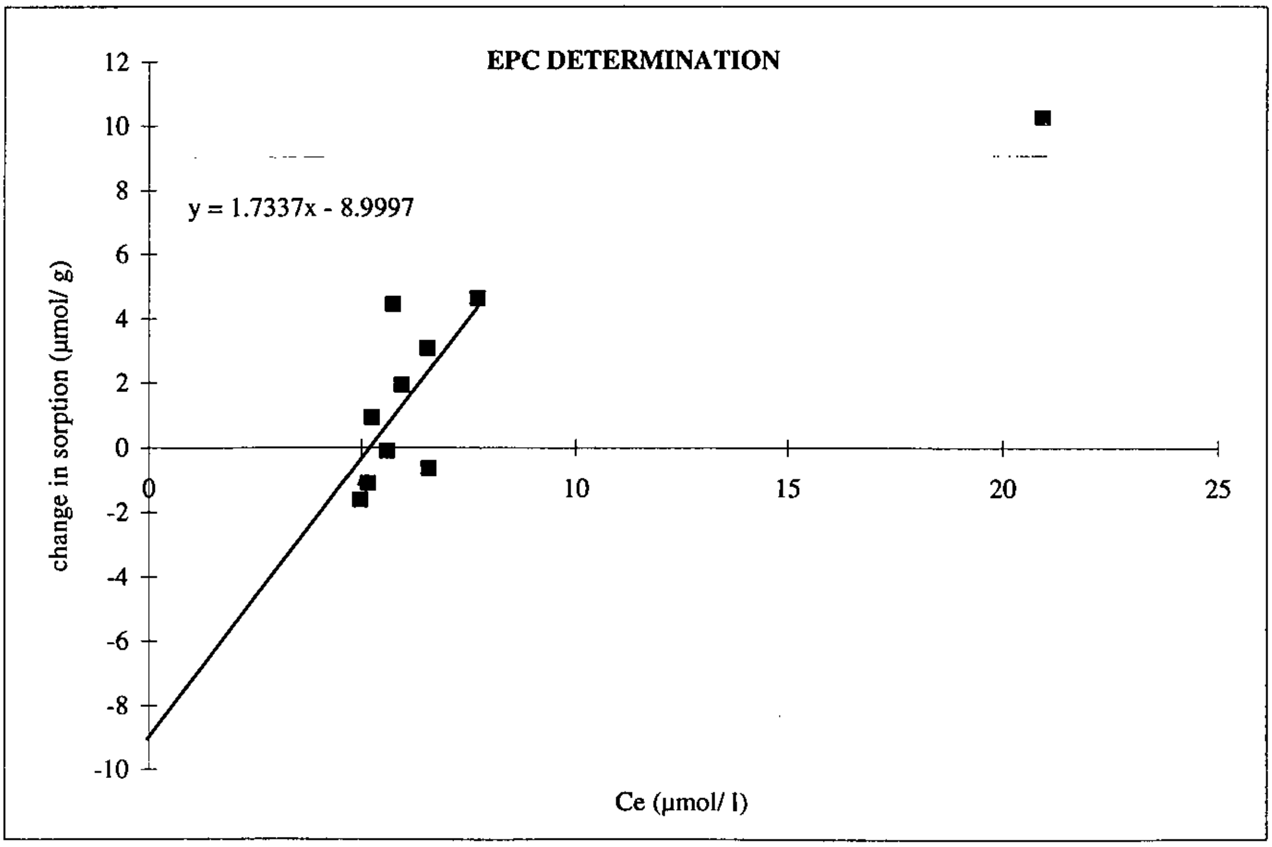


EPC determination of sediment from vertical cores taken from river Blackwater site B
Sample P5 (4 - 6 cm depth from sediment surface)

EPCo DETERMINATION: ANALYSIS 29/4/96				
weight of wet sediment/ g	weight of dry sediment/ g	initial [P] (μmol/ l)	[P] at 24 h (μmol/ l)	dN (μmol/ g dry wt)
4.74	2.03	0	6.56	-0.65
2.20	0.94	0	5.14	-1.09
1.43	0.61	0	4.96	-1.62
2.65	1.13	5	5.60	-0.11
2.40	1.03	10	5.23	0.93
2.18	0.93	15	5.94	1.94
2.04	0.87	20	6.53	3.08
2.01	0.86	25	5.73	4.46
1.32	0.57	50	20.92	10.27
4.25	1.82	50	7.70	4.64

% water of sediment = 57.11
Organic matter as % of dry weight = 16.34
Total phosphorus of sediment = 452 μmol/ g
Total Calcium of sediment = 602 μmol/ g
Total Iron of sediment = 1065 μmol/ g

SRP of river water = 93.0 μmol/ l
SRP of sediment pore water = 6.4 μmol/ l
TDP of sediment pore water = 8.9 μmol/ l
EPCo = 5.2 μmol/ l
Kd = 1734 l/ kg
ni = 9.0 μmol/ g

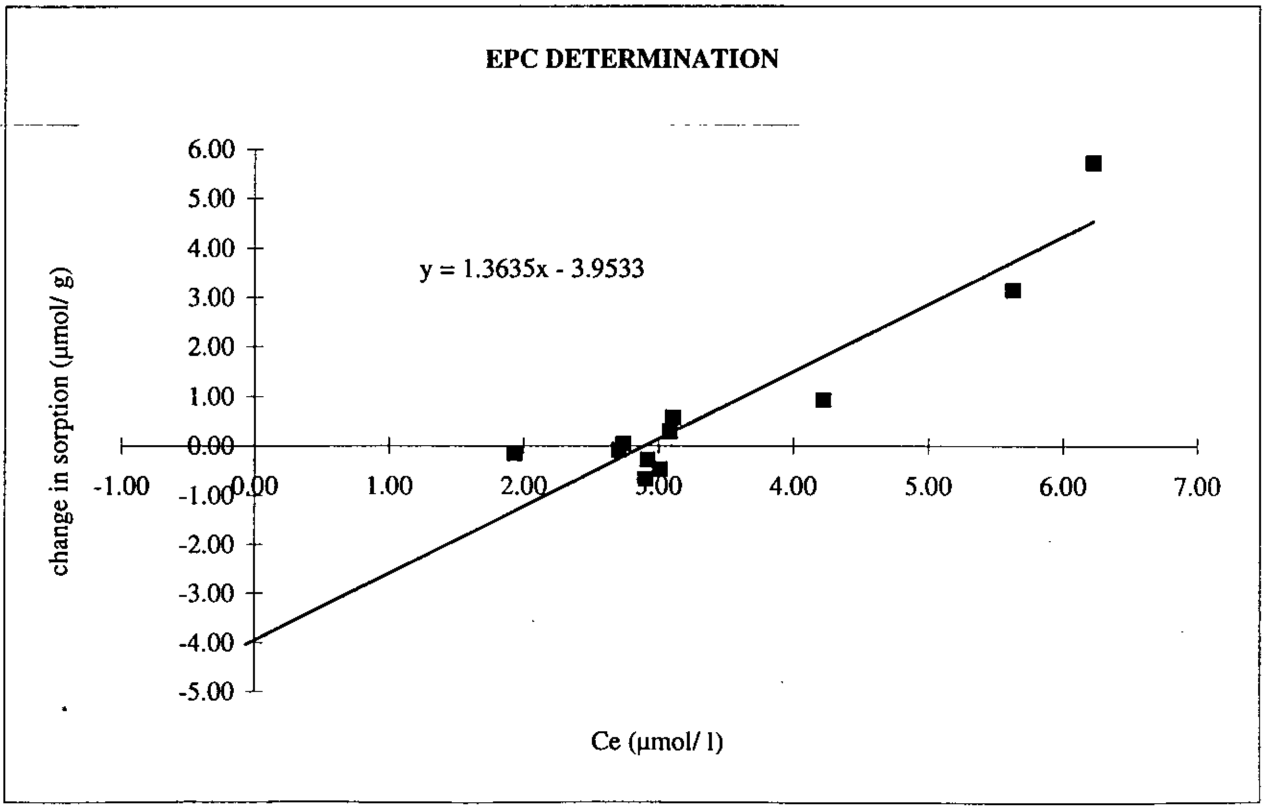


EPC determination of sediment from vertical cores taken from river Blackwater site B
Sample P6 (6 - 10 cm depth from sediment surface)

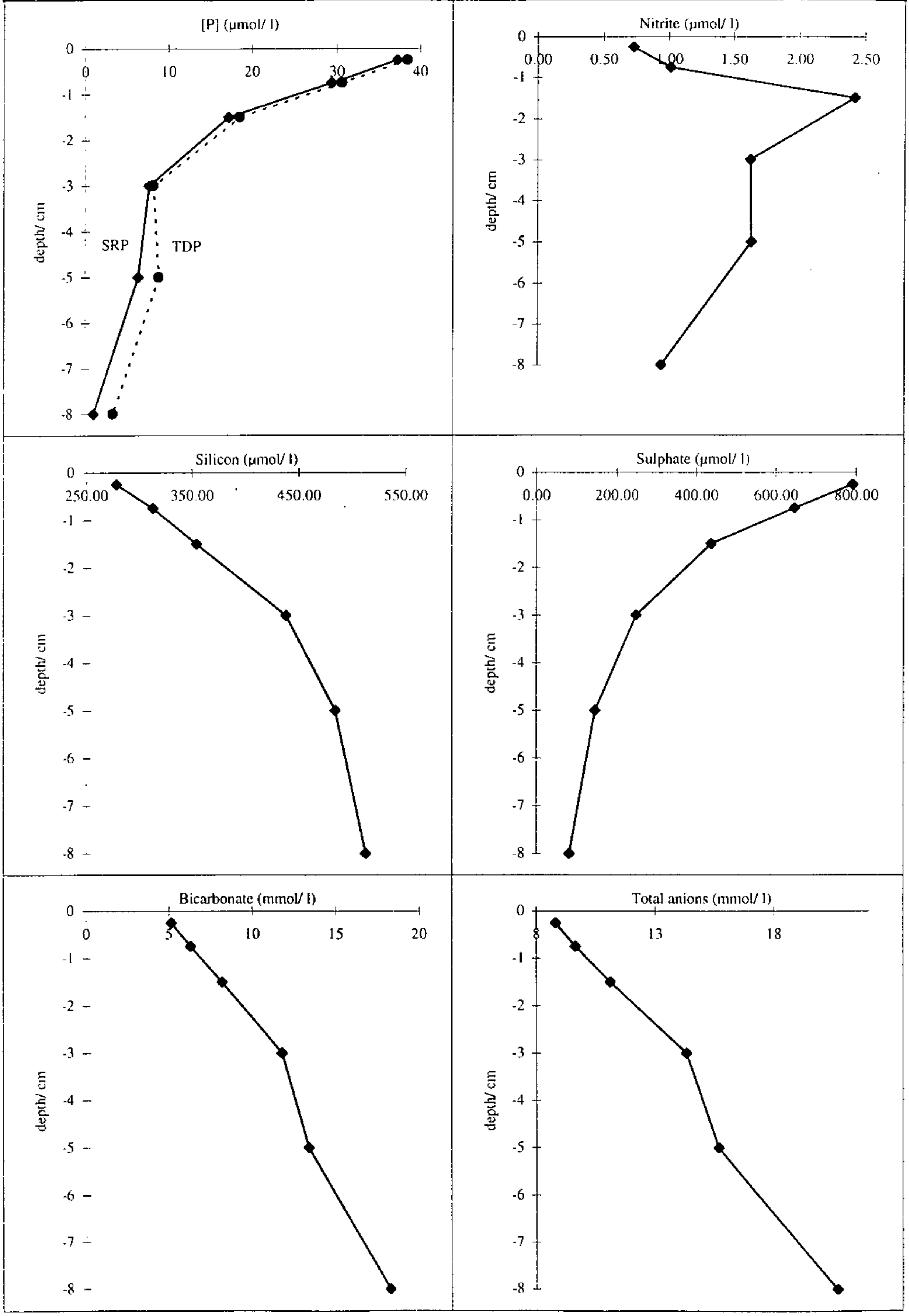
EPCo DETERMINATION: ANALYSIS 29/4/96				
weight of wet sediment/ g	weight of dry sediment/ g	initial [P] (µmol/ l)	[P] at 24 h (µmol/ l)	dN (µmol/ g dry wt)
4.07	2.43	0	1.93	-0.16
2.11	1.26	0	3.01	-0.48
1.45	0.86	0	2.91	-0.67
2.26	1.35	1	2.92	-0.28
2.55	1.52	2	2.71	-0.09
2.21	1.32	3	2.74	0.04
2.20	1.32	5	3.09	0.29
2.30	1.37	7	3.11	0.57
2.08	1.24	10	4.22	0.93
2.07	1.23	25	5.63	3.14
2.56	1.53	50	6.22	5.72

% water of sediment = 40.23
Organic matter as % of dry weight = 9.53
Total phosphorus of sediment = 167 µmol/ g
Total Calcium of sediment = 313 µmol/ g
Total Iron of sediment = 524 µmol/ g

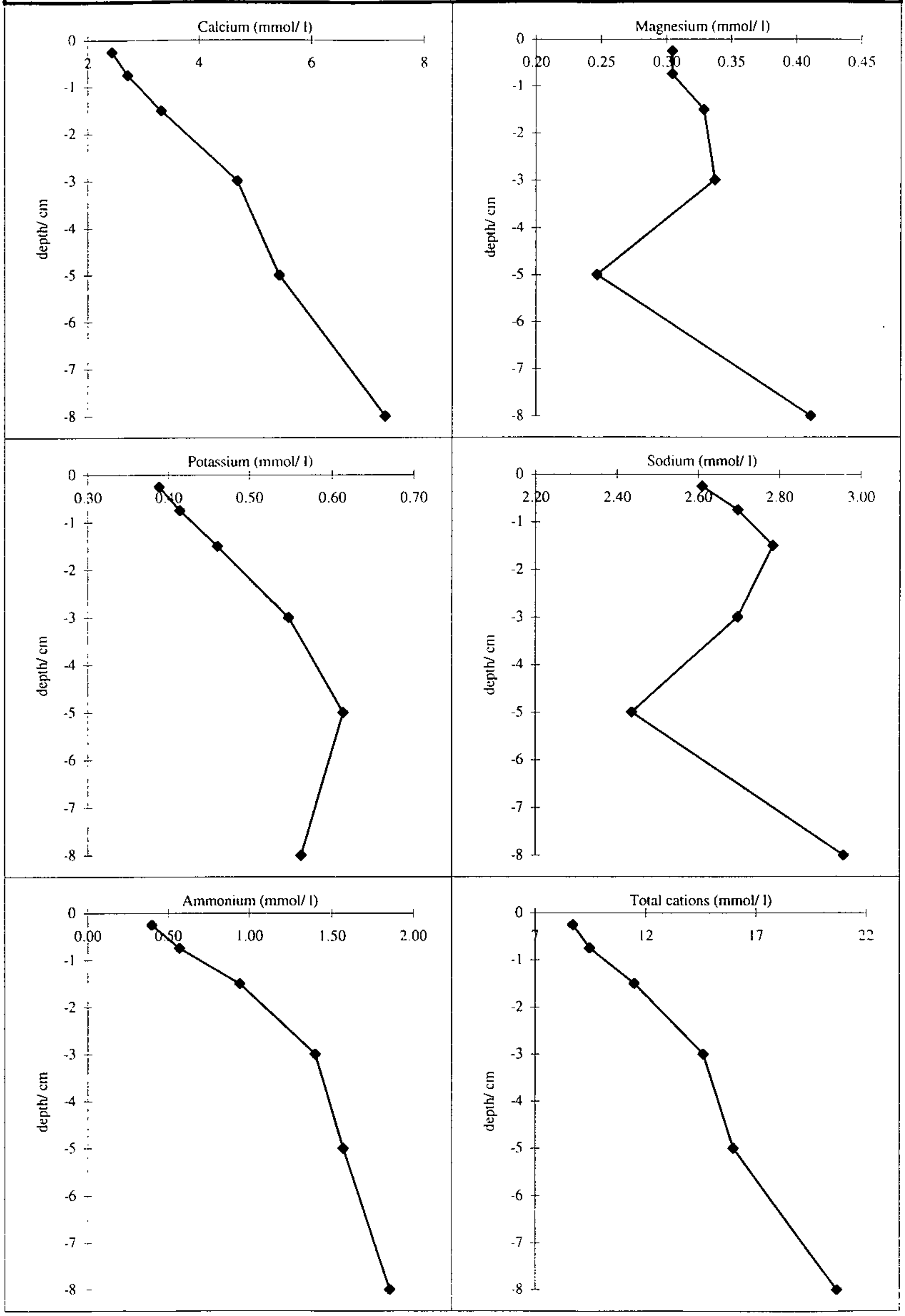
SRP of river water = 93.0 µmol/ l
SRP of sediment pore water = 1.0 µmol/ l
TDP of sediment pore water = 3.4 µmol/ l
EPCo = 2.9 µmol/ l
Kd = 1364 l/ kg
ni = 4.0 µmol/ g



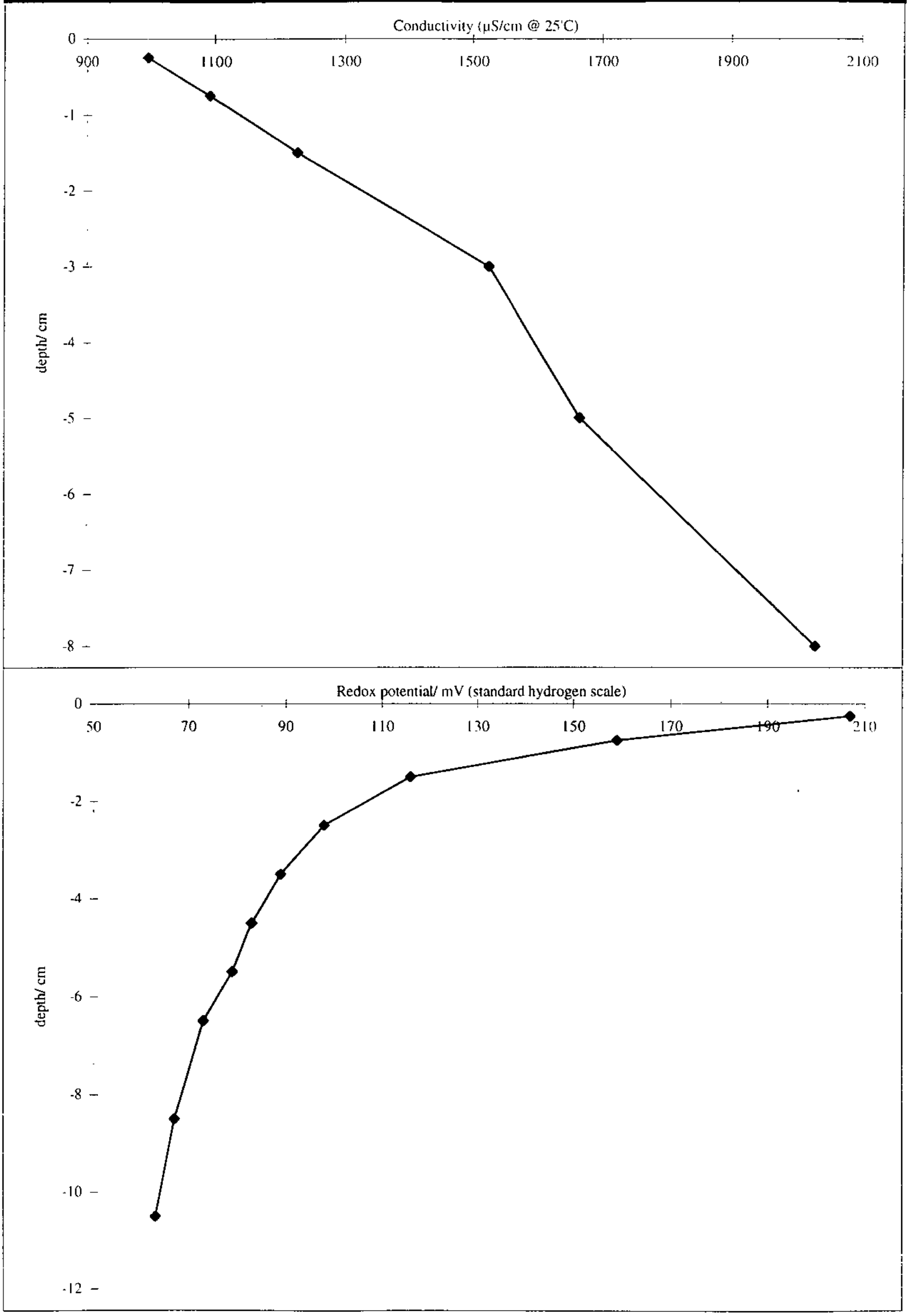
CONCENTRATION PROFILES OF MAJOR ANIONS IN SEDIMENT PORE WATER FROM VERTICAL CORES TAKEN FROM RIVER BLACKWATER SITE B



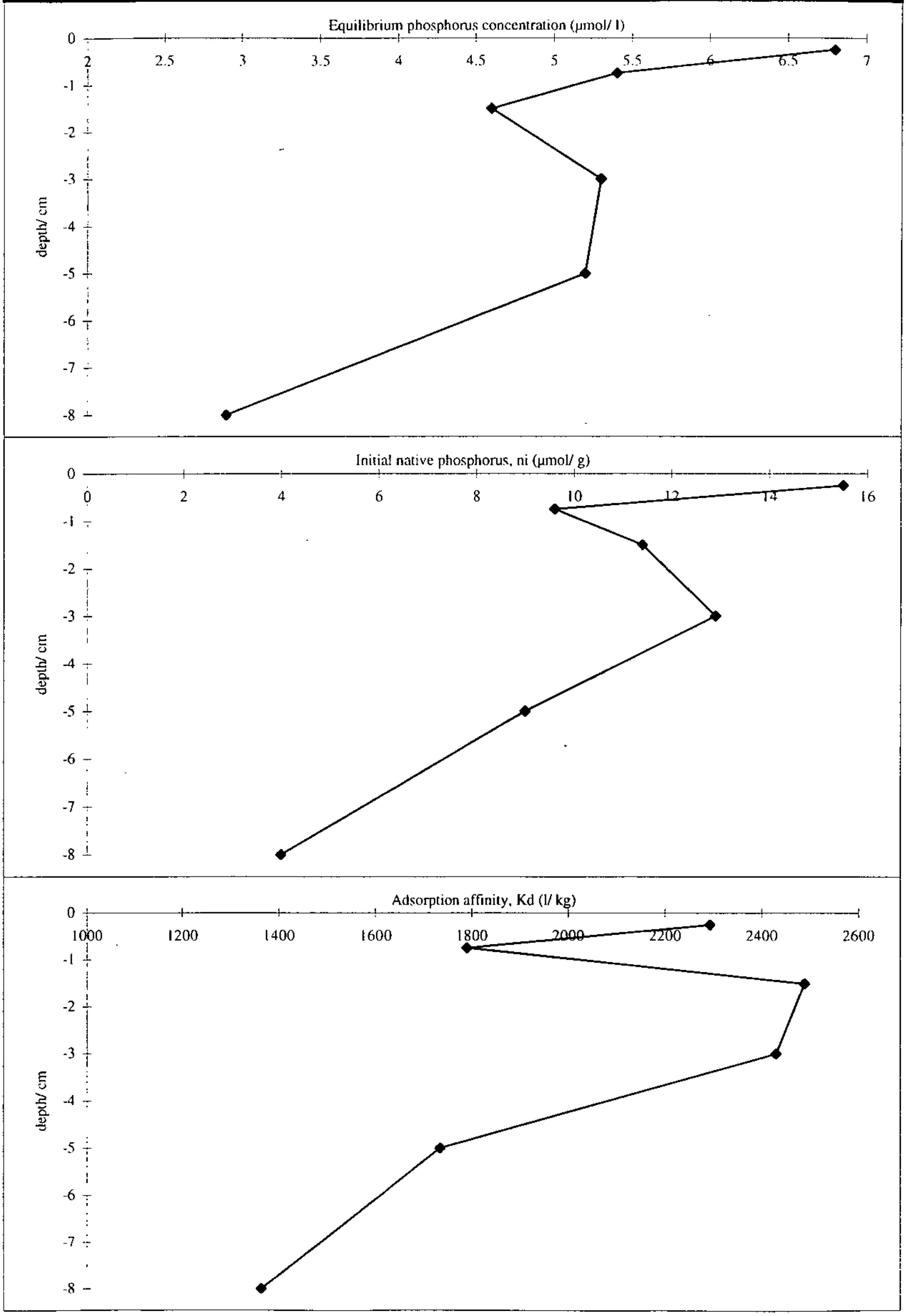
CONCENTRATION PROFILES OF MAJOR CATIONS IN SEDIMENT PORE WATER FROM VERTICAL CORES TAKEN FROM RIVER BLACKWATER SITE B



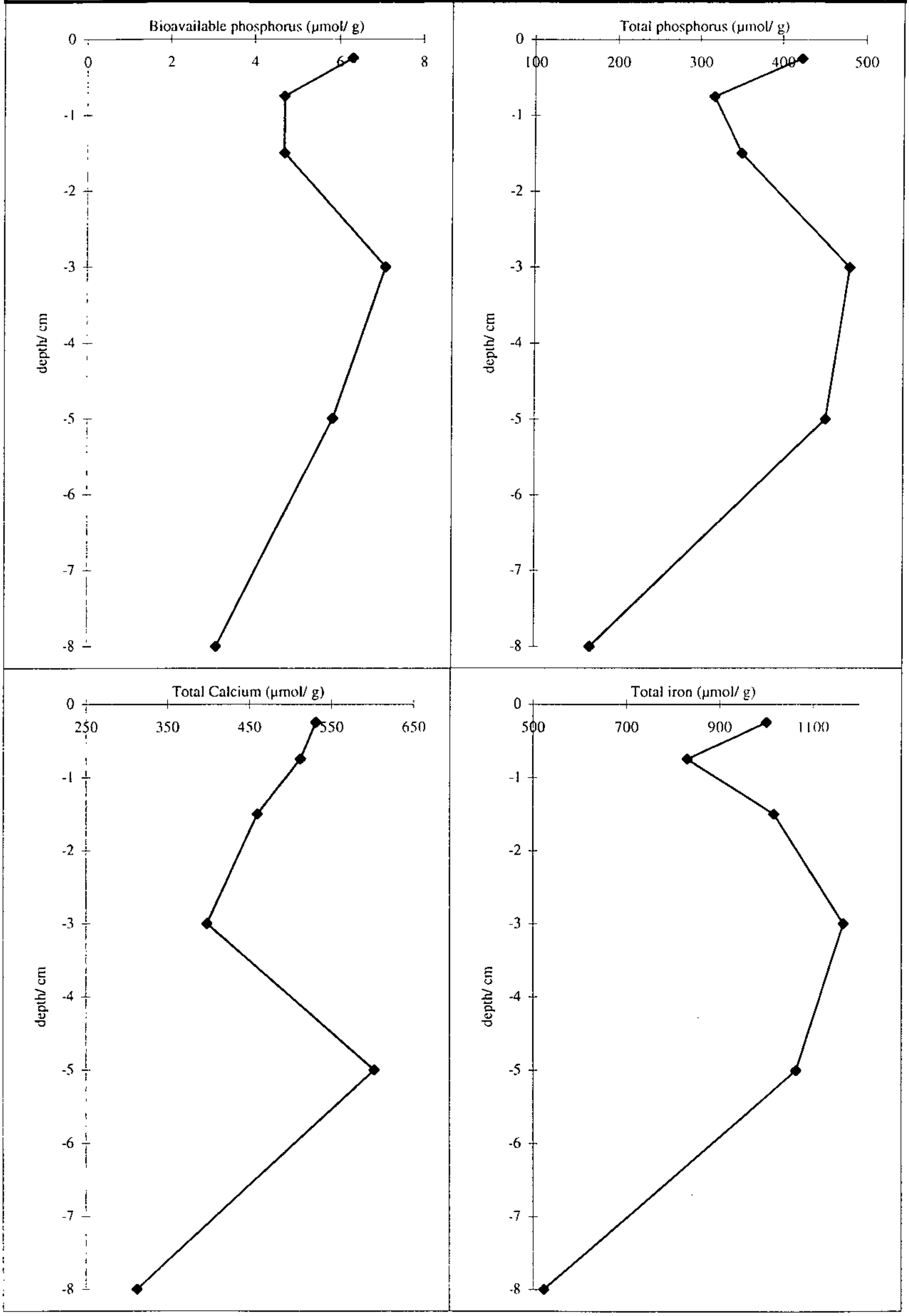
PHYSICO-CHEMICAL CHARACTERISTCS OF SEDIMENT PORE WATER FROM VERTICAL CORES TAKEN FROM RIVER BLACKWATER SITE B



PROFILES OF SEDIMENT CHARACTERISTCS FROM VERTICAL CORES TAKEN FROM RIVER BLACKWATER SITE B

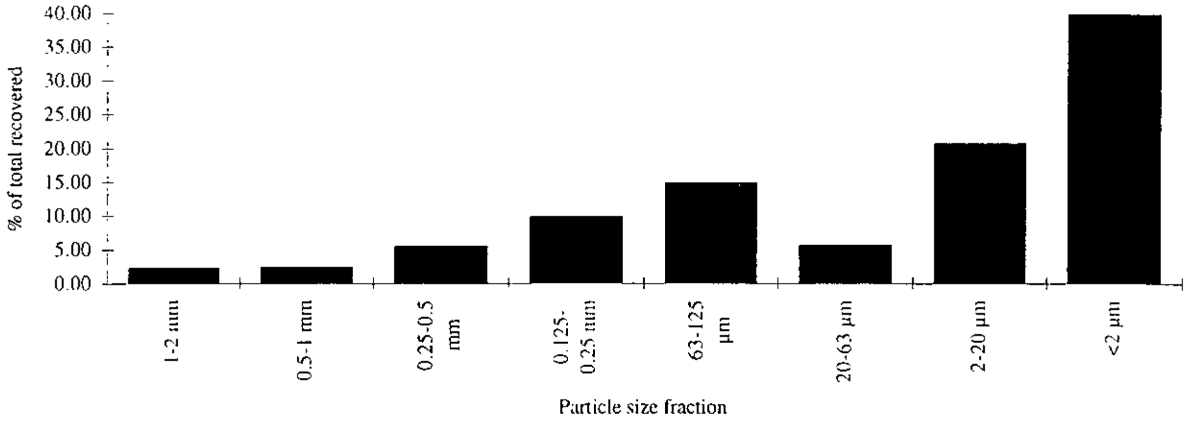


PROFILES OF SEDIMENT CHARACTERISTCS FROM VERTICAL CORES TAKEN FROM RIVER BLACKWATER SITE B

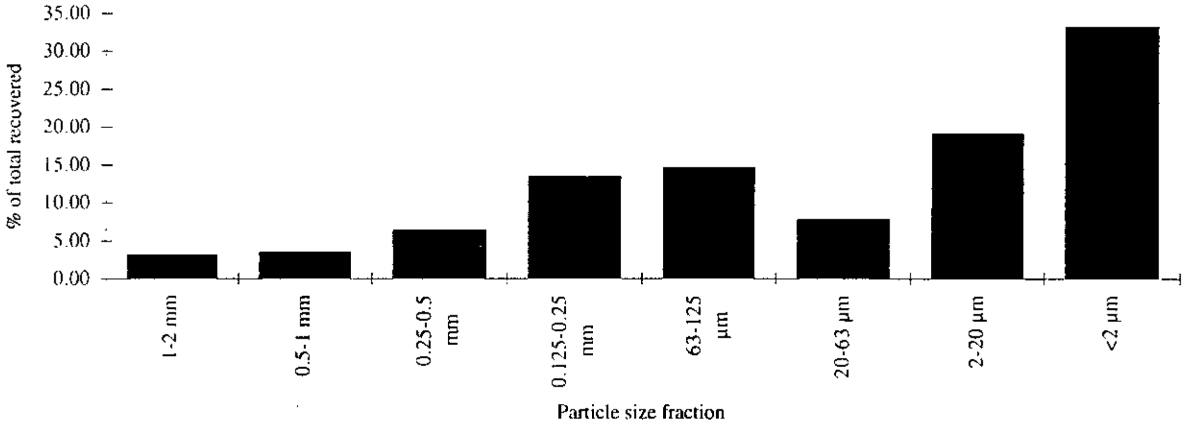


PARTICLE SIZE DISTRIBUTION OF SEDIMENTS FROM VERTICAL CORES TAKEN FROM RIVER BLACKWATER SITE B 18/4/96

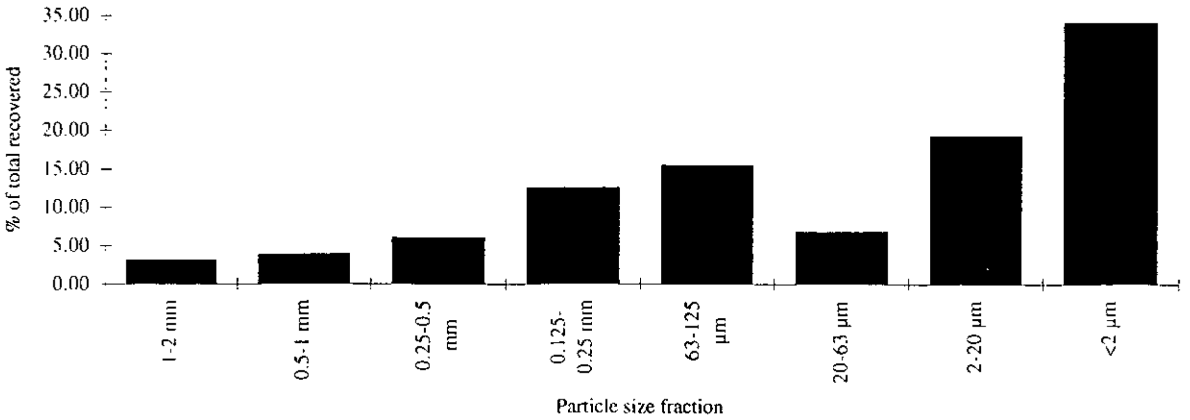
**Blackwater core pofile:
sample P1 (0-0.5 cm depth from sediment surface)**



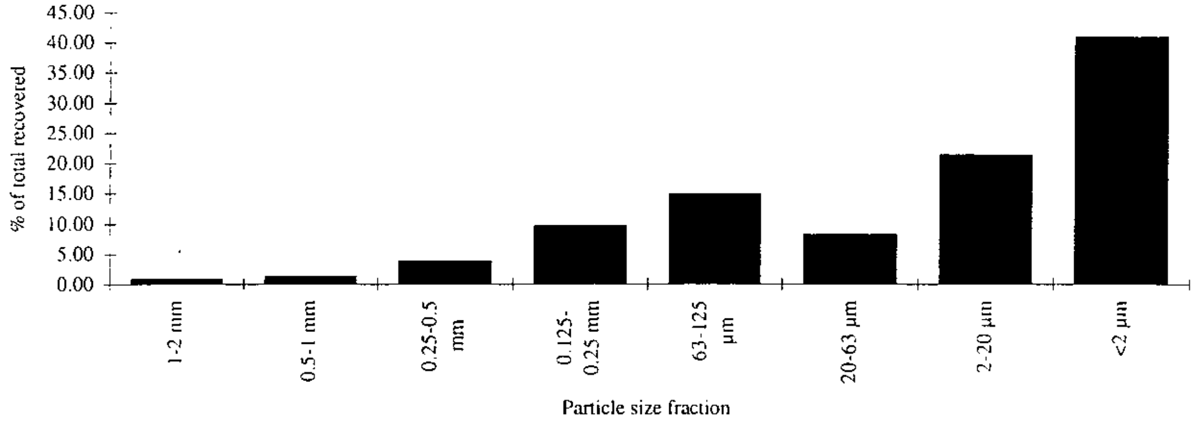
**Blackwater core pofile:
sample P2 (0.5-1 cm depth from sediment surface)**



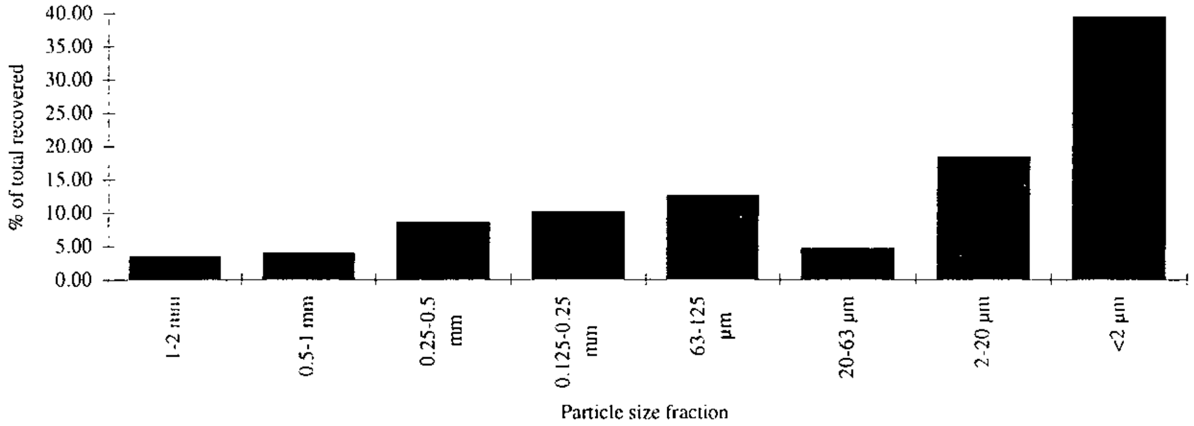
**Blackwater core pofile:
sample P3 (1-2 cmdepth from sediment surface)**



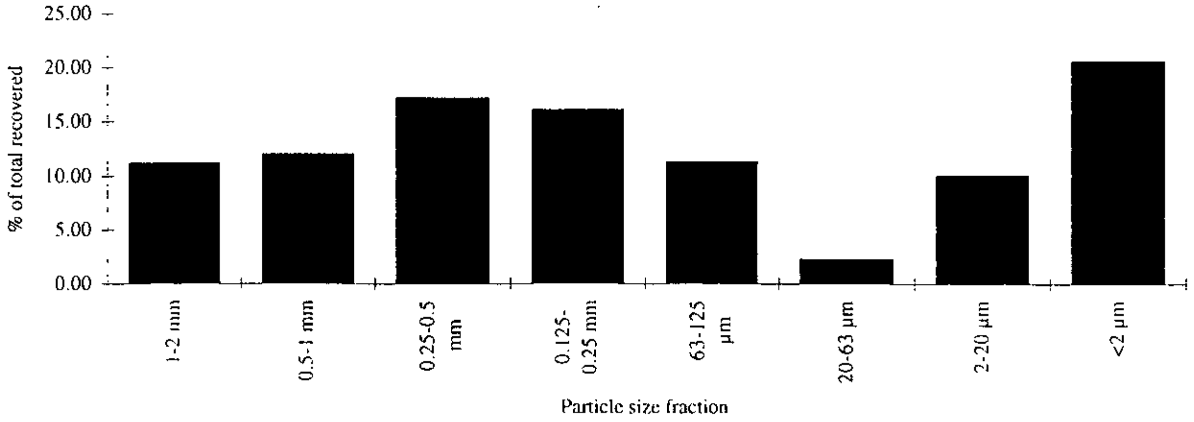
PARTICLE SIZE DISTRIBUTION OF SEDIMENTS FROM VERTICAL CORES TAKEN FROM RIVER BLACKWATER SITE B 18/4/96



Blackwater core pofile:
sample P4 (2-4 cmdepth from sediment surface)



Blackwater core pofile:
sample P5 (4-6 cm depth from sediment surface)



Blackwater core pofile:
sample P6 (6-10 cm depth from sediment surface)

PARTICLE SIZE DISTRIBUTION OF SEDIMENTS FROM VERTICAL CORES TAKEN FROM RIVER BLACKWATER SITE B 18/4/96