

TI059 j1/6



Institute of  
Freshwater  
Ecology

RJ 1 ab.  
APRIL  
1997

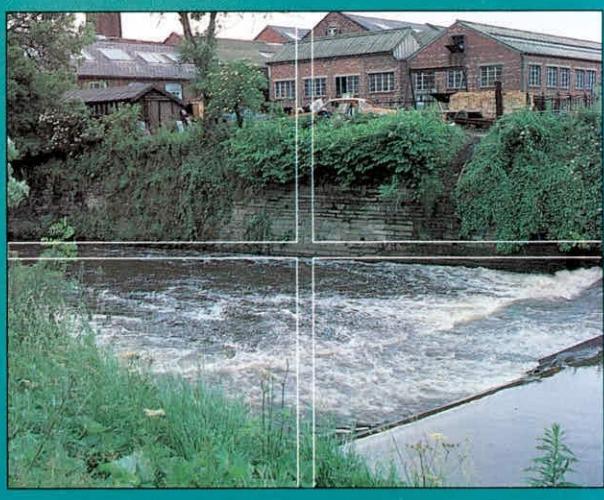
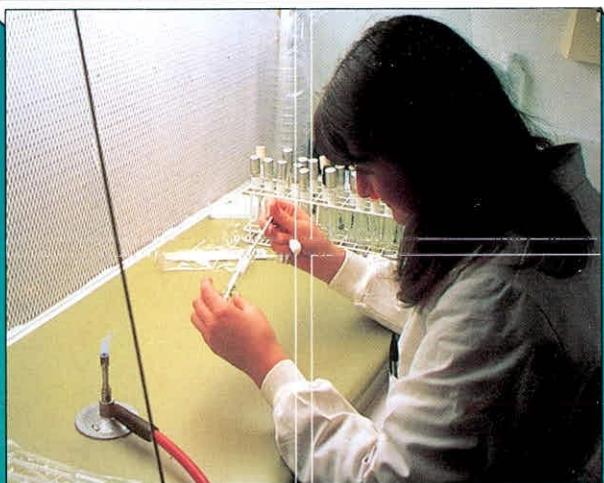
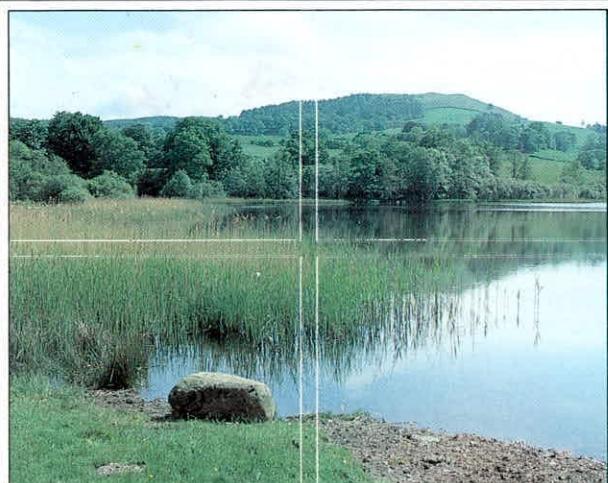
# Assessment of the potential for phosphorus reduction in river waters

W.A. House DSc CChem FRSC

F.H. Denison HNC

S.M. Smith

R.Sadak



**Centre for  
Ecology &  
Hydrology**

**Natural Environment Research Council**

Institute of Freshwater Ecology  
Institute of Hydrology  
Institute of Terrestrial Ecology  
Institute of Virology & Environmental Microbiology



**Institute of  
Freshwater  
Ecology**

**River Laboratory**  
East Stoke, Wareham  
Dorset BH20 6BB  
United Kingdom

*Telephone +44 (0)1929 462314  
Facsimile +44 (0)1929 462180  
Email*

## **Assessment of the potential for phosphorus reduction in river waters**

**W.A. House DSc CChem FRSC  
F.H. Denison HNC  
S.M. Smith  
R.Sadak**

Project Leader:	<b>W.A. House</b>
Report Start Date:	<b>1 September 1996</b>
Report End Date:	<b>1 April 1997</b>
Report To:	<b>Department of the Environment Romney House, 43 Marsham Street London, SW1P 3PY</b>
Contract No:	<b>EPG/1/9/09</b>
IFE Report Ref. No:	<b>RL/T11059j1/6</b>

**Centre for  
Ecology &  
Hydrology**

Institute of Freshwater Ecology  
Institute of Hydrology  
Institute of Terrestrial Ecology  
Institute of Virology & Environmental Microbiology

Natural Environment Research Council

## **INTELLECTUAL PROPERTY RIGHTS**

### **CONFIDENTIALITY STATEMENT**

*'In accordance with our normal practice, this report is for the use only of the party to whom it is addressed, and no responsibility is accepted to any third party for the whole or any part of its contents. Neither the whole nor any part of this report or any reference thereto may be included in any published document, circular or statement, nor published or referred to in any way without our written approval of the form and context in which it may appear.'*

## **CONTENTS**

<b>GLOSSARY</b>	<b>2</b>
<b>SUMMARY</b>	<b>3</b>
<b>1. INTRODUCTION</b>	<b>3</b>
<b>2. LABORATORY METHODS</b>	<b>4</b>
<b>3. FLUVARIUM CHANNEL EXPERIMENTS</b>	<b>4</b>
<b>4. FURTHER WORK</b>	<b>6</b>
<b>5. PAPER FOR SUBMISSION TO WATER RESEARCH</b>	<b>7</b>
<i>Main results from the research on the R. Wey</i>	
<b>APPENDIX 1. Fluvarium channel sediment profiles</b>	<b>30</b>

## 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.
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 <sub>0</sub> is the EPC of a sediment containing only native phosphorus ie. when the sediment is in contact with a solution with SRP=EPC <sub>0</sub> , there is no net flux of SRP.
K <sub>d</sub>	Distribution coefficient in units of dm <sup>3</sup> kg <sup>-1</sup> . 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 <sub>i</sub>	Initial adsorption amount. The initial concentration of SRP associated with the sediment prior to sorption. n <sub>i</sub> is normally < BAP for sediments.
OM	Organic matter content expressed as a percentage of the dry weight measured by combustion at 550 °C
PP	Particulate phosphorus. Difference between TP and TDP, ie that phosphorus associated with the particulate phase of size > 0.45 :m.
SRP	Soluble reactive phosphorus. Soluble phosphorus measured after filtration through a 0.45 :m membrane filter without acid digestion.
STW	Sewage treatment works.
TDP	Total dissolved phosphorus. Filtered through 0.45 :m membrane filter but subject to acid digestion prior to analysis.
TP	Total phosphorus. Unfiltered and subject to acid digestion prior to analysis.
f <sub>i</sub>	Flux in the ith river section; mmol s <sup>-1</sup>
q <sub>i</sub>	Discharge in the ith river section; m <sup>3</sup> s <sup>-1</sup>
c <sub>i</sub>	Concentration of SRP in the ith river section; :mol dm <sup>-3</sup> or mmol m <sup>-3</sup>
p <sub>c<sub>i</sub></sub> , p <sub>q<sub>i</sub></sub>	Concentration and discharge of point-source in ith section

## SUMMARY

Further site visits to the R. Blackwater have been completed (27/8/97 and 6/11/96). New experiments have been started using the fluvarium channel to investigate the kinetics of the development of vertical profiles in SRP (and other chemicals including nutrients) in surface sediment from site B of the R. Blackwater.

The first experiment was done in dark conditions over a 6 week period in the winter and resulted in substantial chemical gradients developing for the nutrients including phosphorus. The results show a large flux of soluble phosphorus from the bed-sediment to the overlying water. Further work has also shown that the EPC<sub>0</sub> of this sediment is dependent on the dissolved oxygen concentrations in the solution..

The second experiment, begun in early March, is to investigate the development of phosphorus (and other chemicals) profiles and measure fluxes to/from the sediment in light conditions with associated algal biofilms on the sediment.

A research paper on the work completed on the R. Wey is also attached. This is to be submitted for publication as soon as possible.

## 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.

## 3. FLUVARIUM CHANNEL EXPERIMENTS

Research has continued with more intensive studies of the development of concentration profiles of phosphorus, other nutrients and major-ions, as well as metal contaminants (as part of other projects), in the R. Blackwater sediment. Previous reports to DoE have highlighted the differences in release and uptake kinetics found for the R. Blackwater sediment in comparison with the rivers Gt. Ouse and Wey. The site immediately downstream from the sewage discharge at Aldershot town contains deposits of fine sediment with high concentrations of total phosphorus (contents of 200-450 µmol g<sup>-1</sup> were measured in the sediment cores discussed in the last report (RL/T11059J1/5). The river water is softer than the Gt. Ouse and Wey and the surface sediments contain less calcium and typically <1 % calcite. Therefore coprecipitation of phosphorus with calcite, found in the Wey and Gt. Ouse, is unlikely to be important at this site. The purpose of the studies is to:

1. obtain information about the variations of SRP with depth in the bed-sediment - and what depth resolution at the water-sediment interface is required to estimate fluxes,
2. measure the relative amounts of SRP and TDP in the sediment pore water,
3. measure redox profiles - possibly linked to measurements with micro-electrodes (100 µm tip) for dissolved oxygen and,
4. measure the effects of redox potential (related to dissolved oxygen concentration) on the measurement of EPC<sub>0</sub>.

The work was planned in two stages:

**Stage 1: Profile development in dark, cold conditions.** Sample sediment from the R. Blackwater from site B, sieve to < 2 mm size and mix. Determine the chemistry of the pore

water of the sediment and then place in the fluvarium channel to settle. Recirculate a solution of 2 mM CaCl<sub>2</sub> over the sediment in dark conditions during the winter at a constant and known velocity and measure the concentration of solutes including SRP, Si and nitrate at predetermined times over a period of approximately 6 weeks with the overlying water well aerated. At the end of this period, measure as many profiles as possible with electrodes and then slice the sediment at intervals of 2.5 mm, 5 mm, 1,2,3 and 4 cm depth to isolate porewater for a full chemical analysis - with precautions to avoid oxygenation of the sediment or porewater.

**Stage 2:** *Profile development in the light during the spring period.* As above but starting the experiment in March and allowing natural light to enter the fluvial section of the channel. This work is being done in conjunction with the Department of Biology at Birmingham University who have an interest in biological processes in algal biofilms (Drs B.S.C. Leadbeater and M. Callow). This work is planned to finish on the 18 May when electrode profiles will be measured and the sediment sliced as in stage 1.

A research grant from The Leverhulme Foundation has just started with the purpose of developing a phosphate micro-electrode (10 µm tip) to measure concentration gradients in algal biofilms and surface sediments. Such measurements will give us a better insight into processes occurring at the interface and another technique for measuring phosphate fluxes to or from the overlying water.

The following field sampling has been completed:

1. 27 August 1996- normal sampling on the R. Blackwater. The experiments with the fluvarium channel were changed so that two batches of sediment were collected. The first was used to measure the release of SRP in low DO conditions and the second to examine release/uptake as previously. This meant the last experiment was in low DO conditions for comparison with the results from the first batch.
2. 6 November 1996 - normal sampling; the fluvarium channel was used for stage 1 as described above.
3. 11 March 1997- visit to site B only for the fluvarium channel experiment- stage 2.

The experimental work for stage 1 is now complete with some of the work on the dissolved silicon profile submitted for publication in the J. Chemical Society, Faraday I (Zhmud and House, Release kinetics and concentration profile of dissolved silicon in compacted sediments). The results for phosphorus have not been examined in detail. Stage 2 is now underway and looks very promising with the sediment developing a biofilm of diatoms soon after the start.

As examples, some results from stage 1 are shown in Appendix 1. The SRP concentration increased sharply from the surface layer ≈ 40 µmol dm<sup>-3</sup> to over 250 µmol dm<sup>-3</sup> at a depth of 3 cm indicating the release of SRP to the overlying solution. Similarly Si, Ca and alkalinity gave steep profiles with the dissolution of calcium minerals and silica/silicates in the sediment. In both instances, the concentrations increased above the initial pore water concentration which is strong evidence for dissolution reactions combined with diffusive transport determining the kinetics of the development concentration profile.

#### **4. FURTHER WORK**

It is planned to complete stage 2 - measurements of the development of sediment profiles of SRP (and other nutrients) in the R. Blackwater sediment. The water companies will again be contacted to obtain a revision for the date when changes to the STW's will occur. After this, field sampling will be planned to enable the effects of the reduction in SRP inputs to be assessed.

## **5. PAPER FOR SUBMISSION TO WATER RESEARCH: Main results from the research on the R. Wey.**

### **Phosphorus Transport in a Lowland River**

William A. House and Frank H. Denison

*Institute of Freshwater Ecology, River Laboratory, East Stoke, Wareham, Dorset, BH20 6BB, U.K.*

---

**Abstract -** Seasonal changes in the concentration of phosphorus and other nutrients along a section of the river Wey in southern England are reported. Measurements of the water chemistry upstream and downstream of a point-discharge together with the analysis of surface bed-sediments indicates the accumulation of phosphorus in surface sediments in the spring and summer followed by a decrease in the autumn and winter. The profiles in the concentration of soluble reactive phosphorus (SRP) along a stretch of river are modelled by simulating the net loss of SRP using the Elovich equation and a parabolic equation. The results are compared with measurements of the release and uptake (in oxic and anoxic waters) in a laboratory fluvium channel. The net loss of SRP in the spring survey are much greater than expected from the uptake of the bed-sediment alone as determined in the fluvium channel experiments whereas the net uptakes estimated from the summer and autumn surveys are much less and in closer agreement with data from laboratory experiments.

### **INTRODUCTION**

The transport and storage of phosphorus in fluvial systems is important to our understanding of the impact of point and diffuse sources in catchments and subsequently in estuaries and coastal waters (Sharpley *et al.*, 1995). Unlike nitrate, dissolved inorganic phosphorus interacts strongly with sediments and is involved in various precipitation/ dissolution reactions, e.g. with calcium carbonate/phosphate and iron/aluminium oxide minerals (Golterman, 1985; Lucotte and d'Anglejan, 1988; Fox, 1989). In systems where distinct point-sources can be identified, little is currently known about how river bed-sediments respond to enhanced concentrations in the overlying water and whether such interactions act as a short or long-term sink of phosphorus. Advances in this area have been limited because of the complex nature of the composition of natural sediments, their associated pore water chemistry and biota. Hence a semi-empirical approach to identify the key "in-stream" processes is essential to understand the seasonal factors which affect translocation of both the dissolved and particulate fractions of phosphorus.

The Land Ocean Interaction Study (LOIS, Natural Environment Research Council, UK) has shown the importance of both inorganic, organic and particulate associated phosphorus in the transport from rivers in the Humber catchment draining approximately 25 % of England and Wales, (House *et al.*, 1997). Part of this research has identified the importance of point-sources of phosphorus in these rivers although, because of the large size of the catchments, it is difficult to assess the relative contribution of "in-stream" processes to the amount of phosphorus transferred to the inter-tidal zone. In small catchments it is easier to assess the impact of specific point-sources on river beds and their associated flora and study

how the interactions with the bed-sediments affect the concentrations in the overlying water. The purpose here is to study how the transport of soluble reactive phosphorus (SRP) in the R. Wey, a lowland hard water river with a major point-source input (> 10,000 people equivalent sewage treatment works, STW), is affected by "in-stream" processes and examine changes in the bed-sediment properties at sites upstream and downstream of a major sewage discharge.

## METHODS

### *Field Sampling*

The R.Wey in southern England (Figure 1), was visited on four occasions: autumn 1994 and winter, spring, summer of 1995. On each visit the following measurements were made at each site, labelled A-F in Figure 1: pH, river temperature, dissolved oxygen, electrical conductivity, river width, depth and velocity profile of the river at 1m intervals. Water samples were taken for major-ion analyses and suspended solids determination as well as total phosphorus (TP) analysis. A separate aliquot of *ca* 250 ml was filtered on-site through a 0.45 mm cellulose nitrate membrane, transported in a cold-box for soluble reactive phosphorus (SRP), total dissolved phosphorus (TDP), nitrate + nitrite, soluble reactive silicon and dissolved calcium measurements. At each site samples of surface sediment (< 5 cm depth) were randomly taken across the river section within a section of approximately 10 m. These samples were sieved on-site through a 2 mm stainless steel mesh, mixed together and transported in a cold-box to the laboratory. They were stored at 4 °C in the dark prior to further analysis. Surface sediments were also taken at site C in four stainless steel trays (30 cm length) for deployment in a fluvium channel. These unsieved sediments were transported with a minimum of disturbance in contact with river water in plastic trays covered with foil, and installed in the fluvium channel as quickly as possible after sampling (< 3 h).

### *Analytical methods*

Temperature, pH, DO and conductivity, major-ions, suspended solids and nutrients were measured as described previously (House and Denison, 1997). Measurements of water flow were made with an ultra-sonic sensor (SENSA RC2). Total phosphorus concentrations in the sediments were determined by the ignition method of Andersen (1976). The concentrations of total calcium and iron in the digest were measured by atomic absorption. Total organic matter (OM) was determined by ignition at 550 °C for 17 h. Bioavailable phosphorus (BAP) was estimated using the iron oxide-impregnated filter paper (10 cm x 2 cm, Whatman No. 541) by the method of Sharpley (1993). Tests indicated a recovery of 90 % from a solution containing one strip in 20 mmol of KH<sub>2</sub>PO<sub>4</sub> dissolved in 2 mmol dm<sup>-3</sup> CaCl<sub>2</sub>.

The particle size fractionation was by wet sieving (63 mm to 2 mm size) and the pipette method described by Gee and Bauder (1986) for particles < 63 mm in size, with bands of 1-2, 0.5-1, 0.25-0.5, 0.125-0.25, 0.063-0.125 mm and 20-63, 2-20 and <2 mm. X-ray diffraction of the sediment was done using a Philips PW 1380 horizontal goniometer with 1710 diffraction control.

### *Adsorption experiments*

Wet sediment (1.5 - 10 g as dry weight) was placed in 250 ml high density polypropylene copolymer centrifuge bottle together with 200 ml of 2 mmol dm<sup>-3</sup> CaCl<sub>2</sub> solution pre-chilled to 10 °C. SRP was added as KH<sub>2</sub>PO<sub>4</sub> to obtain initial concentrations up to 15 mmol dm<sup>-3</sup>. The suspensions were then placed in the dark in an orbital incubator at 10 +/- 0.5 °C for a 24 h. Following centrifugation (g<sub>av</sub>=6000), the supernatants were filtered (0.45 mm cellulose nitrate) and analyzed for SRP by the method of Murphy and Riley (1962).

### *Fluvium channel experiments*

The fluvium channel has been described previously (House *et al.*, 1995b; House and

Denison, 1997). The temperature of the channel was controlled by a continuous flow of water from the nearby R. Frome circulated through a tank containing the channel. In brief the equipment permits the control of the water velocity and depth over the bed-sediment, the gas atmosphere, the concentration of oxygen in the water by air and nitrogen lines and the pH, temperature and dissolved oxygen in the water to be automatically monitored *via* a computer interface. The solution flow was continually measured using a turbine flow-transducer placed downstream of the recirculating pump. Filtered samples were taken automatically (0.45 mm cellulose nitrate membrane), and delivered to a collection bottle. The system of tubes, membrane housing and syringe pump were flushed prior to each sampling and the tube connected to the sample collector was flushed with air after each collection.

Three experiments were performed:

(1) After transportation, the small amount of fines leached from the sediment was returned to the trays which were immediately placed in the fluvium channel. Before adding the background electrolyte ( $21 \text{ dm}^{-3}$  of  $2 \text{ mmol dm}^{-3}$   $\text{CaCl}_2$ ), the pH and dissolved oxygen (DO) sensors were calibrated. The overlying solution was sampled at 0, 15 and 30 mins; thereafter the automatic sampler operated at 1 h intervals for about 48 h.

(2) The uptake of SRP was investigated over 48 h by the augmentation of SRP concentration in the overlying water to  $40\text{-}50 \text{ mmol dm}^{-3}$ .

(3) The net release of SRP was also evaluated by depleting the dissolved oxygen concentration in the channel by the addition of  $\text{Na}_2\text{SO}_3$  solution in sufficient quantity to react with all the dissolved oxygen. The solution was continually purged with high purity nitrogen gas (99.999%).

#### *Macrophyte surveys*

During the spring and summer 1995 visits to the river, a 100 m length of river was surveyed for macrophytes at each site, 50 m above and 50 m below the sampling point. This comprised of listing the taxa present, estimation of the percentage cover by each taxon and total macrophyte cover as a percentage of the river bed area.

#### **THEORY**

##### *Interaction of SRP with bed-sediments*

The interaction of soluble reactive phosphorus with sediments is complex because of the heterogeneous nature of the matrix and the effects of biological processes such as microbial uptake or release and bioturbation effects of benthic organisms. For such systems a semi-empirical approach is appropriate with the kinetics of the net uptake or release described by:

(a) The Elovich equation (Chien and Clayton, 1980),

$$dn(t) / dt = a \exp(-bn(t)) \quad (1)$$

which integrates in the limits of  $t=0$  and  $n=0$ :

$$n(t) = (1/b) \ln(1 + abt) \quad (2)$$

where  $a=dn(0)/dt$ ,  $b$  is a constant and  $n(t)$  is the amount of phosphorus influx per unit area at time,  $t$ .

(b) A parabolic equation of the form (House *et al.*, 1995a; 1995b):

$$dn(t) / dt = k_p [c(t) - EPC_o]^2 \quad (3)$$

where  $k_p$  is the parabolic rate constant,  $c(t)$  is the concentration of SRP in the overlying solution at time,  $t$ , and  $EPC_o$  is the equilibrium phosphate concentration defined below. The constant,  $a$ , in equation(2) may be substituted from equation (3) to give:

$$n(t) = (1/b) \ln[1 + k_p bt(c(t) - EPC_o)^2] \quad (4)$$

The  $EPC_o$  may be obtained experimentally by either measuring the steady-state concentration

of SRP in a solution overlying the bed-sediment in particular conditions relevant to the sampling site or from experiments with suspended bed-sediment to determine the sorption and desorption behaviour. The sorption isotherm may be interpreted by the equation:

$$\Delta n_a(t) = K_d c(t) - n_i \quad (5)$$

where  $\Delta n_a(t)$  is the change in the amount of SRP sorbed relative to the initial amount present in the sediment,  $K_d$  is the sorption constant describing the linear isotherm,  $c(t)$  is the SRP concentration in solution at time  $t$  (taken as 24 h), and  $n_i$  is the initial amount sorbed to the sediment before any changes occur- sometimes referred to as the “native” inorganic phosphorus amount (House *et al.* 1995a). When  $\Delta n_a=0$  then  $c(24h)=EPC_0$ , i.e. that concentration of SRP in contact with the sediment which leads to no net change in the SRP concentration in solution.

The interaction of SRP with bed-sediments in the R. Wey was simulated by dividing the river reach into 1 km sections and associating the following parameters with each section,  $j$ : width,  $w_j$ ; depth of water,  $d_j$ ,  $EPC_{0j}$  as well as information on minor tributaries and point-discharges in the section. The latter were quantified by dilution ratios of the point-inputs,  $r_j$ :

$$r_j = qp_j / qr_j \quad (6)$$

where  $qp_j$  and  $qr_j$  are the discharges of the point-input (here minor tributaries are considered as point-inputs to the main river) and main river at the point of the input in the  $j$  th section respectively. Parameters characterizing the net uptake/release of SRP along the whole river,  $k_p$  (equation 3) and  $b$ ,  $k_p$  (equation 4) were included in the model.

The flux of SRP passing out of the  $(j+1)$  river section,  $f_{j+1}$ , was computed by a recursive procedure, e.g for the parabolic equation (3):

$$f_{j+1} = f_j + qp_{j+1}cp_{j+1} - k_p w_j \left( \frac{f_j + qp_j cp_j}{qr_j} - EPC_{0j} \right)^2 \quad (7) \text{ so that:}$$

$$cr_j = f_j / qr_j \quad (8)$$

where  $cp_j$  and  $cr_j$  are the SRP concentrations in the point-input and main river sections respectively. A similar equation was used incorporating equation (4) to describe the interactions of SRP with the bed-sediments. A Mathcad computer program was developed to permit the optimization of the parameters  $k_p$  or  $b$  (equation 4) and  $k_p$  (equation 3) to obtain the best agreement between the measured profile of SRP along a section of river and the calculated concentrations from equations (7 and 8). The program also permitted a comparison of the measured and computed river discharges,  $qr_j$ , and adjustment of minor tributary inputs through the parameters,  $r_j$ , to obtain a water balance along the study section.

#### *Relationship between river discharge and concentration*

If the mass flux at any point in a river is  $c_i q_i$  where  $c_i$  and  $q_i$  are the concentration and discharge of the point-sources ( $i=p$ ), diffuse inputs ( $i=d$ ) and base-flow components ( $i=b$ ), then from a mass-balance and the assumption that  $q_p c_p \gg q_b c_p$  and  $Q > q_B + q_p$  (House and Warwick, 1997) leads to the dilution equation:

$$c = (q_p c_p + m_{net}) / Q + c_d \quad (9)$$

$$c = \alpha / Q + c_d \quad (10)$$

where  $c$  is the concentration of SRP and  $m_{net}$  the losses or gains caused by internal processes.

#### *Chemical speciation*

The possibility for the precipitation of calcite and various calcium phosphate minerals was investigated in detail using a chemical speciation program developed in Mathcad. This was done for calcium hydroxyapatite (HAP), octacalcium phosphate (OCP), tricalcium phosphate

(TCP) or amorphous calcium phosphate by an iterative method using the dissociation and solubility constants listed by Hartley *et al.*, (1996, 1997) and activity coefficient from the Davis equation. The saturation index, SI, with respect to a particular mineral phase was calculated from:

$$SI = \log[IAP / K_{so}] \quad (11)$$

where IAP is the ion-activity product for the lattice ions and  $K_{so}$  is the thermodynamic solubility at the temperature of the river water (House and Denison, 1997).

## RESULTS AND DISCUSSION

The concentrations of the selected determinands in the water at sites A to F (see Figure 1) measured over one year (autumn 1994 - summer 1995) are shown in Table 1. The concentration of soluble unreactive phosphorus (SUP) is calculated from the difference: TDP-SRP and is mainly composed of organophosphorus and inorganic polyphosphates (Denison *et al.*, 1997). The concentration of phosphorus associated with particulate matter (PP/ mmol dm<sup>-3</sup>) is calculated from the difference between total phosphorus determined on unfiltered samples and total dissolved phosphorus, (TP-TDP). The concentration of phosphorus in the suspended material, PSS in mmol g<sup>-1</sup>, is PP/SS where SS is the concentration of suspended solids in the sample. During the summer sampling, the stream at site B was dry. Suspended solids were not measured in the autumn sampling. As a result of the combined errors in the measurements the difference between TDP and SRP or TP and TDP for some samples are below the limit of determination and are excluded from the table.

The R. Wey is a particularly hard water river with the highest calcium concentration of 3.9 mmol dm<sup>-3</sup>. Changes in dissolved oxygen, silicon and pH from site C in the spring visit reflect biological activity in the river, e.g. the uptake of silicon by diatoms and photosynthesis changing the dissolved oxygen and carbon dioxide concentrations. The results from the chemical speciation analysis show that the hardness of the water and high concentration of SRP lead to supersaturations with respect to all the minerals at some time during the study, i.e.  $SI > 0$  (Figure 2). The highest values occurred for HAP although this phase is unlikely to form before the precursor phase, OCP. The highest supersaturations with respect to calcite ( $SI=1.7$ ) occurred during the spring with a systematic increase between sites C to F, (Figure 3). Lower saturations were calculated from the data for the summer and autumn visits but still with a progressive increase downstream. Generally, the equilibrium partial pressures of carbon dioxide,  $P_{CO_2}$ , are highest at site A (10-16 matm compared to the atmospheric partial pressure of 0.34 matm) and decreased in the spring, summer and autumn on passage downstream to site F (0.4-4 matm). In the winter visit, when the river was in spate,  $P_{CO_2}$  values did not decrease but remained high along the entire stretch leading to conditions of undersaturation with respect to calcite at all sites apart from C, (Figure 3).

The concentration of nitrate is not noticeably affected by the STW input and not elevated in the winter as a result of increased surface/sub-surface run-off. However, there is evidence for the loss of nitrate from the water during the visit in the summer when the concentration decreases systematically downstream from site C to site F. This amounted to approximately 130 mmol m<sup>-2</sup> d<sup>-1</sup> calculated from single concentration, stream dimension and water velocity measurements at each site and extrapolation between sites. This loss incorporates denitrification in the sediments, e.g. denitrification rates for rivers between 2 and 100 mmol m<sup>-2</sup> d<sup>-1</sup> have been reported in the literature (1972; Hill, 1981), and uptake by the macrophytes and algae; high net losses were not observed in the spring.

During the high flow in February 1995, the transport of phosphorus is mainly by suspended material (Figure 4), with a relatively minor contribution from SRP. There is a

difference in the percentage transport of the three fractions shown in Figure 4 for site A and the downstream sites as a result of the supplementation of SRP from the STW. At the other downstream sites, SRP is the main form contributing > 60% of the total phosphorus transported. SUP is also an important contribution in the spring and summer amounting to between 14 and 30 % of the TDP at sites C to E.

The assumption that  $q_p c_p > c_b c_b$  invoked for the dilution equation (9) is valid for sites C to F when  $q_b c_b \approx 0.1$  and  $q_p c_p \approx 10 \text{ mmol s}^{-1}$ . Apart from the low flow period in the summer when  $Q \approx q_B + q_p$ , the second assumption is also realistic. Linear regression analysis of all data for each site (site F was excluded because only 3 measurements were made), leads to values of  $\alpha$  and  $c_d$  shown in Table 2. As expected, site A shows poor agreement with equation (10) because point-sources are not important. However, the other sites give reasonable agreement with  $\alpha$  decreasing downstream from site C reflecting the influence of  $m_{net}$  (flux of SRP lost from the water during passage downstream). Values of the parameter,  $c_d$ , characterizing the concentration of SRP in the diffuse inflow, are in reasonable agreement at the three sites and much larger than those determined in the Gt. Ouse river (typically  $< 1 \text{ mmol dm}^{-3}$ , House and Denison, 1997). This is also reflected in the high concentrations of SRP measured in the winter during relatively high flow conditions. The values of  $\alpha$  may be compared to the estimated point-input from the STW (see Table 3) of  $7.8\text{--}14.3 \text{ mmol s}^{-1}$  in agreement with  $\alpha$  at site C ( $9.51 \text{ mmol s}^{-1}$ ) which is nearest to the STW discharge where  $m_{net}$  is likely to be smallest.

The results from the analysis of surface sediments, BAP and isotherm measurements are summarized in Table 4. The isotherm parameters,  $EPC_0$ ,  $n_i$  and  $K_d$  were calculated by linear regression of the isotherm data plotted according to equation (5). The particle-size distributions of the sediments from sites C, E and F were similar and different from sites A and D (Figure 5). The sediment from site D was from a deeper and slow flowing section of river, much finer in composition and gave higher distribution coefficients,  $K_d$ 's, BAP's,  $n_i$ 's and total phosphates contents than the other sediments (Table 4). The main mineral components at site C were quartz (69%), calcite (28%), haematite (1%) and K-feldspars (2%). The clay fraction ( $< 2 \mu\text{m}$  in size) was mainly expandable clays (71%), illite (25%) and kaolinite (4%). Temporal changes in the particle-size distribution of the surface bed-sediments at sites C, E and F were similar with the coarsest sediments found in the autumn 1994 (approximately 50 %  $< 1 \text{ mm}$ ) and the finest sediments in the summer (approximately 70 %  $< 1 \text{ mm}$ ). There was a systematic increase in the proportion of fine material between the winter and summer periods indicating the accumulation of a lower size fraction during low flow conditions.

The  $EPC_0$ 's were generally much lower than the corresponding concentrations of SRP in the overlying water indicating a net uptake of SRP by the bed-sediments at the time of sampling. Only three samples were found where the  $EPC_0 >$  SRP concentration; two of these at site A with a very low SRP concentrations and the other at site F (although this difference was  $< 0.20 \mu\text{mol dm}^{-3}$ ). There was a poor correlation between SRP and  $EPC_0$  when all the data were combined; however the individual seasonal correlations were good with  $EPC_0$  increasing with the SRP concentration in the overlying water (95% confidence limit,  $R^2$  between 0.5 and 0.8). Multivariate analysis showed that the best correlations were between  $K_d$ ,  $n_i$  and the TP content of the sediment and the clay fraction ( $R^2 > 0.6$ ). The iron oxide BAP values were always greater than the "native phosphorus",  $n_i$ , calculated from the isotherm measurements which is in agreement with previous results (House and Denison, 1997).

There is an increase in both the total calcium and phosphorus contents of the sediment from the winter to summer. The high supersaturations with respect to calcite (Figure 3) will lead to precipitation in the spring-autumn period, particularly in algal biofilms (Hartley *et al.* 1996). The changes in calcium content permit an estimate of the amount of SRP coprecipitated (House, 1990) - this amounts to approximately 53, 2, 4 and 16 % of the measured change in phosphorus content at sites C to F respectively. The increase in phosphorus content above that predicted by this mechanism is a result of other processes such as sorption to clays, biological assimilation and settling of suspended matter during low flow. The phosphorus contents of the sediment are lower in the winter and autumn, probably as a result of scouring of the river bed of organic material and fine sediments (see for example the high values of PSS shown in Table 1 for the winter sampling).

The conditions in the fluvium channel during the three main experiments with the bed-sediments are shown in Table 5. The parameters calculated from the phosphorus release and uptake from the Elovich and parabolic equations are collected in Table 6. For the first experiments, involving the release of SRP from the sediment, the final concentration of SRP in the channel is compared with the  $EPC_0$  concentration measured in the adsorption experiments. As shown, the final SRP concentrations in the spring and summer closely approach the corresponding  $EPC_0$  value at the end of 48 h; the experiment in the autumn was only over 24 h. Reduction of the oxygen concentration in the overlying water (see Table 5), led to a stabilization of the SRP concentration and, in some instances, to a slight increase (generally  $< 5 \text{ mmol dm}^{-3}$ ). This may be explained by an increase in the  $EPC_0$  of the surface sediment as a result of either the pH or redox changes at the solution-sediment interface (House and Denison, 1997).

The concentration profiles of SRP measured over the river section were modelled using equations (7) and (8). The program permitted:

- (a) Adjustment of the dilution ratio,  $r_1$ , with the STW discharge and concentration of SRP taken as shown in Table 4 to obtain agreement with the measured SRP concentration at site C.
- (b) Adjustment of the water flow from minor tributaries (Figure 1) to obtain agreement with the water discharge measured at the sites downstream of the sewage input (assumes that the SRP concentration in the tributary water is the same as at site A)
- (c) Comparison of the expected discharge at the gauging station at Farnham (Figure 1) with the information supplied by the Environmental Agency (UK).

The generated SRP profile for the river was compared with the measurements to obtain the optimum parameters describing the net uptake by the system. This was done by either fixing  $b$  in the Elovich equation to the value measured in the fluvium channel and optimizing the parabolic parameter,  $K_p$ , (equation 4) or using the parabolic model and optimizing  $K_p$  (equation 3). These methods gave very similar profiles, examples of which are shown in Figure 6 for each of the sampling dates. The optimum parameters are listed in Table 7. The results from the winter sampling show that the system is almost conservative with some indication of the release of SRP to the water. However, this is small ( $< 7\%$  of the total flux) and difficult to quantify because of the uncertainties in the contributions of the minor tributaries and the effects of the interaction of phosphorus with relatively high suspended sediment load. This is in contrast to the spring when large losses of SRP were measured as a result of the biological activity noted in the discussion of Table 1. The optimum  $K_p$  was much greater than determined from the fluvium channel experiments suggesting the importance of benthic algae, surface biofilms and macrophyte growth. This was confirmed by the macrophyte survey; the dominant

plants were *Cladophora* sp. covering  $\approx$  70 % of the river bed at site C and  $\approx$  50% at sites D and E. Other species such as *Ranunculus pectinatus*, most abundant at site E with 25 % and 40 % coverage in the spring and summer respectively, and *Phalaris arundinacea* at sites A to C. In the summer the loss to the bed-sediment, as estimated from the fluvium channel results, is approximately 65 % of the total loss observed at site F. Again macrophyte coverage of the bed was important at all the sites with percentage total coverage estimated between 60 and 95%. In contrast, in the autumn the uptake found in the field was approximately half that predicted from laboratory experiments probably as a result of the aerobic respiration of organic detritus from algal and macrophyte decay, e.g. the flux of SRP in the water at site F was approximately  $4.1 \text{ mmol s}^{-1}$  compared with a calculated flux from the fluvium channel experiments of  $8.7 \text{ mmol s}^{-1}$ .

## CONCLUSIONS

Seasonal changes influence the transport of phosphorus in this system with evidence for the accumulation of phosphorus in low flow periods in the spring and summer and scouring of bed-sediments in the autumn and winter storms, i.e. decrease in fine material and total phosphorus in the bed-sediments. As shown by the application of equation (7), the role of bed-sediments in the uptake of SRP may be estimated by a comparison of the kinetic parameters measured in the fluvium channel experiments with observations of the SRP profiles along a stretch of river. Although the site upstream of the STW contained a lower concentration of TP than those downstream, there was no systematic change in the phosphorus content along the rest of the section. There was evidence for the coprecipitation of phosphorus with calcite in the sediments but the changes in Ca:P ratio between the winter and summer were much smaller than predicted by a coprecipitation model.

## Acknowledgement

We thank the Department of the Environment, DoE (Grant EPG/1/9/09) for financial support, Dr E. McIntosh of DoE for discussions, A. Nowosielski and J. Bennett of the Environmental Agency (Thames Region), A. Hopwood of the Thames Water Utilities for their help and supplying chemical and discharge data and G.P Irons, S.M. Smith and R. Sadak for assistance with the chemical analysis.

## REFERENCES

- Andersen J.M. (1976) An ignition method for the determination of total phosphorus in lake sediments. *Water Res.* **10**, 329-331.
- Chien, S.H. and Clayton, W.R. (1980) Application of the Elovich equation to the kinetics of phosphate release and sorption in soils, *Soil Sci. Soc. Am. J.*, **44**, 265-8.
- Denison, F.H., Haygarth, P.M., House, W.A. and Bristow, A.W. (1997), The measurement of organophosphorus and polyphosphate compounds during dissolved phosphorus analysis of environmental samples: comparison of methods, *Intern. J. Environ. Anal. Chem.*, (in preparation)
- Gee G.W. and Bauder J.W. (1986) Particle-size analysis. In *Methods of Soil Analysis* (Ed. by Klute A.), American Soc. Agronomy, Soil Science Soc. America, Wisc.
- Fox, L.E. (1989) A model for inorganic control of phosphate concentrations in river waters, *Geochimica et Cosmochimica Acta*, **53**, 417-428.
- Golterman, H.L. (1985) The geochemistry of the Rhine and Rhone. 5, Synthesis and conclusions, *Annls. Limnol.*, **21**, 191-201.
- Hartley, A.M., House, W.A., Leadbeater, B.S.C. and Callow, M.E., (1996) The use of microelectrodes to study the precipitation of calcite upon algal biofilms, *J. Colloid Interface*

*Sci.*, **183**, 498-505.

- Hartley, A.M., House, W. A., Callow, M.E., and Leadbeater, B.S.C.(1997) Coprecipitation of phosphate with calcite in the presence of photosynthesizing green algae, *Water Res.*, (in press).
- Hill, A.R. (1981) Nitrate- nitrogen flux and utilization in a stream ecosystem during low summer flow, *Canadian Geog.*, **25**, 225-239.
- House, W.A. (1990) The prediction of phosphate coprecipitation with calcite in freshwaters, *Water Res.*, **24**, 1017-1023.
- House, W.A. and Denison, F.H. (1997) Nutrient dynamics in a lowland stream impacted by sewage effluent: Great Ouse, England, *Sci Total Environ.*, in press.
- House, W.A. and Warwick, M.S. (1997) Hysteresis of solute concentrations and discharge in rivers during storms, *Water Res.*, (submitted).
- House, W.A., Denison, F.H. and Armitage, P.D. (1995a) Comparison of the uptake of inorganic phosphorus to a suspended and stream bed-sediment, *Water Res.*, **29**, 767-779.
- House, W.A., Denison, F.H., Smith, J.T. and Armitage, P.D. (1995b) An investigation of the effects of water velocity on inorganic phosphorus influx to a sediment, *Environ. Pollution*, **89**, 263-271.
- House, W.A., Leach, D., Warwick, M.S., Whitton, B.A., Pattinson, S.N., Ryland, G., Pinder, A., Ingram, J., Lishman, J.P., Smith, S.M., Rigg, E. and Denison, F.H., Nutrient Transport in the Humber rivers, (1997) *Sci. Total Environ.*, **194/195**, 303-320.
- Lucotte, M. and d'Anglejan, B. (1988) Processes controlling phosphate adsorption by iron hydroxides in estuaries, *Chemical Geology*, **67**, 75-83.
- Murphy J. and Riley J.P. (1962) A modified single solution method for the determination of phosphate in natural waters. *Analytica Chim. Acta*. **27**, 31-36.
- Sharpley, A.N. (1993) An innovative approach to estimate bioavailable phosphorus in agricultural runoff using iron oxide impregnated paper. *J. Envir. Qual.* **22**, 597-601.
- Sharpley, A.N., Hedley, M.J., Sibbesen, E., Hillbricht-Ilkowska, A., House, W.A. and Ryszkowski, L. (1995) Phosphorus transfers from terrestrial to aquatic ecosystems. In: *Phosphorus in the Global Environment, Transfers, Cycles and Management*, ed. H. Tiessen, John Wiley and Sons, Chichester, ch 11.

Table 1. Summary of the field data, dissolved calcium, nutrient and suspended solids concentrations for the river Wey. Sites codes are: A: upstream of the STW inflow; B: a minor tributary entering the main river above the STW; C: immediately downstream of the STW inflow; D, E and F are downstream at approximately 2.5, 3.5 and 7 km from the STW discharge. SRP is soluble reactive phosphorus, TDP is total dissolved phosphorus, TP is total phosphorus, SS is suspended solids, PP is the concentration of phosphorus associated with the suspended solids and PSS is the concentration of phosphorus in the suspended material expressed with respect to the mass of suspended solids.

Date: 13 February 1995	WINTER						
SITE	A	B	C	D	E	F	Mean
T/ °C	9.4	9.1	9.5	9.4	9.3	9.2	9.32
pH	7.18	7.50	7.25	7.10	7.21	7.00	7.21
Conductivity/ $\mu\text{S cm}^{-1}$ @ 25 °C	527	588	558	520	572	588	558.8
Dissolved Oxygen/ %	96	98	99	ND	90	96	96
Dissolved Calcium/ mmol dm <sup>-3</sup>	2.38	2.59	2.59	2.34	2.62	2.77	2.55
Nitrate/ mmol dm <sup>-3</sup>	0.33	0.57	0.46	0.47	0.50	0.53	0.48
Silicon/ $\mu\text{mol dm}^{-3}$	150	216	202	181	219	216	197
SRP/ $\mu\text{mol dm}^{-3}$	2.46	9.10	16.43	13.62	16.95	13.04	11.93
TDP/ $\mu\text{mol dm}^{-3}$	4.52	8.17	44.48	22.48	24.22	25.07	21.49
TP/ $\mu\text{mol dm}^{-3}$	5.31	8.19	>200	42.19	>200	>200	
SUP/ $\mu\text{mol dm}^{-3}$	2.06	-	28.05	8.86	7.27	12.03	9.56
PP/ $\mu\text{mol dm}^{-3}$	0.79	0.02	>155	19.71	>175	>175	
SS/ mg dm <sup>-3</sup>	27.9	8.9	15.8	26.8	16.7	20.9	19.5
PSS/ $\mu\text{mol g}^{-1}$	28.3	2.2	9817	735.4	10479	8387	4908
Discharge/ $\text{m}^3 \text{s}^{-1}$	0.55		1.76	1.85	2.34	2.55	1.81
Date: 8 May 1995	SPRING						
SITE	A	B	C	D	E	F	Mean
T/ °C	13.7	15.7	15.0	15.2	15.8	16.2	15.3
pH	7.36	8.14	7.65	7.97	8.20	8.76	8.01
Conductivity/ $\mu\text{S cm}^{-1}$ @ 25 °C	605	787	701	687	654	642	679
Dissolved Oxygen/ %	92	132	75	102	118	142	110
Dissolved Calcium/ mmol dm <sup>-3</sup>	2.94	3.47	3.10	3.06	3.15	3.05	3.13
Nitrate/ mmol dm <sup>-3</sup>	0.36	0.54	0.43	0.42	0.42	0.41	0.43
Silicon/ $\mu\text{mol dm}^{-3}$	171	128	204	157	161	124	157
SRP/ $\mu\text{mol dm}^{-3}$	1.30	2.24	23.25	16.30	13.88	13.04	11.67
TDP/ $\mu\text{mol dm}^{-3}$	1.90	2.20	33.40	21.89	18.40	12.20	15.00
TP/ $\mu\text{mol dm}^{-3}$	3.75	2.50	36.90	23.00	19.40	18.30	17.31
SUP/ $\mu\text{mol dm}^{-3}$	0.60	-	10.15	5.59	4.52	-	3.33
PP/ $\mu\text{mol dm}^{-3}$	1.85	0.30	3.50	1.11	1.00	6.10	2.31
SS/ mg dm <sup>-3</sup>	12.6	8.0	16.0	5.0	12.4	7.0	10.16
PSS/ $\mu\text{mol g}^{-1}$	146.8	37.5	218.7	222.1	81.0	871.2	262.9
Discharge/ $\text{m}^3 \text{s}^{-1}$	0.21		0.38	0.40	0.54	0.61	0.43

Table 1. continued

Date: 7 August 1995		SUMMER						
SITE		A	B	C	D	E	F	Mean
T/ °C		19.6	-	19.5	19.2	17.9	17.9	18.8
pH		7.30	-	7.29	7.67	7.64	7.93	7.57
Conductivity/ $\mu\text{S cm}^{-1}$ @ 25 °C		681	-	818	746	764	741	750
Dissolved Oxygen/ %		53	-	60	67	73	72	65
Dissolved Calcium/ mmol dm <sup>-3</sup>		2.86	-	3.01	3.03	3.02	3.12	3.01
Nitrate/ mmol dm <sup>-3</sup>		0.25	-	0.68	0.50	0.49	0.32	0.45
Silicon/ $\mu\text{mol dm}^{-3}$		191	-	304	256	299	308	272
SRP/ $\mu\text{mol dm}^{-3}$		2.58	-	67.8	43.6	41.0	34.9	38.0
TDP/ $\mu\text{mol dm}^{-3}$		3.50	-	80.0	50.5	53.5	40.0	45.5
TP/ $\mu\text{mol dm}^{-3}$		7.00	-	83.0	51.0	54.0	41.0	47.2
SUP/ $\mu\text{mol dm}^{-3}$		0.92	-	12.2	6.92	12.5	5.13	7.5
PP/ $\mu\text{mol dm}^{-3}$		3.5	-	3.0	0.5	0.5	1.0	1.7
SS/ mg dm <sup>-3</sup>		8.6	-	4.5	5.6	4.1	3.1	5.18
PSS/ $\mu\text{mol g}^{-1}$		407.0	-	666.7	89.3	122.0	322.6	321.5
Discharge/ $\text{m}^3 \text{s}^{-1}$		0.05	-	0.15	0.19	0.19	-	0.14
Date: 21 September 1995		AUTUMN						
SITE		A	B	C	D	E	F	Mean
T/ °C		12.3	11.3	13.7	14	14	13	13.1
pH		7.41	7.63	7.46	7.54	7.75	8.08	7.65
Conductivity/ $\mu\text{S cm}^{-1}$ @ 25 °C		543	804	730	671	681	663	682
Dissolved Oxygen/ %		90	69	58	55	81	100	75
Dissolved Calcium/ mmol dm <sup>-3</sup>		2.83	3.87	3.78	3.58	3.21	3.05	3.39
Nitrate/ mmol dm <sup>-3</sup>		0.30	0.16	0.34	0.38	0.38	0.37	0.32
Silicon/ $\mu\text{mol dm}^{-3}$		164	258	253	215	251	267	235
SRP/ $\mu\text{mol dm}^{-3}$		1.30	4.42	68.8	51.0	58.1	48.6	38.7
TDP/ $\mu\text{mol dm}^{-3}$		1.43	4.64	74.7	52.0	54.4	44.9	38.7
TP/ $\mu\text{mol dm}^{-3}$		2.85	6.10	73.7	52.3	55.0	ND	38.0
SUP/ $\mu\text{mol dm}^{-3}$		0.13	0.22	5.9	1.0	-	-	0
PP/ $\mu\text{mol dm}^{-3}$		1.42	1.46	-	0.3	0.6	ND	0.6
Discharge/ $\text{m}^3 \text{s}^{-1}$		0.11		0.25	0.27	0.26	0.55	0.29

Table 2. Results of the analysis by the dilution equation (10)

site code	a/ mmol s <sup>-1</sup>	C <sub>d</sub> /mmol dm <sup>-3</sup>	R <sup>2</sup>
A	0.031	1.63	0.12
C	9.51	11.10	0.75
D	7.78	7.78	0.67
E	7.48	11.20	0.51

Table 3. Parameters used to model the profile of SRP along the river section. Key: GS: The Environmental Agency gauging station at Farnham (NGR: SU853473). r<sub>1</sub> is the dilution ratio (equation 6) for the STW at Alton.

sampling date	STW discharge / m <sup>3</sup> s <sup>-1</sup>	SRP concentration / mmol dm <sup>-3</sup>	q <sub>p</sub> c <sub>p</sub> / mmol s <sup>-1</sup>	GS / m <sup>3</sup> s <sup>-1</sup>	dilution ratio, r <sub>1</sub>
winter	0.15	51.7	7.8	3.03	0.42
spring	0.12	93.6	10.8	0.77	0.30
summer	0.09	126	11.3	0.36	1.10
autumn	0.13	115	14.3	0.45	1.50

Table 4. Comparison of the properties of the surface bed-sediments from the main river sites.  $EPC_0$  is the equilibrium phosphorus concentration,  $K_d$  is the distribution coefficient (equation 5),  $n_i$  is the native phosphorus concentration (equation 5). BAP is biologically available phosphorus by iron oxide stripping.

Date: 13 February 1995		WINTER					
Site		A	C	D	E	F	Mean
Organic matter/ % by mass		1.47	1.61	3.06	1.89	1.68	1.94
Total phosphorus/ $\mu\text{mol g}^{-1}$		4.29	19.12	28.01	14.01	10.13	15.11
Total calcium/ $\mu\text{mol g}^{-1}$		1245	1177	1084	1021	898	1085
Total iron/ $\mu\text{mol g}^{-1}$		270	416	596	227	249	351.5
BAP/ $\mu\text{mol g}^{-1}$		0.82	1.73	4.32	1.58	9.25	3.54
$EPC_0/\mu\text{mol dm}^{-3}$		1.72	9.27	3.80	5.90	5.28	5.19
$K_d/\text{dm}^3 \text{kg}^{-1}$		77.1	94.2	140.4	95.3	64.3	94.25
$n_i/\mu\text{mol g}^{-1}$		0.13	0.87	0.53	0.56	0.34	0.49
Date: 8 May 1995		SPRING					
Site		A	C	D	E	F	Mean
Organic matter/ % by mass		1.54	1.72	2.43	3.03	1.68	2.08
Total phosphorus/ $\mu\text{mol g}^{-1}$		4.72	22.36	24.46	17.91	ND	17.36
Total calcium/ $\mu\text{mol g}^{-1}$		894	1439	1270	1566	ND	1292
Total iron/ $\mu\text{mol g}^{-1}$		168.6	240.3	670.5	230.4	ND	327.5
BAP/ $\mu\text{mol g}^{-1}$		1.45	3.91	6.84	3.30	2.89	3.68
$EPC_0/\mu\text{mol dm}^{-3}$		2.55	10.19	13.34	11.76	13.23	10.21
$K_d/\text{dm}^3 \text{kg}^{-1}$		55.4	54.0	56.6	65.0	35.4	53.3
$n_i/\mu\text{mol g}^{-1}$		0.14	0.55	0.76	0.76	0.47	0.54
Date: 7 August 1995		SUMMER					
Site		A	C	D	E	F	Mean
Organic matter/ % by mass		5.98	2.67	4.19	3.87	2.34	3.81
Total phosphorus/ $\mu\text{mol g}^{-1}$		2.73	28.93	216.77	40.41	45.29	66.83
Total calcium/ $\mu\text{mol g}^{-1}$		1204	1692	1460	1138	1441	1387
Total iron/ $\mu\text{mol g}^{-1}$		348.0	146.5	708.2	175.8	115.4	298.8
BAP/ $\mu\text{mol g}^{-1}$		0.97	1.71	2.51	1.78	1.14	1.62
$EPC_0/\mu\text{mol dm}^{-3}$		0.45	5.33	2.47	3.97	4.09	3.26
$K_d/\text{dm}^3 \text{kg}^{-1}$		691.2	70.3	444.9	131.1	103.3	288.2
$n_i/\mu\text{mol g}^{-1}$		0.31	0.38	1.10	0.52	0.42	0.55
Date: 21 September 1994		AUTUMN					
Site		A	C	D	E	F	Mean
Organic matter/ % by mass		1.54	1.58	4.52	2.00	1.27	2.18
Total phosphorus/ $\mu\text{mol g}^{-1}$		1.86	5.88	287.3	4.12	3.81	60.6
Total calcium/ $\mu\text{mol g}^{-1}$		-	-	-	-	-	-
Total iron/ $\mu\text{mol g}^{-1}$		-	-	-	-	-	-
BAP/ $\mu\text{mol g}^{-1}$		0.46	1.96	2.95	1.95	1.19	1.70
$EPC_0/\mu\text{mol dm}^{-3}$		2.15	14.37	1.91	6.94	7.31	6.54
$K_d/\text{dm}^3 \text{kg}^{-1}$		68.1	36.7	1061.8	65.4	36.9	253.8
$n_i/\mu\text{mol g}^{-1}$		0.15	0.53	2.03	0.45	0.27	0.68

Table 5. Summary of the solution conditions measured during the experiments with the fluvium channel: (a) the initial release of SRP to solution, (b) net uptake of SRP after augmentation of the overlying solution and (c) net release of SRP from the sediment when the dissolved oxygen concentration in the overlying water was reduced. Key: DO- dissolved oxygen.

	Conditions	Temperature/ °C		pH		DO/ %	
		min.	max.	min.	max.	min.	max.
Winter 1995	Release, oxic	9.1	10.9	7.01	8.29	93	106
	Uptake, oxic	8.0	10.3	7.77	7.96	94	105
	Release, low DO	9.0	9.3	8.50	9.06	0	2
Spring 1995	Release, oxic	14.2	19.5	7.15	8.17	84	101
	Uptake, oxic	12.1	17.6	7.95	8.15	93	103
	Release, low DO	14.1	17.0	8.75	9.24	0	3
Summer 1995	Release, oxic	18.4	22.8	7.35	7.93	84	101
	Uptake, oxic	19.4	23.6	7.92	8.21	81	110
	Release, low DO	19.8	24.0	8.39	8.84	0	4
Autumn 1994	Release, oxic	13.0	14.9	7.50	7.79	84	99.6
	Uptake, oxic	12.0	15.4	7.69	7.86	88	105
	Release, low DO	11.3	13.9	8.11	8.62	2	5

Table 6. Results from the fluvium channel experiments. The parabolic rate constant,  $K_p$ , (equation 3) is in  $m^4 \text{ mmol}^{-1} s^{-1}$ . The Elovich parameters a and b (equation 2) are in  $\mu\text{mol m}^{-2} h^{-1}$  and  $m^2 \text{ mmol}^{-1}$  respectively. Values in brackets are standard deviations, or for the values of the final SRP concentration, the appropriate  $EPC_0$ 's are given in brackets. Note: \* values calculated with  $EPC_0$  measured on 21 September 1994.

Date	$K_p / 10^8$	Elovich, a	Elovich, b	Final SRP/ $\mu\text{mol dm}^{-3}$
Release from sediment				
21 November 1994	8.44 (0.09)*	68.94 (2.85)	2.15 (0.12)	6.8 (14.4)
13 February 1995	8.11 (0.08)	29.44 (1.24)	2.70 (0.16)	4.6 (9.3)
8 May 1995	145(25)	56.65 (3.58)	1.25 (0.11)	9.8 (10.2)
7 August 1995	117 (14)	32.03 (4.92)	3.15 (0.58)	4.4 (5.3)
Uptake by sediment				
21 November 1994	6.13 (0.16)*	148 (8)	0.436 (0.054)	27.12
13 February 1995	2.18 (0.17)	569 (158)	1.80 (0.22)	33.58
8 May 1995	0.98 (0.14)	57.9 (22.4)	1.04 (0.66)	37.13
7 August 1995	1.82 (0.17)	347 (131)	1.36 (0.36)	35.51

Table 7. Results from the modelling of the SRP concentration profiles measured in the river.

season	equation (4) $b/m^2 \text{ mmol}^{-1}$	equation (4) $k_p/10^{-8}$ $m^4 \text{ mmol}^{-1} s^{-1}$	equation (3) $k_p/10^{-8}$ $m^4 \text{ mmol}^{-1} s^{-1}$
winter	2.70	-39.3	-29.4
spring	1.04	122	36.9
summer	1.36	18.0	3.43
autumn	0.436	2.49	2.22

## LEGENDS TO FIGURES

Figure 1. Map showing the location of the sampling sites, minor tributaries and sewage treatment works.

Figure 2. Distribution of the saturation indices, SI, (equation 11) calculated for all the river water samples. Key:  $\times$ : calcite; ■ : calcium hydroxyapatite; ● : octacalcium phosphate; □ : tricalcium phosphate.

Figure 3. Seasonal changes in the supersaturation of the river water with respect to calcite precipitation at sampling site A-F on the R.Wey. Key: W: winter 1995; Sp: spring, 1995; Su: summer, 1995; A: autumn 1994. SI < 0 indicates undersaturation of the water with respect to calcite formation.

Figure 4. Examples of the fractionation of phosphorus at sites A, C and E (see Figure 1). PP: particulate phosphorus; SUP: soluble unreactive phosphorus and SRP: soluble reactive phosphorus.

Figure 5. Mean cumulative particle size distributions for the four sampling times for sites A to F along the R. Wey.

Figure 6. Comparison of the concentration profiles of soluble reactive phosphorus along the R. Wey from site A to Farnham. Key: ●, profile calculated for a conservative system; □, optimized profile calculated using the parabolic equation (3) with the parameters in Table 7 (points joined to aid visualization of the data); ■, measured concentrations of SRP. The sampling times correspond to those given in Table 1.

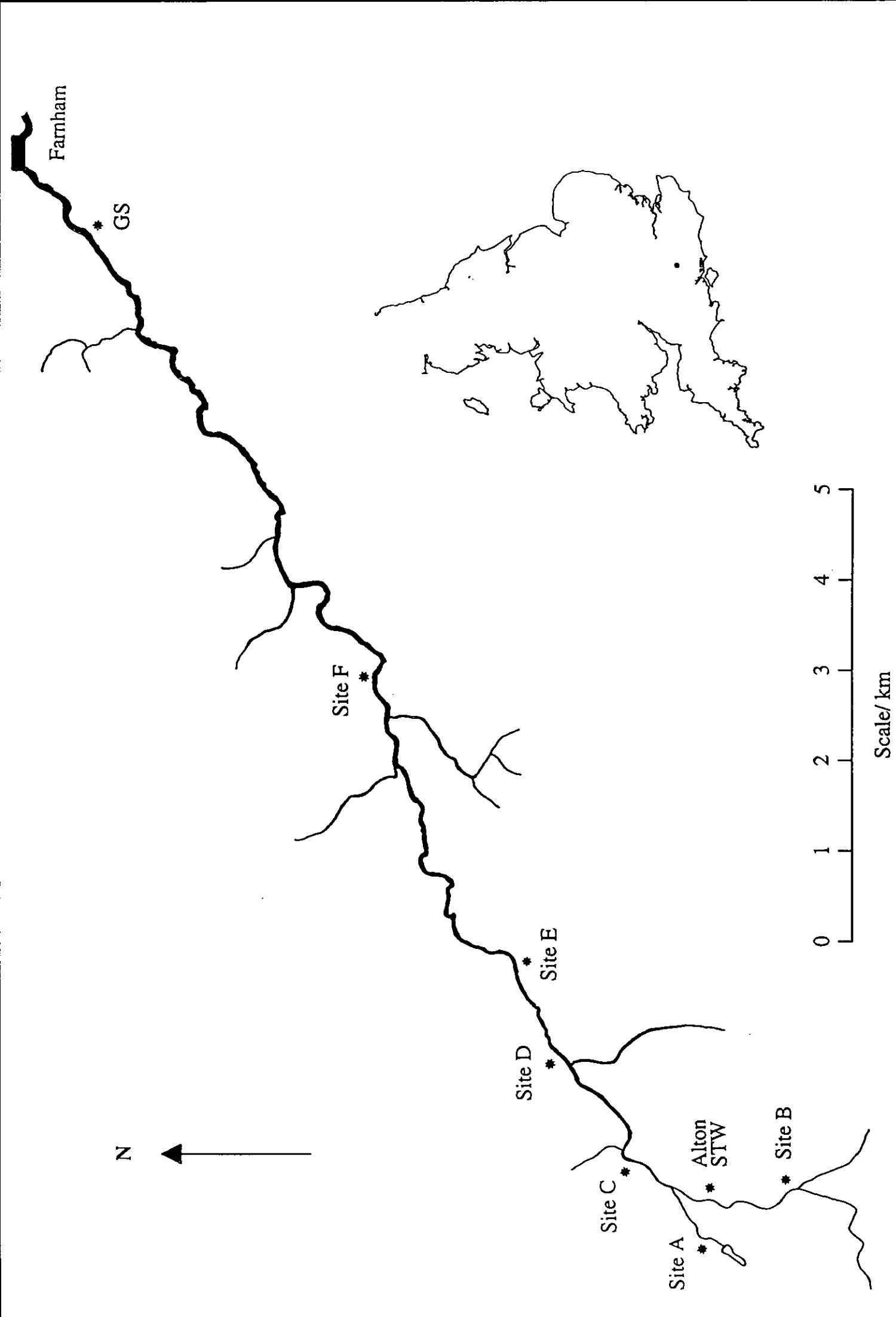


FIG 2.

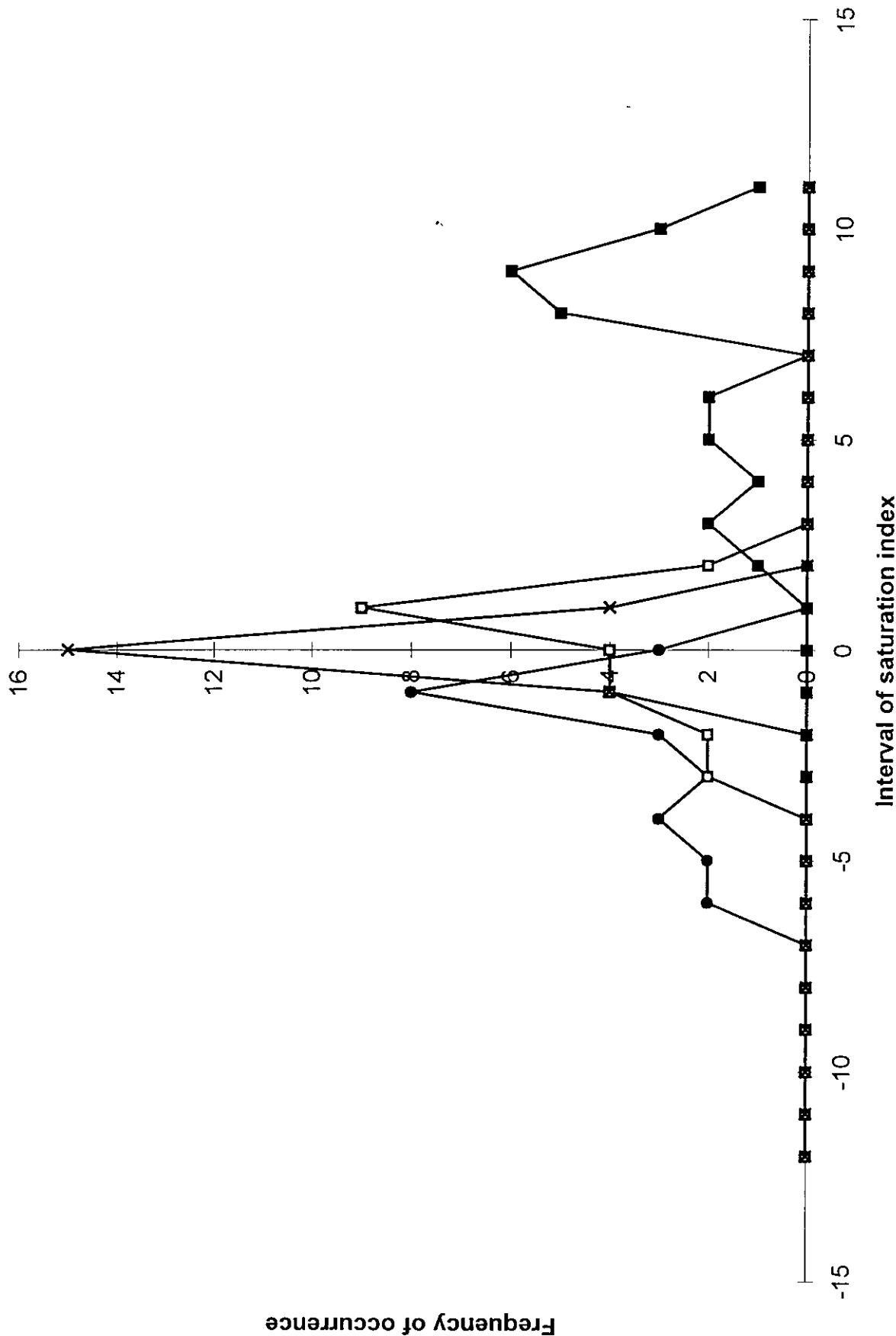
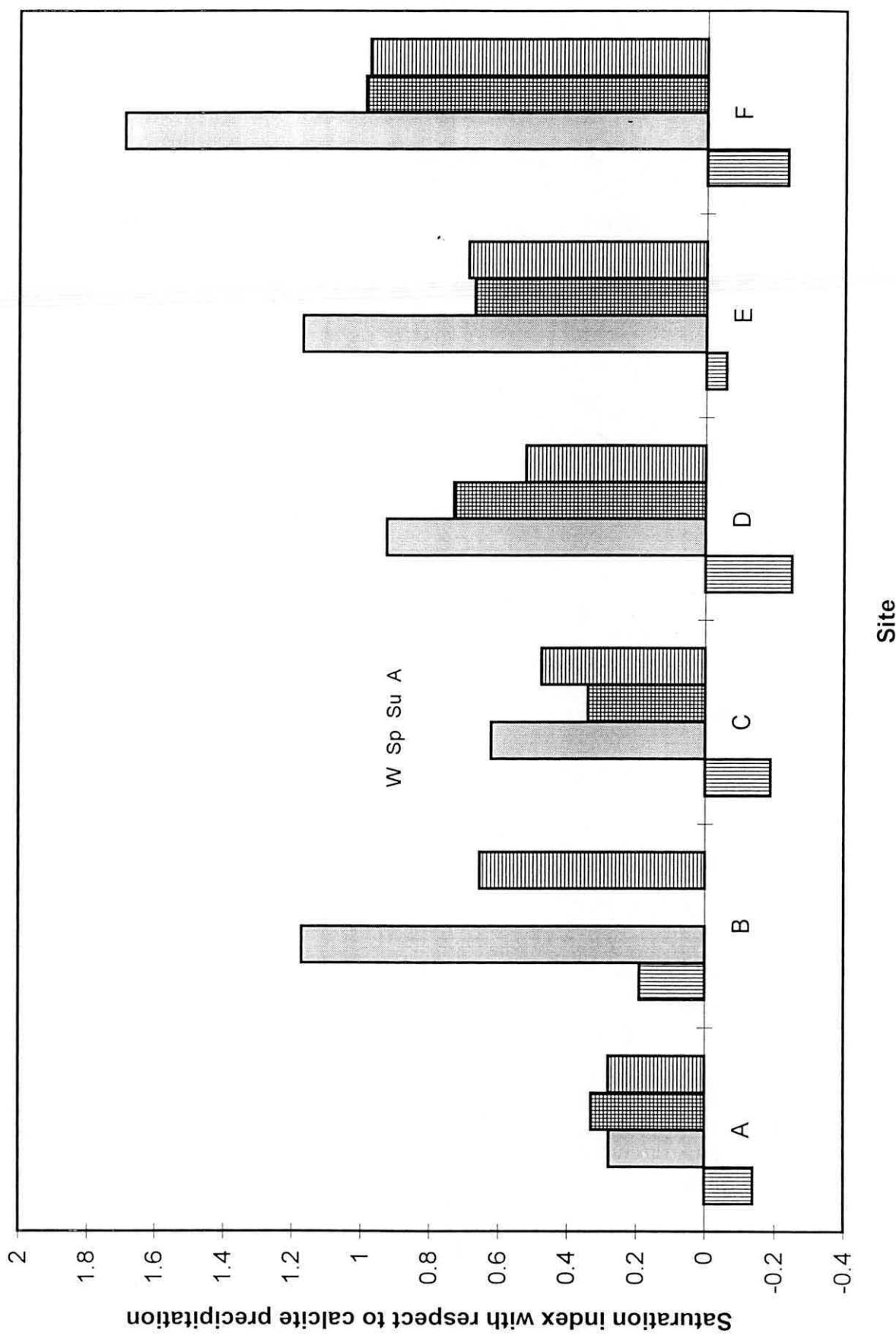
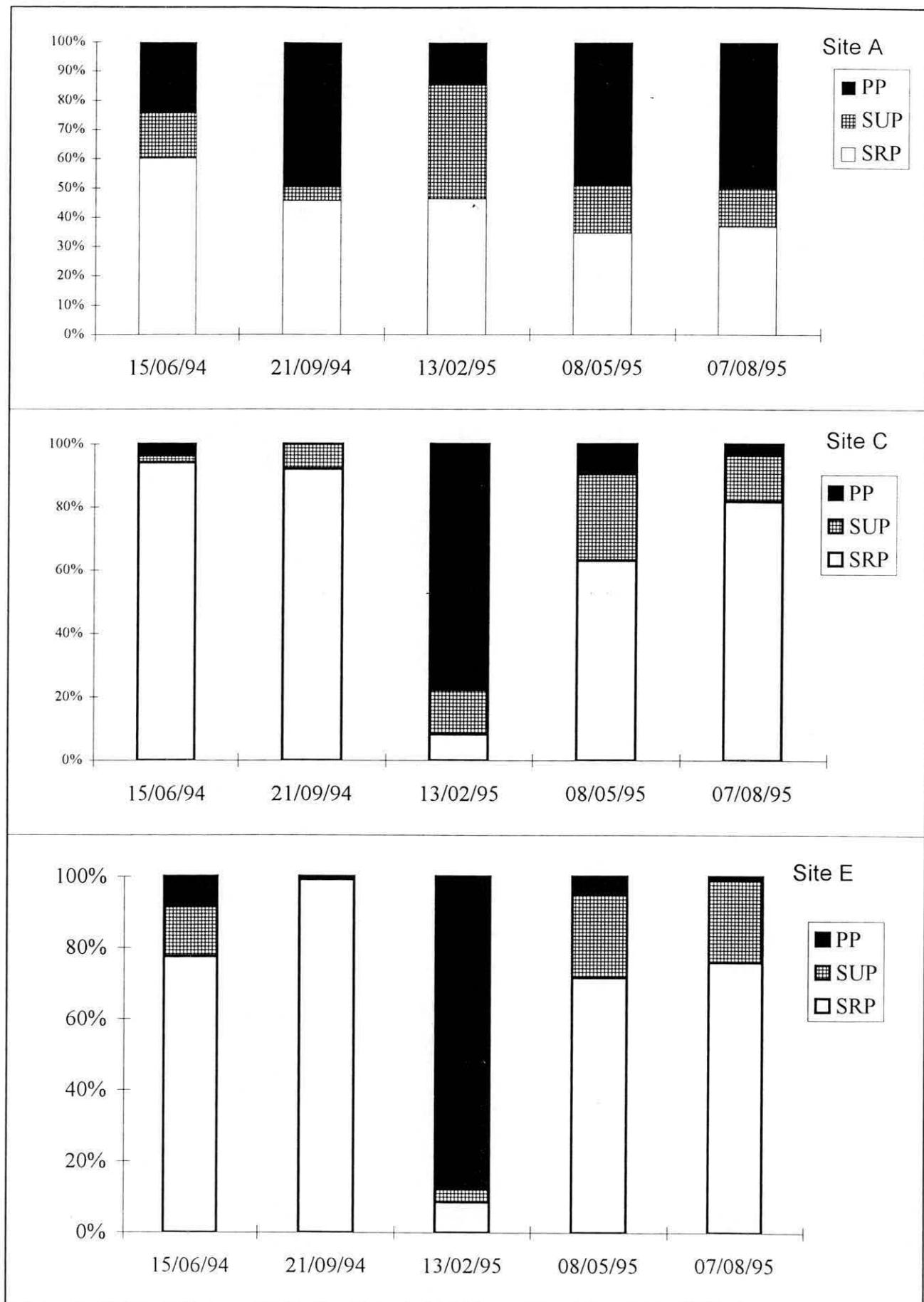
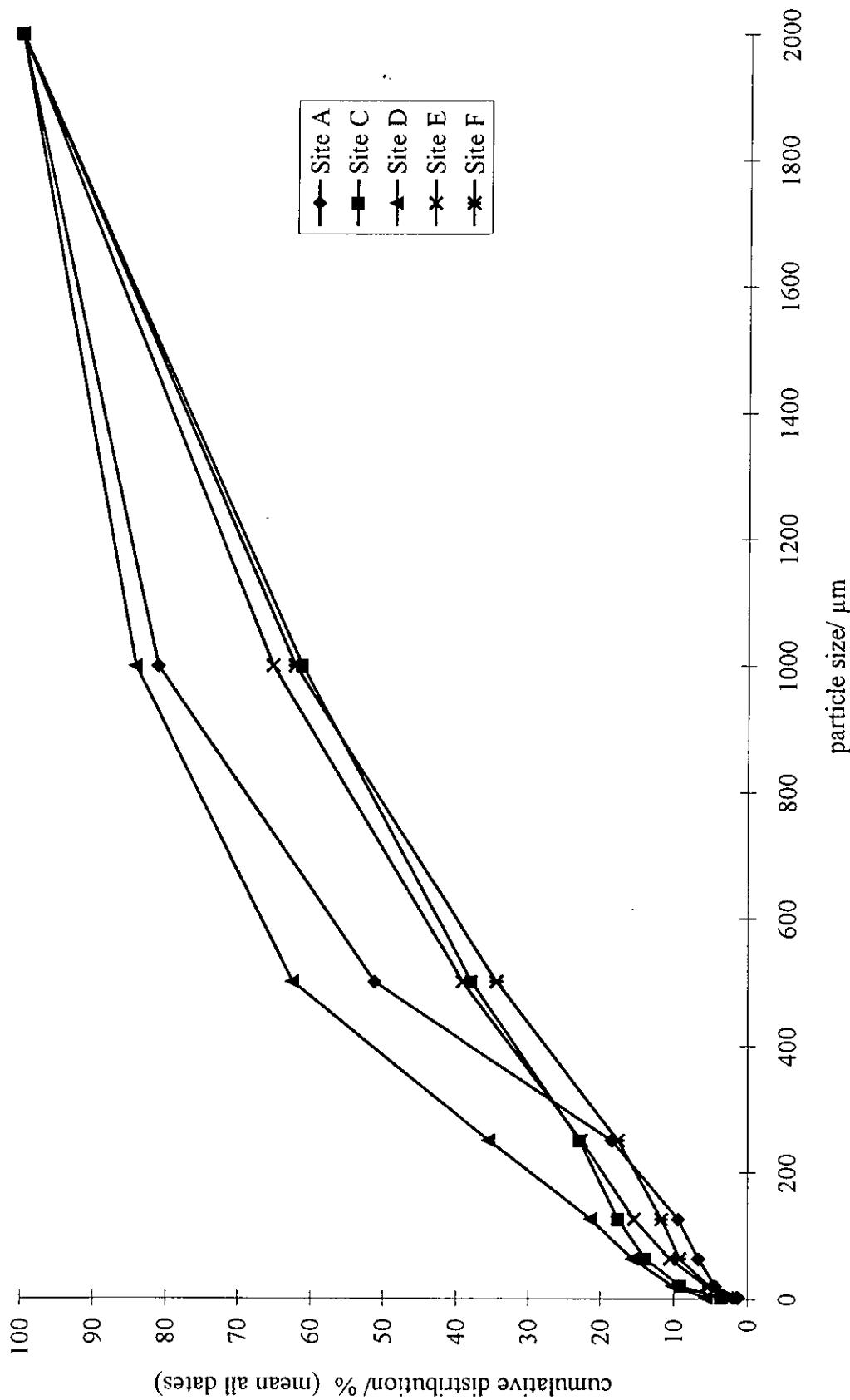
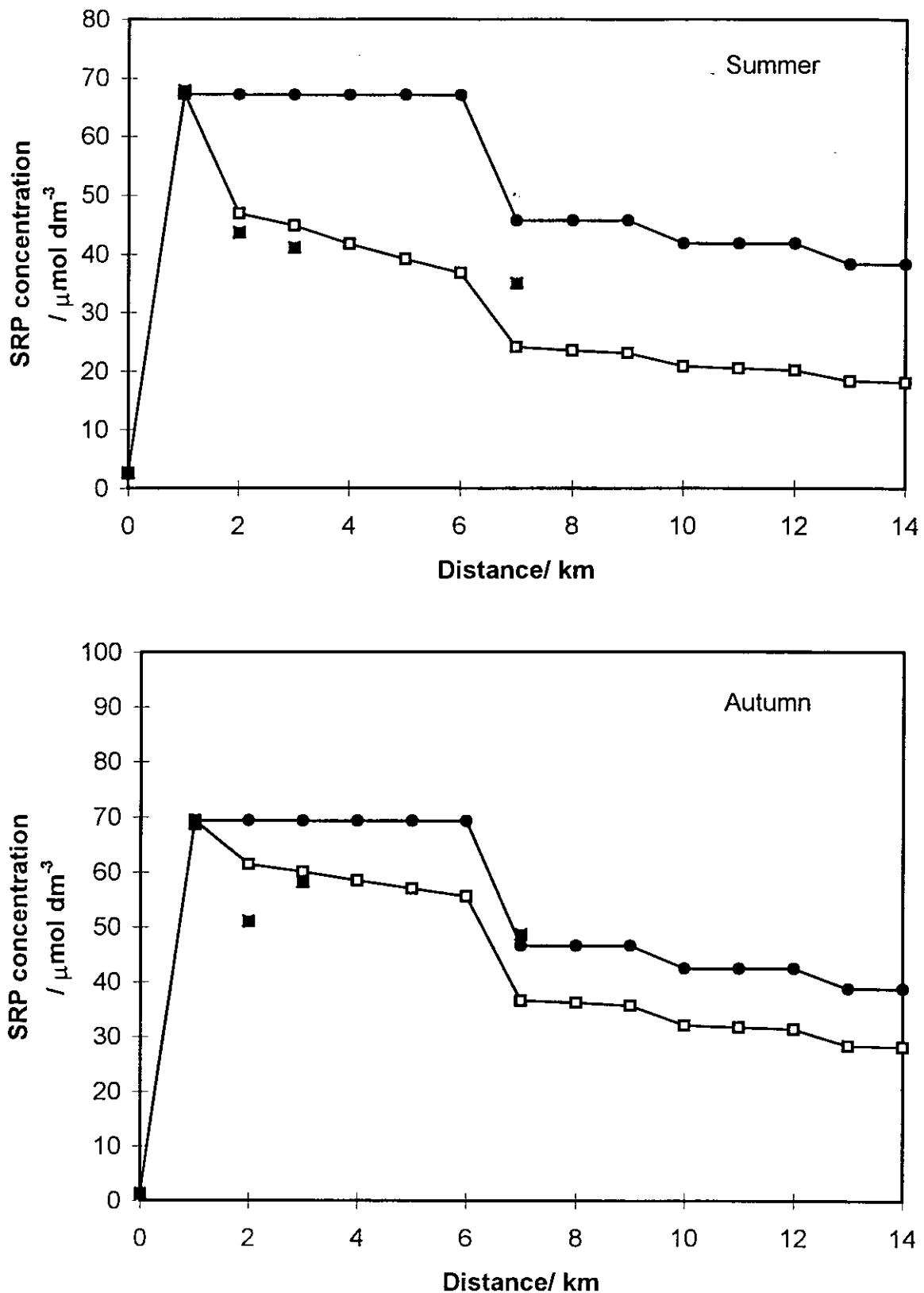


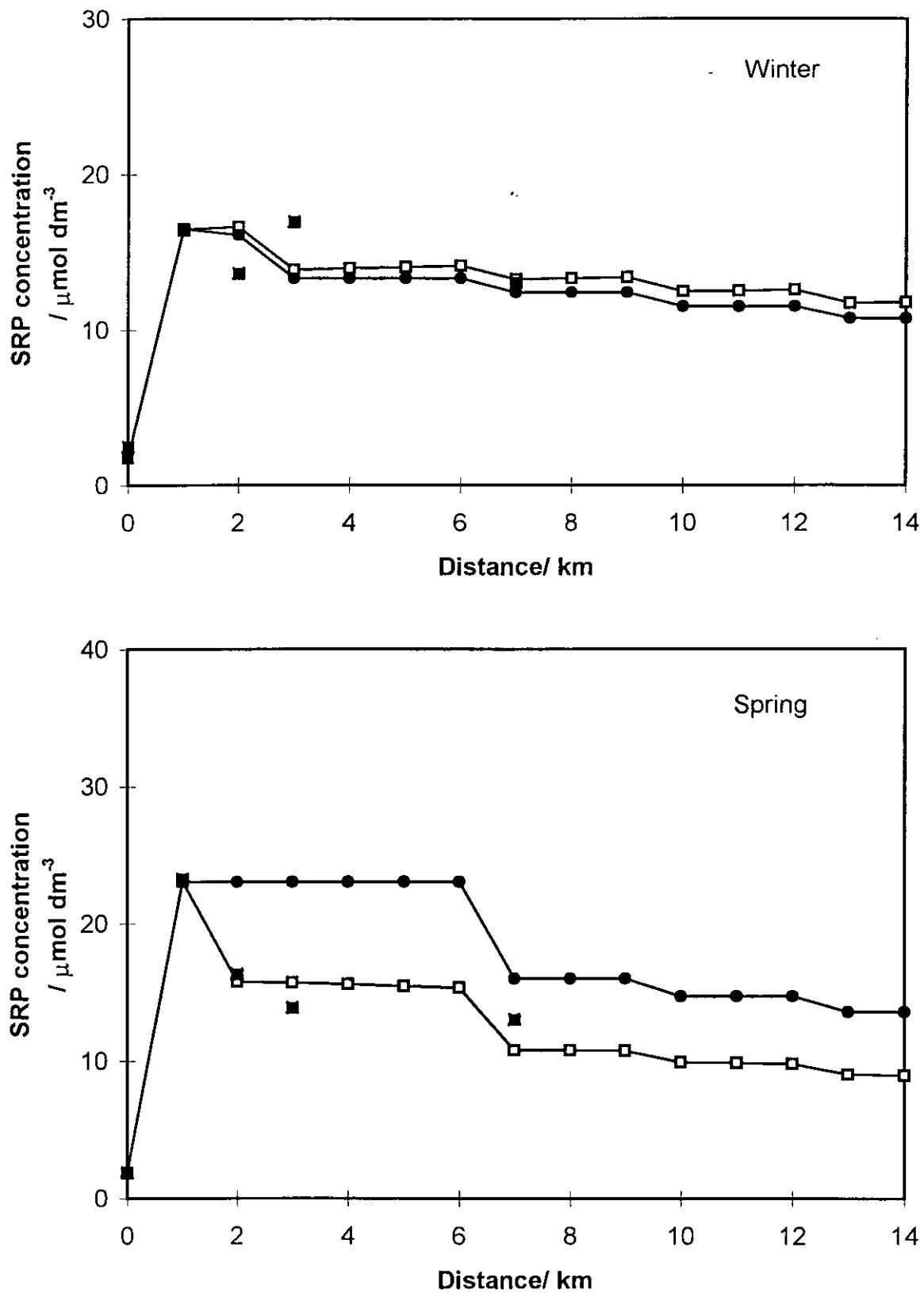
FIG 3











#### APPENDIX 1. Fluvarium channel sediment profiles

Figure illustrating the development of concentration profiles in the R. Blackwater sediment after the sediment was well mixed and then placed in the fluvarium channel to develop a concentration profile over a period of 6 weeks.

