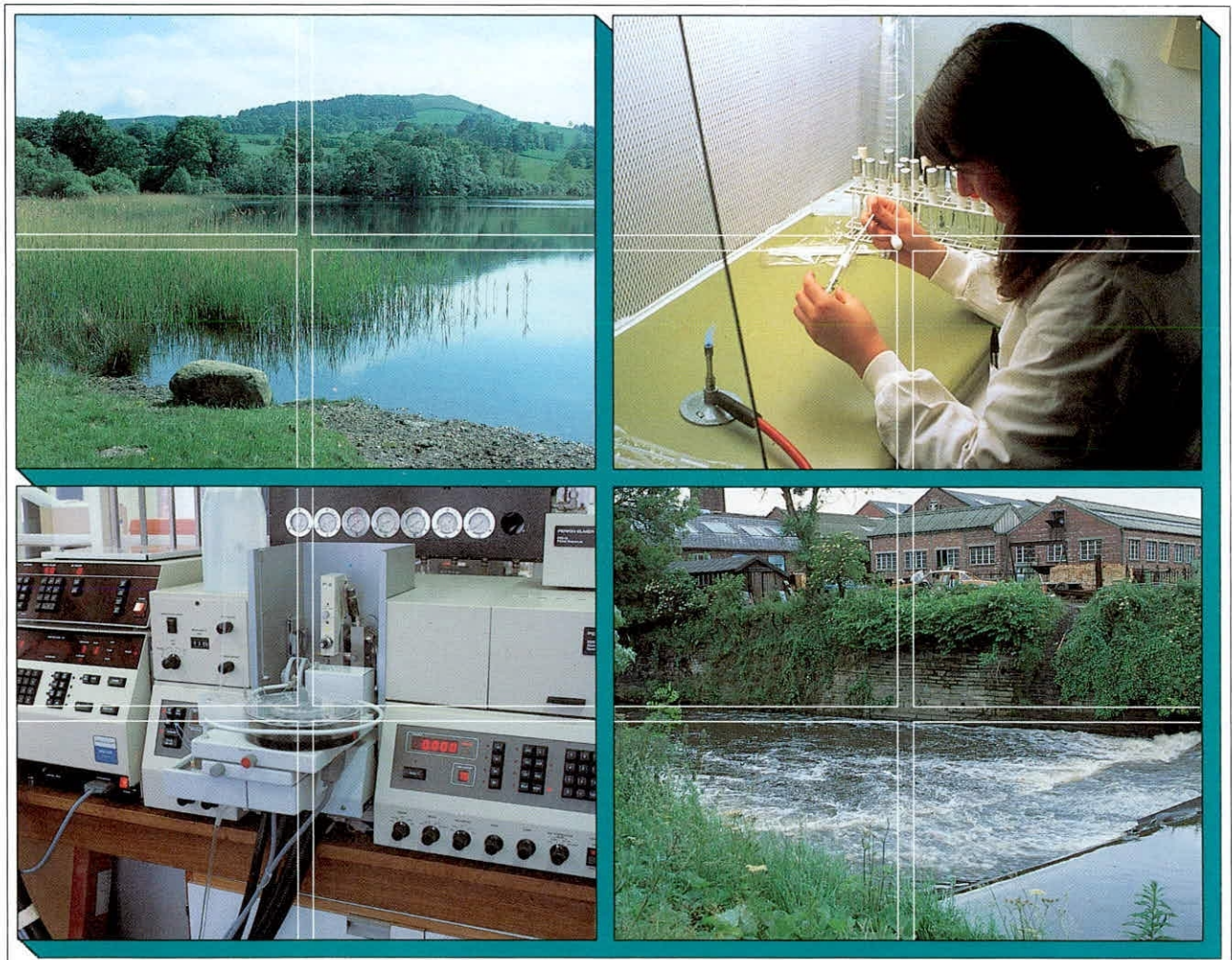




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Assessment of the potential for phosphorus reduction in river waters

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Report Start Date:	1 March 1994
Report End Date:	1 September 1994
Report To:	Department of the Environment Romney House, 43 Marsham Street London SW1P 3PY
Contract No:	EPG/1/9/09
IFE Report Ref. No:	RL/T11059j1/1

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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 $550\ ^\circ C$
PP	Particulate phosphorus. Difference between TP and TDP, ie that phosphorus associated with the particulate phase of size $> 0.45\ \mu m$.
SRP	Soluble reactive phosphorus. Soluble phosphorus measured after filtration through a $0.45\ \mu m$ membrane filter without acid digestion.
STW	Sewage treatment works.
TDP	Total dissolved phosphorus. Filtered through $0.45\ \mu m$ membrane filter but subject to acid digestion prior to analysis.
TP	Total phosphorus. Unfiltered and subject to acid digestion prior to analysis.

SUMMARY

Preliminary site visits of 12 rivers designated Sensitive Areas (Eutrophication) by the DoE have been made to assess their suitability for study in this project. These rivers are the Test, Wey, Creedy/Yeo, Wye/Lugg, Arrow, Blythe, Gipping/Alton Water, Louth Canal, Blackwater, Ant/Burr, Nene and Great Ouse. Several sites in the vicinity of the STWs on each river were examined with chemical analysis of the major nutrients and phosphorus fractions. Chemical measurements and water filtration were done on-site at all locations. River bed sediments were also examined and surficial sediments taken for particle size determination when appropriate.

The results from the visits indicate that the rivers Test, Wey, Arrow, Gipping and Louth canal are suitable for further work. As a consequence, a full pilot study on the R. Wey is planned for early September.

A pilot study of the Great Ouse near Brackley has been completed. Four sites in the vicinity of the STW have been examined and bed-sediments taken from each site. Measurements of the total phosphorus concentrations, bioavailable phosphorus and sorption isotherms produced interesting results showing clear differences between the site upstream of the STW and the downstream sites. This information is crucial for the future planning of the sampling and the fluvarium flux studies.

A new and modified fluvarium channel has been constructed and tested. Work is now in progress to complete the automation of the system. This should be completed in 1 month ready for the start of the phosphorus flux studies using bed-sediments from the pilot study sites.

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 of prediction using criteria developed above and measured at selected sites.

2. 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.

3. PRELIMINARY SITE VISITS (task 1)

The site visits were planned as part of the first nine months work to select appropriate river sections and candidate sites on each river and undertake a pilot study of water and sediment samples from selected rivers. The preliminary site visits were necessary to choose appropriate sites for more intensive pilot studies (task 2). The main purpose of the work was to gain first hand knowledge of the sites, examine the bed-sediments and make measurements of the key nutrients including three phosphorus fractions with particular attention to maintaining sample integrity by filtration of the samples on site.

3.1 Sites

All the planned preliminary site visits have been completed as follows:

1. R. Test (Andover) four sites.
2. R. Wey (Alton) five sites.
3. R. Creedy/Yeo (Credon) five sites.
4. R. Wye/Lugg (Hereford) five sites.
5. R. Arrow (Redditch) five sites.
6. R. Blythe (Barston) four sites.
7. R. Gipping/Alton water (Needham Market/Stowmarket) four sites.
8. Louth Canal (Louth)/ four sites.
9. Blackwater (Aldershot) one site.
10. R. Ant (Stalham) two sites.
11. R. Nene, two sites.
12. Gt. Ouse/Foxcote & Hyde Lane Pit (Brackley), four sites.

3.2 Measurements

On site work involved the following:

- (a) Sampling the water and on-site filtration for measurements of SRP, TDP, Si, NO₃ and Ca.
- (b) Measurements of pH, T, conductivity and oxygen concentrations.
- (c) Recording the site location, general features of the site including the presence of diatoms, filamentous algae and macrophytes, the type of sediment and suitability for sediment sampling.
- (d) Sampling the bed-sediment at selected sites and testing the use of the Ekman sediment sampler when appropriate.

Samples were filtered using a 0.45 µm cellulose nitrate membrane filter. Samples for total phosphorus measurement were taken on-site and placed in 100 ml glass Duran 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 NO₃, all analysed within 1 day of returning.

The sites were chosen from those listed in the Urban Waste Water Treatment Directive of Sensitive Areas (Eutrophication) issued by DoE (News release 303, 18 May 1994). The sites included all those mentioned in the project steering committee meeting of 23 February 1994. Sites at which the NRA considered that phosphorus removal is not required at qualifying sewage treatment works because it is unlikely to have an effect on eutrophication were excluded. The R. Thames (and cut-off and relief channel) were also excluded because of the intention of the NRA to implement catchment studies to determine phosphorus inputs.

A summary of the information from each of the sites is collated below together with a figure showing the change in the different phosphorus fraction in the water downstream of the STW (Tables 1 to 9). On each river, a site upstream of the STW was also sampled although the restricted access to the river at some sites meant this was not as close to the STW as desirable. Little attempt was made at this stage to evaluate other possible point-sources of phosphorus in the up-stream areas. The sites where important tributaries entered the rivers are also shown; again no attempt was made to quantify other inputs from land drainage or small streams entering in the downstream sections. This aspect of the study will be addressed in the pilot study, although complex drainage patterns and channel divisions, eg in water meadows, were noted as they are important factors in the choice of the sites for more intensive study.

3.3 Results

1. R. Test (Table 1)

Sites were visited between Stockbridge and Wherwell with site 3 downstream of the STW and close to the confluence with the R. Anton. The STW has an appreciable effect on all the P fractions immediately downstream of the input with the SRP concentration reducing by about 46 % over a distance of 3.5 km downstream. The bed of this river is dominated by gravel and coarse sand with no evidence of finer materials even in regions of lower flow. As shown in the particle size distributions, the 1-2 mm size fraction dominates the sediment composition.

2. R. Wey (Table 2)

Sites were visited between Alton and Mill Court, 3.5 km downstream of the STW. A small tributary at the head waters was also sampled (site 5). There was a lot of filamentous algae and diatoms at the downstream sites. All P fractions increased dramatically immediately downstream of the STW (>900 % increase in SRP) with a monotonic decrease in all P fractions downstream. The sediments were mainly sand and gravel. As shown at site 1 the bed-sediment had a greater percentage of finer material than the R. Test sediment (site 2).

3. R. Creedy (Table 3)

Sites were visited on the both the rivers Creedy and Yeo from Cowley to Creedy bridge north of Crediton. This is one of the softer water rivers visited (calcium concentration of about 1 mM). The P fraction did not show the trends noted for the rivers Test and Wey of increasing P immediately downstream of the STW with a systematic decrease in all the fractions downstream. It was also noted at site 2 that the river was particularly turbid because of the

runoff of clay from the catchment; this led to the increase in TP at this site compared to the other sites visited. There was evidence of bank erosion at some of the sites. The bed sediment varied in character from gravels, sand banks and some areas with silt. No sediments were collected from these sites. The evidence from this visit is that the river is not influenced by the STW input and judging from the gradual increase in P concentrations downstream diffuse inputs or other point-sources are important for this river.

4. R. Wye (Table 4)

Sites were visited between Hoarwithy in the south (about 21 km from the STW inputs) and upstream of the Hereford (Eign and Rotherwes) STWs. The SRP at the upstream site is low (about 1 μM) and increased by 160 % at the site immediately downstream of the works. The R. Lugg was also sampled at a site immediately above the confluence with the Wye. As shown in the Figure, the higher concentration of P in the R. Lugg (presumably from the Leominster STW) leads to an appreciable increase in the concentration of all P fractions in the R. Wye. This did not decrease appreciably at the downstream site suggesting that other inputs are important in this section of the river. Changes in pH, [Ca] and [Si] were also noted along this section although some of these are clearly linked with the influence of the R. Lugg. The bed-sediment was mainly gravel with some associated finer material. The particle size distribution of the sediment from site 2 indicates the predominance of the 1-0.25 mm size fraction.

5. R. Arrow (Table 5)

Sites were visited between Alcester and Studley. The Studley site was about 2 km upstream of the Sperrall STW. As shown, the phosphorus concentrations downstream of the STW were very high with a gradual decrease at the downstream sites. Both silicon and nitrate showed similar changes. This is a very hardwater river and there is the possibility of heterogenous reactions such as calcium phosphate formation or coprecipitation of phosphate with calcite in the bed sediments. Extensive beds of filamentous algae were seen at all the sites. The sediment was variable in size with a predominance of gravels and sands at all sites but with areas of finer loam material.

6. R. Blythe (Table 6)

Sites were visited between Barston in the south to Blyth Bridge near Coleshill in the north. The TP at the upstream site was very high compared with the other P fractions. The SRP and TDP increased below the STW but showed little change with distance downstream. This is unusual and suggests that other inputs of phosphorus are important downstream or that the bed-sediment is already saturated. Both silicon and nitrate showed little change downstream. The sediment was again very variable in size; the material collected from site 2 was mainly in the 0.5-0.125 mm size fraction with less of the coarser sand fraction found at other sites such as the R. Test (site 2) and R. Wye (site 2). Filamentous algae and submerged macrophytes were found at all the sites.

7. R. Gipping (Alton Water) (Table 7)

Sites were visited between Stowmarket and Great Blakenham with two upstream sites (1 and 2) above the Stowmarket STW, site 3 downstream of the Stowmarket STW but upstream of the Needham Market STW and a downstream site below Needham Market STW. The SRP is already quite high at both the upstream sites (see Table). For example, at site 2 the river was in very low flow conditions and also many ducks were seen in the area. Extensive areas

of filamentous algae were noted at the upstream site 1. The phosphorus concentrations all decreased at site 4 although more information is needed to see whether this continues to the Sroughton intake to Alton Water. The sediment was variable with much gravel at the downstream site; the 1-0.25 mm size fraction dominated in the sediment at site 4 with only a little fines.

8. Louth Canal (Table 8)

Sites were visited between Louth and Thoresby Bridge in the north. The SRP concentration at the upstream site in Louth was low ($0.77 \mu\text{M}$) and increased dramatically downstream of the sewage input. All the phosphorus concentrations decreased systematically downstream. At sites 2 and 3 there was extensive beds of macrophytes and evidence of algal growth. The sediment was variable but that from site 4 was anaerobic below the surface ($<5 \text{ cm}$) and was composed of fines dominated by the $< 2 \mu\text{m}$ size fraction. This type of sediment is likely to have a high affinity and capacity for phosphorus sorption.

9. R. Ant (Table 9)

Only two sites were visited, (Wayford Br. near Smallburgh in the north and Ludham Br. near Horning in the south), to measure the difference between the upstream and downstream locations of the Stalham STW input. A sediment sample was collected from the downstream site at Ludham Bridge. The size fractionation showed the dominance of the 1-0.125 mm fraction with little fines. The TP at these sites was very high relative to the SRP and TDP fractions indicating the importance of particulate phosphorus in this water body. No doubt the extensive boat activity in the area accounts for the abnormally high TP. The R. Ant (and also the R. Bure) have complex networks which are not amenable to the type of mass balance study planned for this project.

10. R. Blackwater (Table 9)

Only sites upstream of the STW at Aldershot were visited. The headwaters run through an urban area and the river is best described as a drainage ditch which in places appears littered and in poor condition. The stream also ran through a road improvement scheme in Aldershot. Although the measured SRP at the site was low, the TP was appreciable and greater than expected. The reason for this is uncertain although suspended green algae was evident at this site. The sediment was gravels with some trapped fines.

11. R. Nene (Table 9)

Two sites were visited: (a) site 1 at Elton downstream of the Willow Brook and sewage from Corby and (b) site 2 south of Wellingborough near Great Doddington and downstream of Great Billing, Broadholme and Whilton STWs. Sediment collection at both these sites would be difficult because of large boulders. The results indicate an appreciable difference in the P fractions at these sites. The complex network of channels and lakes of the R. Nene make this a difficult river to study. Further work would need to identify a STW of interest so that the effort could be directed to a single stretch of the river.

12. R. Great Ouse

A preliminary visit on 19.3.94 to four sites on the Gt Ouse near Brackley indicated that the SRP concentration was $1.3 \mu\text{M}$ below the STW, increasing to $4.9 \mu\text{M}$ at Westbury which is 4 km below the sewage input and then decreased downstream. Other measurements were made but are not reported here in full. On the basis of this initial survey, it was decided to

do a full pilot study of this river in the vicinity of Brackley STW and to include a site on the river closer to the STW. The results of this pilot study are given in section 4 below.

TABLE 1

PRELIMINARY SITE VISIT - RIVER TEST (ANDOVER)
15/6/94

Site #	4	3	2	1
NGR of site:	SU 397 408	SU 381 388	SU 362 369	SU 353 352
Time of visit:	11:30	10:40	09:30	09:00
Distance from STW/ km	-2	1	3.5	6

CHEMICAL PARAMETERS				
pH	8.16	8.04	8.09	7.91
Temperature (°C)	16.2	16.1	15.3	15.4
Conductivity (µS/cm@25°C)	ND	ND	ND	ND
DO (%)	136%	122%	99%	96%
SRP (µM)	1.99	7.97	3.67	3.73
TDP (µM)	2.22	8.88	4.62	4.53
TP (µM)	4.04	10.65	6.66	5.57
Non-M&R reactive fraction (µM)	0.23	0.91	0.95	0.8
Particulate Phosphorus (µM)	1.82	1.77	2.04	1.04
Si (µM)	154.9	167.7	159.2	156.3
NO3 (mM)	0.45	0.5	0.46	0.46

PHYSICAL FEATURES				
Width of river (m):	25	30	20	18
Depth of river (m):	1.5	2	1.5	2
Sediment type:	gravel & sand	gravel & sand	gravel	gravel

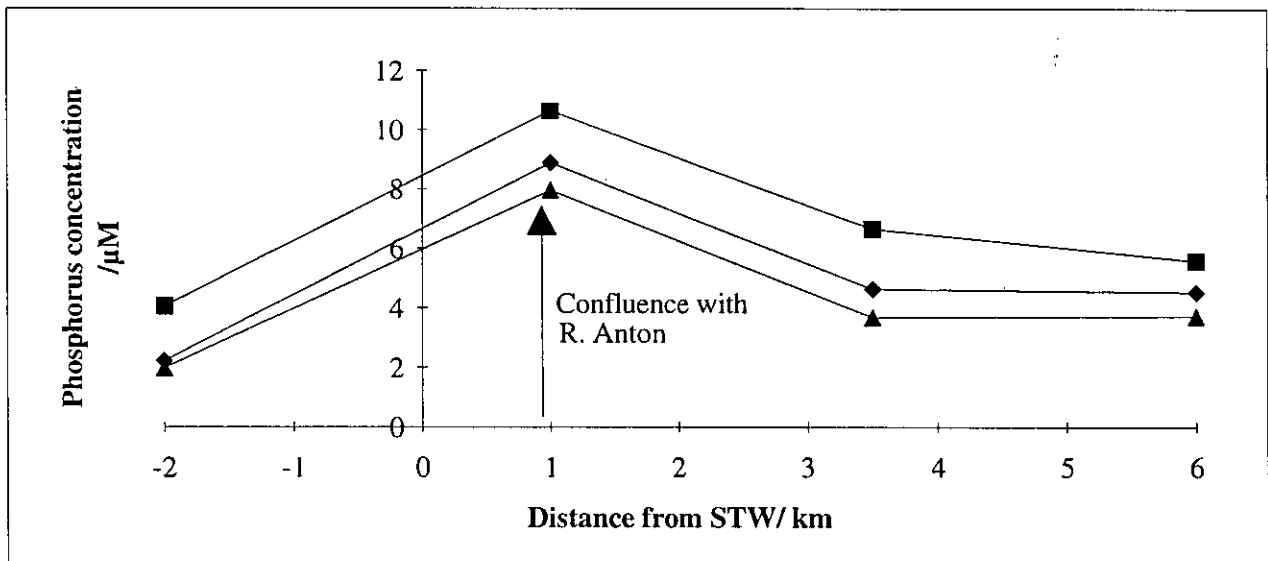


TABLE 2

PRELIMINARY SITE VISIT - RIVER WEY (ALTON)
15/6/94

Site #	5	4	3	2	1
NGR of site:	SU 725 396	SU 729 388	SU 733 404	SU 744 412	SU 756 417
Time of visit:	18:05	16:45	16:10	15:00	14:30
Distance from STW	Tributary	-1	1	2.5	3.5

CHEMICAL PARAMETERS					
pH	7.84	7.92	7.82	8.09	8.04
Temperature (°C)	18.9	18.7	17.1	16.8	18.1
Conductivity (µS/cm@25°C)	ND	ND	ND	ND	ND
DO (%)	ND	91%	93%	116%	139%
SRP (µM)	0.872	2.55	25.83	19.05	14.32
TDP (µM)	1.1	3.21	26.43	22.89	16.91
TP (µM)	1.45	4.74	27.46	23.97	18.48
Non-M&R reactive fraction (µM)	0.228	0.66	0.6	3.84	2.59
Particulate phosphorus (µM)	0.35	1.53	1.03	1.08	1.57
Si (µM)	163.8	158.4	195.1	166.3	161.3
NO3 (mM)	0.34	0.45	0.37	0.4	0.39

PHYSICAL FEATURES					
Width of river (m):	5	2	15	7	15
Depth of river (m):	0.2	0.5	0.2	1 - 1.5	0.5
Sediment type:	gravel & sand	loam	sand & gravel	gravel & sand	gravel & sand

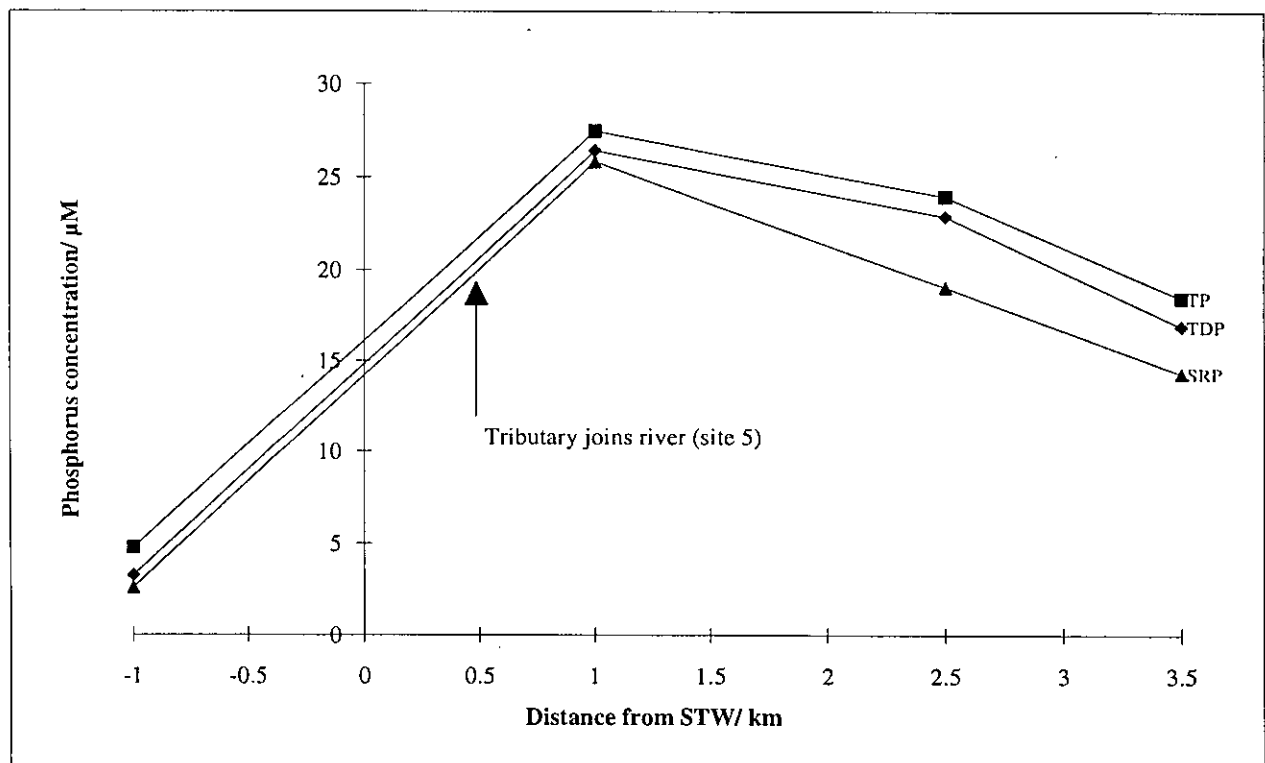


TABLE 3

PRELIMINARY SITE VISIT - RIVER CREEDY
21/6/94

Site #	4	5	3 (YEO)	2	1
NGR of site:	SS 847 012	SS 854 000	SX 856 992	SX 882 985	SX 901 968
Time of visit:	13:30	14:00	13:00	12:15	11:40
Distance from STW/ km	-0.5	1.25	Tributary	4.5	7.5

CHEMICAL PARAMETERS					
pH	7.4	7.39	7.24	7.19	7.65
Temperature (°C)	15.8	16.1	16.2	15.7	14.7
Conductivity (µS/cm@25°C)	379	410	395	436	455
DO (%)	ND	ND	ND	ND	ND
SRP (µM)	6.23	5.55	3.52	6.55	7.43
TDP (µM)	6.93	6.8	4.16	8.18	9.02
TP (µM)	8.28	7.3	4.63	22.46	9.91
Non-M&R reactive phosphorus (µM)	0.7	1.25	0.64	1.63	1.59
Particulate Phosphorus (µM)	1.35	0.5	0.47	14.28	0.89
Si (µM)	175	172	191	175	166
NO3 (mM)	0.454	0.444	0.461	0.516	0.545
Ca++ (mM)	1.03	1.2	1.02	1.13	1.16

PHYSICAL FEATURES					
Width of river (m):	15	10	20	30	20
Depth of river (m):	0.5	0.5	0.5	? >1	0.5 - 1
Sediment type:	gravel & silt	gravel & silt	sand & silt	?	gravel & silt

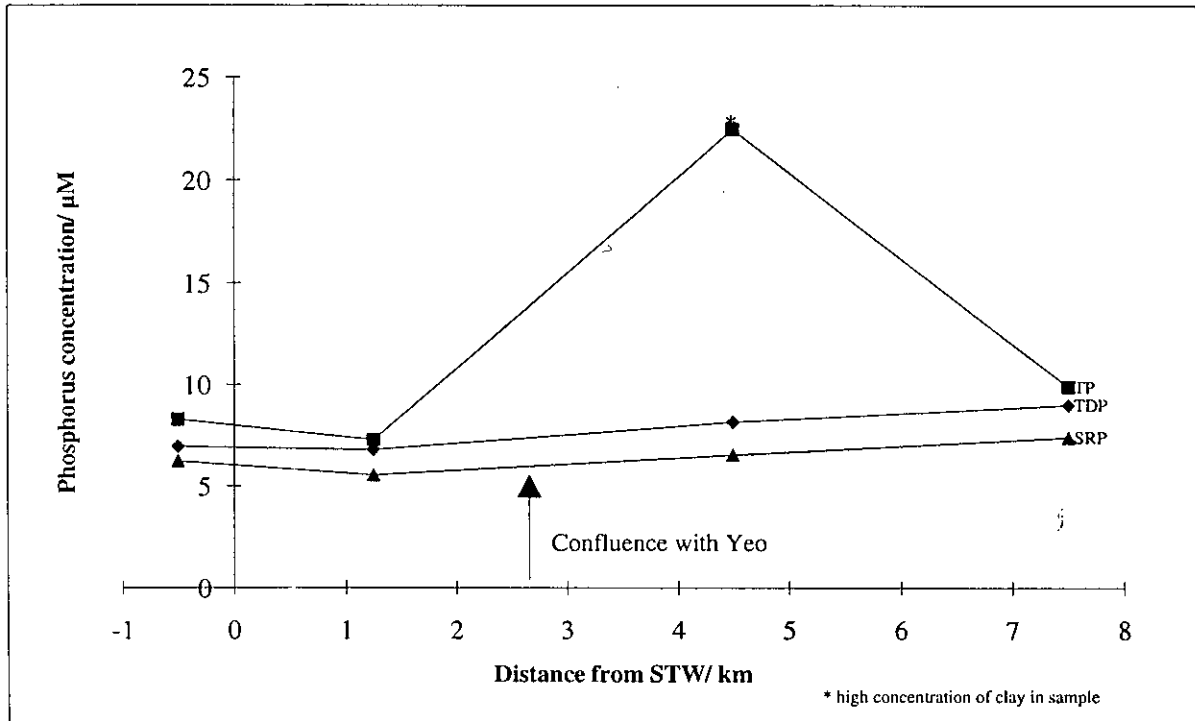


TABLE 4

PRELIMINARY SITE VISIT - RIVER WYE
21-22/06/1994

Site #	4	3	5 (LUGG)	2	1
NGR of site:	SO 517 384	SO 543 374	SO 568 375	SO 568 368	SO 548 295
Time of visit:	09:20	08:55	09:55	18:40	17:45
Distance from STW/ km	-2	3.5	tributary	7.5	21

CHEMICAL PARAMETERS					
pH	7.92	8.35	8.05	8.48	8.55
Temperature (°C)	16.6	16.2	16	17.9	17.7
Conductivity (µS/cm@25°C)	279	287	521	351	371
DO (%)	ND	ND	ND	ND	ND
SRP (µM)	1.1	2.86	6.26	3.84	3.68
TDP (µM)	1.28	3.34	7.31	4.78	4.99
TP (µM)	1.72	5.29	7.88	7.82	8.78
Non-M&R Reactive Phosphorus (µM)	0.18	0.48	1.05	0.94	1.31
Particulate Phosphorus (µM)	0.44	1.95	0.57	3.04	3.79
Si (µM)	44.2	38.1	74.4	47	37.7
NO3 (mM)	0.159	0.167	0.461	0.252	0.266
Ca++ (mM)	1.06	1.04	2.17	1.39	1.41

PHYSICAL FEATURES					
Width of river (m):	50	60	20	60	60
Depth of river (m):	>2	>2	>2	>2	>2
Sediment type:	gravel & silt	loam	gravel & silt	gravel + silt	gravel

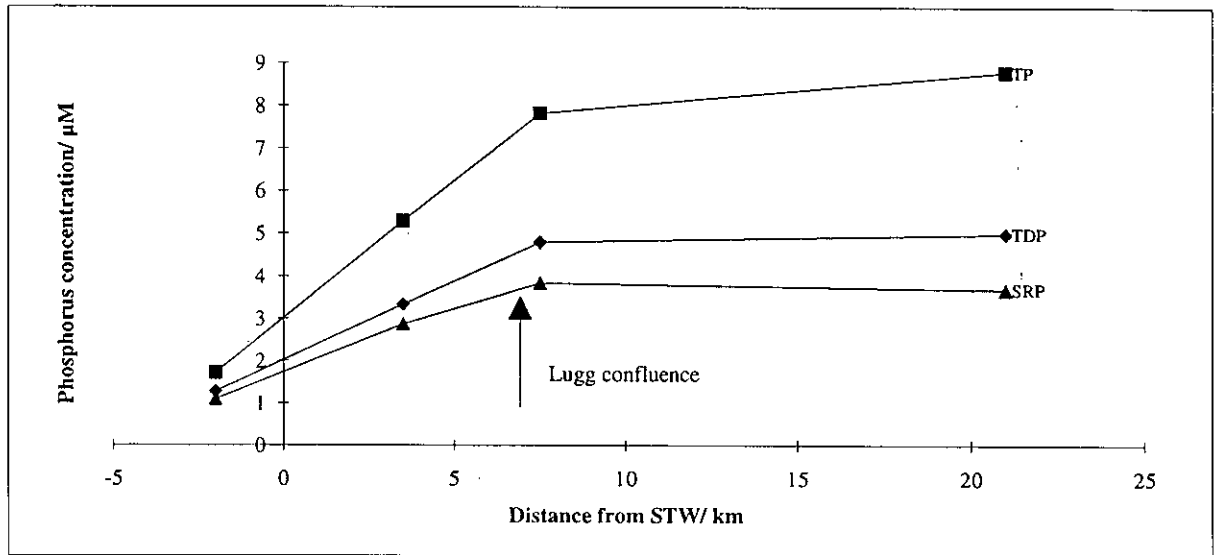


TABLE 5

PRELIMINARY SITE VISIT - RIVER ARROW
22/6/94

Site #	1	2	3	4	5
NGR of site:	SP 077 639	SP 085 623	SP 086 604	SP 092 578	SP 083 514
Time of visit:	14:45	15:25	16:00	16:30	17:05
Distance from STW/ km	-2	0.5	2	5	13

CHEMICAL PARAMETERS					
pH	8.3	8.02	7.32	7.65	7.77
Temperature (°C)	18.7	18.5	18.8	18.6	18.9
Conductivity (µS/cm@25°C)	833	1007	1008	1027	1228
DO (%)	ND	ND	ND	ND	ND
SRP (µM)	22.89	114.29	85.88	67.48	51.66
TDP (µM)	25.41	123.32	94.00	74.77	61.09
TP (µM)	26.71	127.66	115.52	79.71	63.37
Non-M&R Reactive Phosphorus (µM)	2.52	9.03	8.12	7.29	9.43
Particulate Phosphorus (µM)	1.3	4.34	21.52	4.94	2.28
Si (µM)	206	336	323	277	313
NO3 (mM)	0.29	0.74	0.72	0.55	0.57
Ca++ (mM)	2.70	2.69	2.70	2.94	3.85

PHYSICAL FEATURES					
Width of river (m):	15	10	15	15	15
Depth of river (m):	0.05	1	0.1	0.2	2
Sediment type:	sand/loam	gravel + silt	gravel + silt	gravel + silt	sand/loam

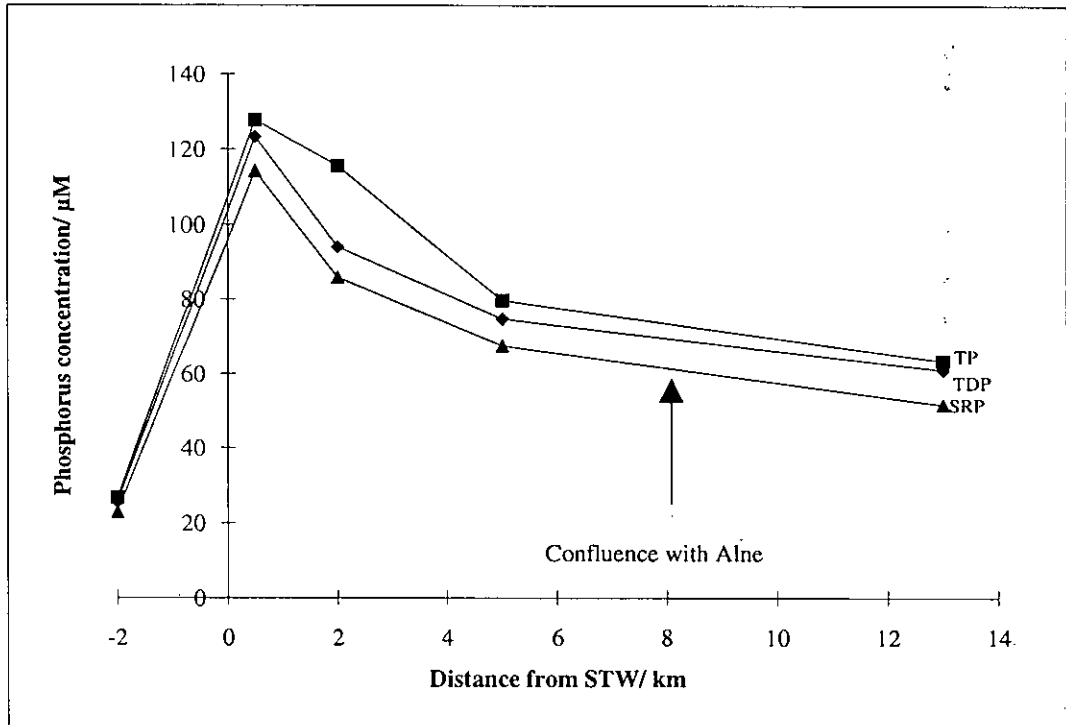


TABLE 6

PRELIMINARY SITE VISIT - RIVER BLYTHE
22/6/94

Site #	1	2	3	4
NGR of site:	SP 218 783	SP 215 814	SP 218 852	SP 211 898
Time of visit:	11:40	11:00	12:40	13:15
Distance from STW/ km	-2	1.5	7	14

CHEMICAL PARAMETERS				
pH	8.06	8.08	8.06	8.18
Temperature (°C)	17.5	17.8	18.1	18.8
Conductivity ($\mu\text{S}/\text{cm}@25^\circ\text{C}$)	751	699	731	755
DO (%)	ND	ND	ND	ND
SRP (μM)	27.18	56.12	56.82	50.14
TDP (μM)	31.24	60.83	65.68	57.2
TP (μM)	97.26	57.86	51.12	57.2
Non-M&R Reactive fraction (μM)	4.06	4.71	8.86	7.06
Particulate Phosphorus (μM)	66.02	-2.97	-14.56	0
Si (μM)	234	267	248	216
NO ₃ (mM)	0.44	0.62	0.65	0.63
Ca ⁺⁺ (mM)	1.80	1.70	1.68	1.73

PHYSICAL FEATURES				
Width of river (m):	8	15	15-20	25-30
Depth of river (m):	0.5	0.2	0.2	2
Sediment type:	sand/loam	gravel + silt	gravel + silt	loam

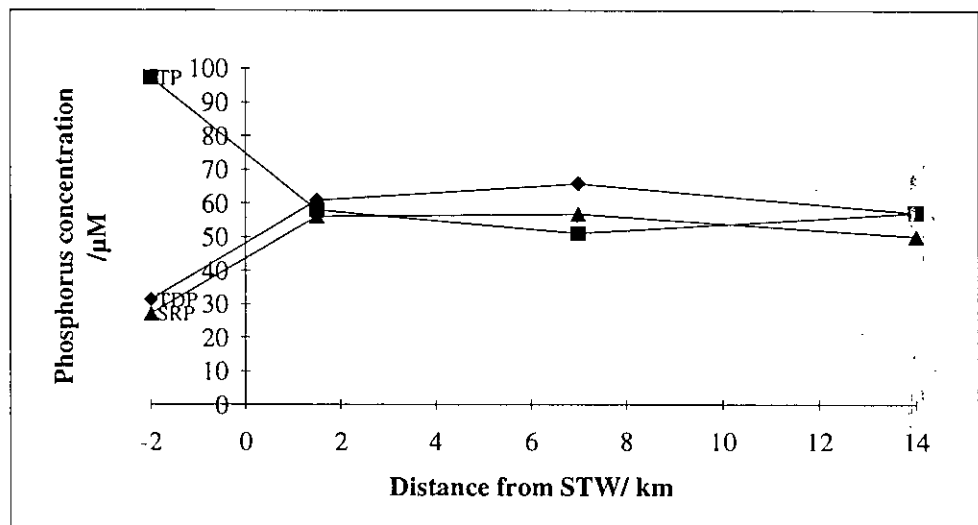


TABLE 7

PRELIMINARY SITE VISIT - RIVER GIPPING
10/08/94

Site #	1	2	3	4
NGR of site:	TM 027 586	TM 051 588	TM 089 554	TM 127 502
Time of visit:	14.20	15.30	15.50	16.25
Distance from STW/ km	-3	-1	5	13

CHEMICAL PARAMETERS				
pH	ND	ND	ND	ND
Temperature (°C)	ND	17.7	17.9	18.2
Conductivity (µS/cm@25°C)	891	997	1031	991
DO (%)	83	90	94	77
SRP (µM)	14.04	24.34	22.05	16.95
TDP (µM)	8	26.57	21.63	17.18
TP (µM)	16.44	38.55	23.93	18.51
Non-M&R Reactive fraction (µM)	-6.04	2.23	-0.42	0.23
Particulate Phosphorus (µM)	8.44	11.98	2.3	1.33
Si (µM)	280.9	273.4	299.1	268.1
NO3 (mM)	0.28	0.36	0.26	0.21
Ca++ (mM)	3.81	4.19	4.06	3.82

PHYSICAL FEATURES				
Width of river (m):	5	15-20	15	30
Depth of river (m):	0.2	0.3	0.2	1
Sediment type:	?	loam	sand/loam	sand/gravel

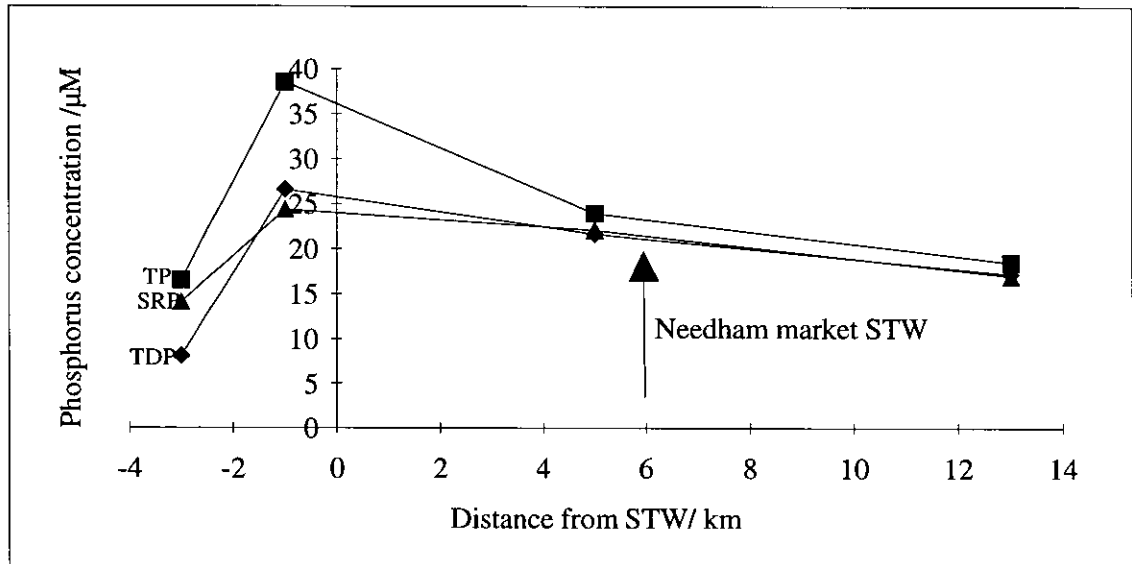


TABLE 8

PRELIMINARY SITE VISIT - LOUTH CANAL
11/08/94

Site #	1	2	3	4
NGR of site:	TF 326 875	TF 364 908	TF 368 946	TF 337 998
Time of visit:	12.45	14.10	14.40	15.15
Distance from STW/ km	-2	4	8	14

CHEMICAL PARAMETERS				
pH	ND	ND	ND	ND
Temperature (°C)	16.6	18.8	17.6	18.4
Conductivity ($\mu\text{S}/\text{cm}@25^\circ\text{C}$)	562	801	639	600
DO (%)	100	101	104	104
SRP (μM)	0.77	31.99	9.33	2.77
TDP (μM)	1.19	34.22	9.68	3.72
TP (μM)	2.74	38.17	10.87	7.35
Non-M&R Reactive fraction (μM)	0.42	2.23	0.35	0.95
Particulate Phosphorus (μM)	1.55	3.95	1.19	3.63
Si (μM)	90.8	188	109.3	36
NO ₃ (mM)	0.76	0.99	0.64	0.30
Ca ⁺⁺ (mM)	2.79	2.49	2.70	2.29

PHYSICAL FEATURES				
Width of river (m):	5	4	30	30
Depth of river (m):	0.3	0.5-1	0.5	3
Sediment type:	gravel	rock	rock/ loam	loam

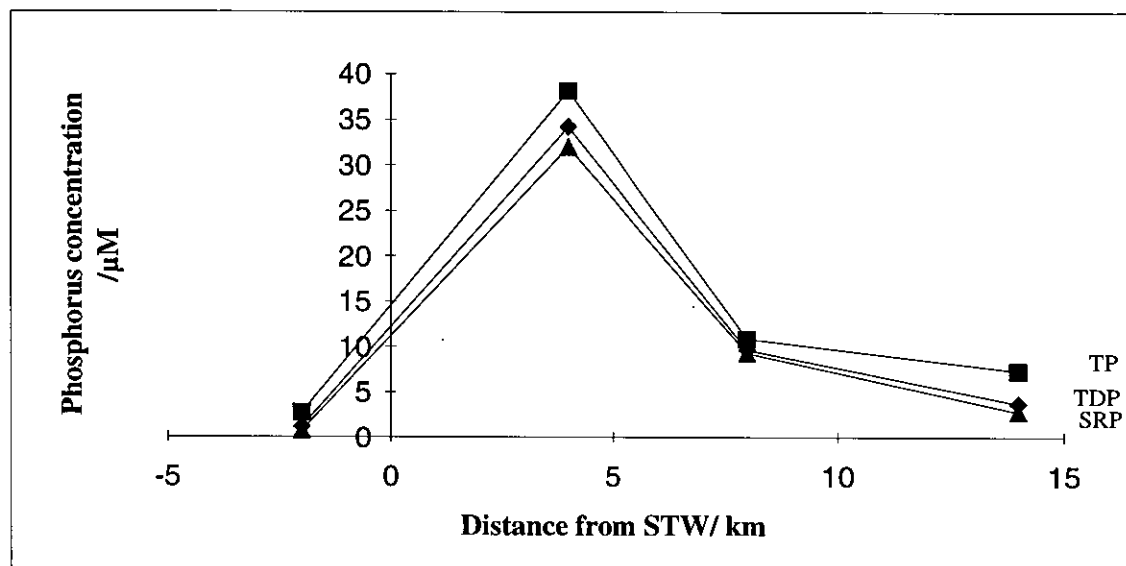


TABLE 9

**ADDITIONAL SITE VISITS AS PART OF PILOT STUDY
1994**

River	Blackwater	Ant 1	Ant 2	Nene 1	Nene 2
NGR of site		TG 373 172	TG 348 247	TL 085 947	SP 877 638
Date of visit	15/6/94	10/08/94	11/08/94	11/08/94	11/08/94
Time of visit	14.00	20.45	9.30	18.20	19.20

CHEMICAL PARAMETERS					
pH	ND	ND	ND	ND	ND
Temperature (°C)	ND	19.7	17.1	18.5	17.9
Conductivity ($\mu\text{S}/\text{cm}@25^\circ\text{C}$)	ND	729	798	969	862
DO (%)	ND	98	86	91	64
SRP (μM)	0.32	0.28	0.85	26.93	52.62
TDP (μM)	0.8	1.06	1.25	24.7	57.24
TP (μM)	7.7	7.87	3.02	30.25	61.8
Non-M&R Reactive Phosphorus (μM)	0.48	0.78	0.4	-2.23	4.62
Particulate Phosphorus (μM)	6.9	6.81	1.77	5.55	4.56
Si (μM)	75.1	14.3	228.6	98.3	120.3
NO ₃ (mM)	0.03	0.06	0.13	0.43	0.58
Ca ⁺⁺ (mM)		2.36	3.24	3.36	2.7

PHYSICAL FEATURES					
Width of river (m)	1	40	50	40	30
Depth of river	0.05	>2	>2	3	2
Sediment type	gravel	?	sand/loam	gravel	large stones

3.4 Recommendations

The expected increase in phosphorus fractions downstream of a STW and then systematic decrease in concentration downstream, is evident for some of the sites visited. This indicates that phosphorus is being retrieved within the river and will ultimately be mainly incorporated in the bed-sediment. Release from the sediment, either in soluble form or sorbed to suspended material is then possible. The rivers which exhibit this trend are:

- R. Test
- R. Wey
- R. Arrow
- R. Gipping
- Louth canal

The other rivers that were visited are more complex in behaviour with either multiple large STWs, such as the R. Nene, or have complex networks, eg the rivers Ant, Burr and Nene, which make a mass balance of phosphorus more difficult and expensive because of the large number of sites needed to monitor the system in any meaningful way. In some rivers such as the Wye and Creedy other nutrient inputs, apart from the STWs identified in the sensitive areas, are important and obviously effect the response of the river to lowering discharges of SRP from the major STWs.

It is interesting to compare the ratios of SRP/TP and SRP/TDP at the keysites on the five rivers identified above. Generally the SRP/TDP ratios are lowest at the upstream sites. The ratio SRP/TDP is similar for all the sites immediately downstream of the STWs and in the range of 89-97 % but generally the ratio decreases downstream because of the preferential uptake of SRP by the sediment and flora or release of soluble organic phosphorous. The SRP/TP ratio is more variable, depending on the local conditions such as surface runoff and resuspension of bed-sediments. The high ratio of SRP/TDP at the sites confirms the bioavailable nature of the dissolved phosphorus in these rivers at the time of sampling. At the moment it is not certain how much of the (TP-TDP) fraction is bioavailable or easily released to the water-column during transit downstream.

TABLE 10 Comparison of the percentage of soluble reactive phosphorus (SRP) of total phosphorus (TP) and total dissolved phosphorus (TDP) for three key sites on each of the selected rivers. The SRP (μM) concentrations are also given for comparison.

river	P ratio	upstream	immediately downstream	furthest downstream
Test	SRP/TP	49	75	67
	SRP/TDP	89	89	82
	SRP/ μM	1.99	7.97	3.73
Wey	SRP/TP	54	95	92
	SRP/TDP	79	97	85
	SRP/ μM	2.55	25.83	16.91
Arrow	SRP/TP	86	90	82
	SRP/TDP	90	93	85
	SRP/ μM	22.89	114.3	51.7
Gipping	SRP/TP	85	63	92
	SRP/TDP	-	92	99
	SRP/ μM	14.04	24.34	16.95
Louth	SRP/TP	28	84	38
	SRP/TDP	65	94	75
	SRP/ μM	0.77	31.99	2.77

4. PILOT STUDY; PROGRESS TO DATE

The pilot study on the Great Ouse at Brackley has been completed. Based on the preliminary site visit, four sites on the Gt. Ouse were selected: upstream in Brackley, below the STW, Fulwell House between Westbury and Finmere and the downstream site in Water Stratford. Three of these sites correspond to NRA monitoring sites and the NRA data for these sites has been supplied by Dr T. Warn, Anglian NRA. The site visits included all the measurements made in the preliminary survey. In addition, the water velocity was measured using an ultrasonic sensor (SENSA RC2), the channel cross-sectional area measured and bed-sediments to a depth of 5 cm sampled and sieved through a 2 mm stainless steel sieve. In the laboratory the water content of the sediment was determined by drying at 105 °C, the organic matter by combustion at 550 °C, the total phosphorus by the method of Andersen (1976), bioavailable phosphorus by the method of Sharpley (1993) as used by House et al (1994), equilibrium phosphorus concentration, EPC_0 , distribution coefficient and initial adsorption amount, n_i , by

the method described by House et al (1994). The particle size distributions were measured using SOP 26/20.7.94 .

4.1 Results

4.1.1 General water analysis

This is a very hardwater river with some possibilities for heterogeneous reactions in the sediment by the formation of calcium phosphates or coprecipitates with calcite. Phosphorus bound in this way will not be released unless the chemistry of the river changes a lot. The nitrate concentration increases as a result of the sewage input but does not change appreciably downstream. Silicon shows only a slight decrease downstream over the whole length studied with a concentration close to the quartz solubility in water and similar in concentration to many chalk streams in southern England. Potassium shows little change whereas sodium increases slightly downstream of the STW. The dissolved oxygen concentration was above the atmospheric equilibrium value at all sites indicating photosynthetic activity in the water.

4.1.2 Phosphorus concentration in the water

The SRP concentration at the upstream site was relatively low with a marked increase below the STW and then a decrease at site 2. There is little difference between the SRP and TDP fractions at site 2 and 3; in contrast the particulate phosphorus (PP) increases at site 3. The non-MR reactive fraction shows a systematic decrease below the sewage inflow. It should now be possible to examine the section between sites 4 and 2, ie up to 4 km below the sewage input, in more detail and look for additional inputs of nutrients in the lower section, ie between Fulwell House and Water Stratford.

4.1.3 Results of the sediment experiments

The organic matter content of the sediments were similar and relatively low. The total phosphorus contents at the upstream and lower downstream sites were similar with an increase at the site immediately downstream of the STW. From the results of the BAP measurements, only a relatively small part of this increase in the sediment past the STW appears to be easily releasable or readily bioavailable. The EPC_0 s are in the range of 3-5 μM at all the downstream sites indicating the net influx of SRP to the sediment at these sites, ie $EPC_0 < \text{SRP}$. The EPC_0 at the upstream site is an order of magnitude lower but still a net uptake of phosphorus by the bed-sediment is expected.

The distribution coefficient gives a measure of the affinity of the sediment to SRP. The highest value is from the first impacted site with a decrease in magnitude at the sites downstream. The lowest value is for the upstream site. The initial adsorption amounts, n_i , are lower than the BAPs and considerably lower than the total phosphorus concentrations of the sediment.

These results provide information important for the modelling work and design of the fluvium experiments. They also provide some measure of the differences between sites as a guide to planning further sampling.

TABLE 11

**PILOT STUDY TO GT. OUSE
BRACKLEY STW 25/5/94**

SITE	1	4	2	3
NGR of site	SP595 368	SP 602 058	SP 627 346	SP 652 341
Distance from STW/ km	-1	1	4	7
pH	8.18	8.37	8.43	8.32
Conductivity (µS/cm)	765	787	794	760
Dissolved Oxygen (%)	105	117	113	139
Temperature	10.7	11.7	11.1	11.1
Flow (m ³ /s)	0.31	0.75	1.25	0.88
Filtered water (0.45 µm)				
Ca ⁺⁺ (mM)	3.64	3.45	3.66	3.79
Mg ⁺⁺ (mM)	0.20	0.19	0.18	0.18
Na ⁺ (mM)	0.69	1.03	0.81	0.83
K ⁺ (mM)	0.08	0.08	0.11	0.10
Alkalinity (mM)	5.30	4.46	5.00	4.91
NO ₃ ⁻ (mM)	0.59	0.75	0.71	0.72
Silica (µM)	130	120	110	100
Soluble Reactive Phosphorus (µM)	1.82	15.07	7.89	8.42
Total Dissolved Phosphorus (µM)	3.13	19.42	10.34	10.59
Non - MR Reactive fraction (µM)	1.31	4.35	2.45	2.17
Unfiltered water				
Total Phosphorus (µM)	3.76	19.89	10.96	11.97
Particulate Phosphorus (µM)	0.63	0.47	0.62	1.38
Sediment sieved 2mm				
% water	21.14	20.61	19.57	22.88
Organic Matter (% of dry wt)	2.36	2.10	2.09	2.57
Total Phosphorus (µmol/g)	19.43	39.38	17.07	23.56
Bioavailable Phosphorus (µmol/g)	0.62	1.43	1.13	1.20
Equilibrium Phosphorus Concentration (µM)	0.41	3.53	4.78	2.93
K _d (dm ³ /kg)	312.40	924.40	736.90	832.90
n _i (µmol/g)	0.13	0.33	0.35	0.24

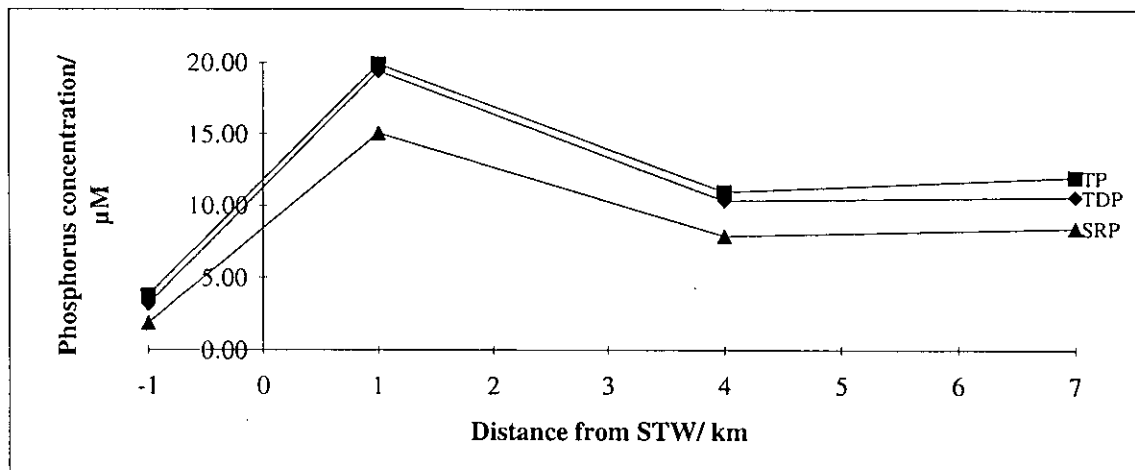


TABLE 12

SITE 1 GREAT OUSE:BRACKLEY STW. SEDIMENT & WATER COLLECTED 25/5/94

EPCo DETERMINATION: ANALYSIS 26/5/94				
weight of wet sediment/ g	weight of dry sediment/ g	initial [P] (μM)	[P] at 24 h (μM)	dN ($\mu\text{mol/g dry wt}$)
2.16	1.71	5	1.65	0.39
2.09	1.65	10	3.71	0.76
2.08	1.64	20	10.30	1.18
4.06	3.20	0	0.37	-0.02
4.15	3.28	5	0.92	0.25
4.17	3.29	10	2.41	0.46
4.08	3.22	20	6.71	0.83
6.07	4.79	0	0.50	-0.02
6.26	4.93	5	0.94	0.16
6.17	4.87	10	1.62	0.34
6.17	4.87	20	4.36	0.64

% WATER OF SEDIMENT = 21.14

ORGANIC MATTER OF SEDIMENT AS % OF DRY MASS = 2.36%

TOTAL PHOSPHORUS OF SEDIMENT = 19.43 $\mu\text{mol/g}$

SRP OF WATER = 1.82 $\mu\text{mol/l}$

TDP OF WATER = 3.13 $\mu\text{mol/l}$

TP OF WATER = 3.76 $\mu\text{mol/l}$

EPCo = 0.41 μM

Kd = 312.4 l/kg

ni = 0.13 $\mu\text{mol/g}$

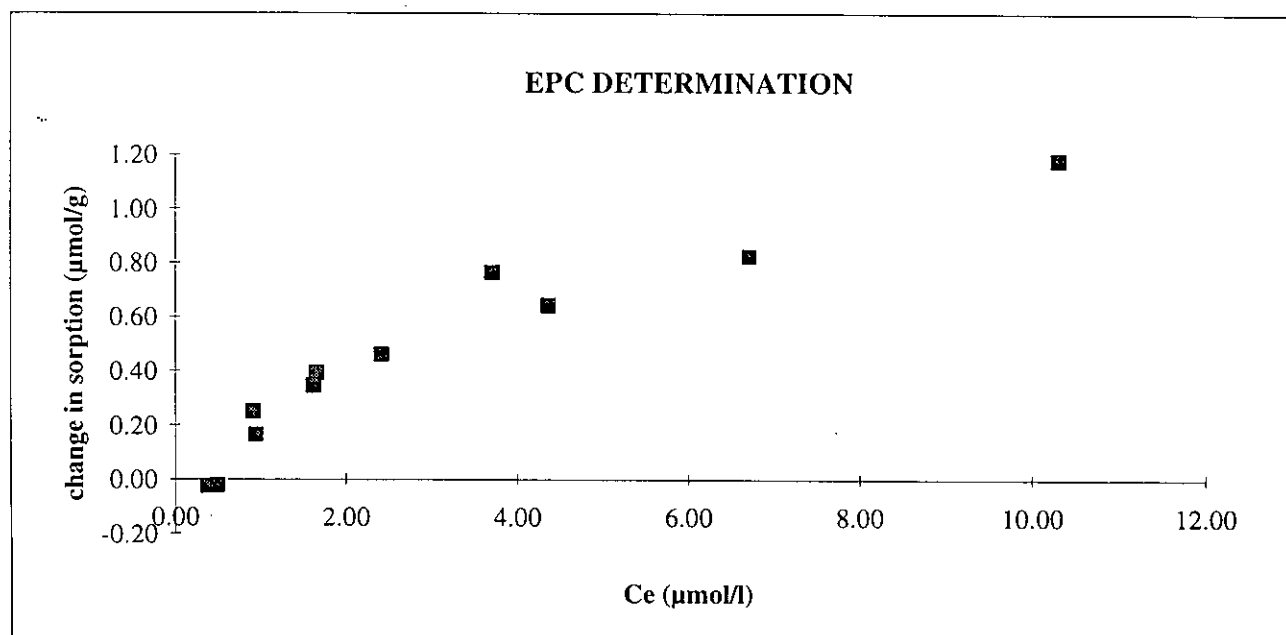


TABLE 13

SITE 2 GREAT OUSE:BRACKLEY STW. SEDIMENT & WATER COLLECTED 25/5/94

EPCo DETERMINATION: ANALYSIS 31/5/94				
weight of wet sediment/ g	weight of dry sediment/ g	initial [P] (μM)	[P] at 24 h (μM)	dN ($\mu\text{mol/g. dry wt}$)
2.20	1.77	0	1.97	-0.22
2.37	1.91	5	4.94	0.01
2.36	1.90	10	7.78	0.23
2.47	1.98	20	15.03	0.50
4.19	3.37	0	2.70	-0.16
4.29	3.45	5	4.66	0.02
4.33	3.48	10	7.17	0.16
4.05	3.26	20	13.08	0.42
6.29	5.06	0	3.09	-0.12
6.33	5.09	5	4.76	0.01
6.17	4.96	10	6.73	0.13
6.01	4.83	20	11.96	0.33

% WATER OF SEDIMENT = 19.57

ORGANIC MATTER OF SEDIMENT AS % OF DRY MASS = 2.09%

TOTAL PHOSPHORUS OF SEDIMENT = 17.07 $\mu\text{mol/g}$

SRP OF WATER = 7.89 $\mu\text{mol/l}$

TDP OF WATER = 10.34 $\mu\text{mol/l}$

TP OF WATER = 10.96 $\mu\text{mol/l}$

EPCo = 4.78 μM

Kd = 736.9 l/kg

ni = 0.35 $\mu\text{mol/g}$

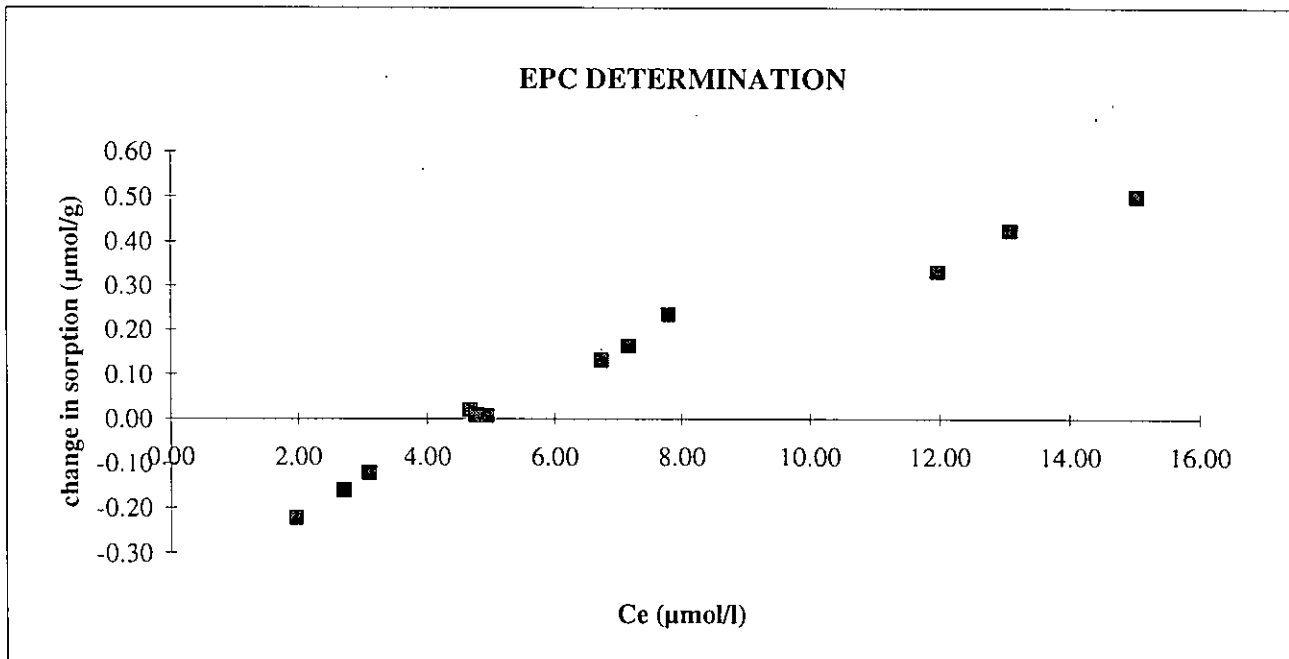


TABLE 14

SITE 3 GREAT OUSE BRACKLEY STW. SEDIMENT & WATER COLLECTED 25/5/94

EPCo DETERMINATION: ANALYSIS 2/6/94				
weight of wet sediment/ g	weight of dry sediment/ g	initial [P] (μM)	[P] at 24 h (μM)	dN ($\mu\text{mol/ g dry wt}$)
2.14	1.65	0	1.38	-0.17
2.03	1.57	5	3.75	0.16
2.04	1.57	10	6.89	0.40
2.33	1.80	20	12.88	0.79
4.30	3.32	0	1.89	-0.11
4.40	3.39	5	3.75	0.07
4.04	3.12	10	5.85	0.27
4.03	3.11	20	11.55	0.54
6.19	4.78	0	2.18	-0.09
6.53	5.03	5	3.57	0.06
6.22	4.79	10	5.56	0.19
6.67	5.14	20	9.02	0.43

% WATER OF SEDIMENT = 22.88

ORGANIC MATTER OF SEDIMENT AS % OF DRY MASS = 2.57%

TOTAL PHOSPHORUS OF SEDIMENT = 23.56 $\mu\text{mol/ g}$

SRP OF WATER = 8.42 $\mu\text{mol/ l}$

TDP OF WATER = 10.59 $\mu\text{mol/ l}$

TP OF WATER = 11.97 $\mu\text{mol/ l}$

EPCo = 2.93 μM

Kd = 832.9 l/kg

ni = 0.24 $\mu\text{mol/ g}$

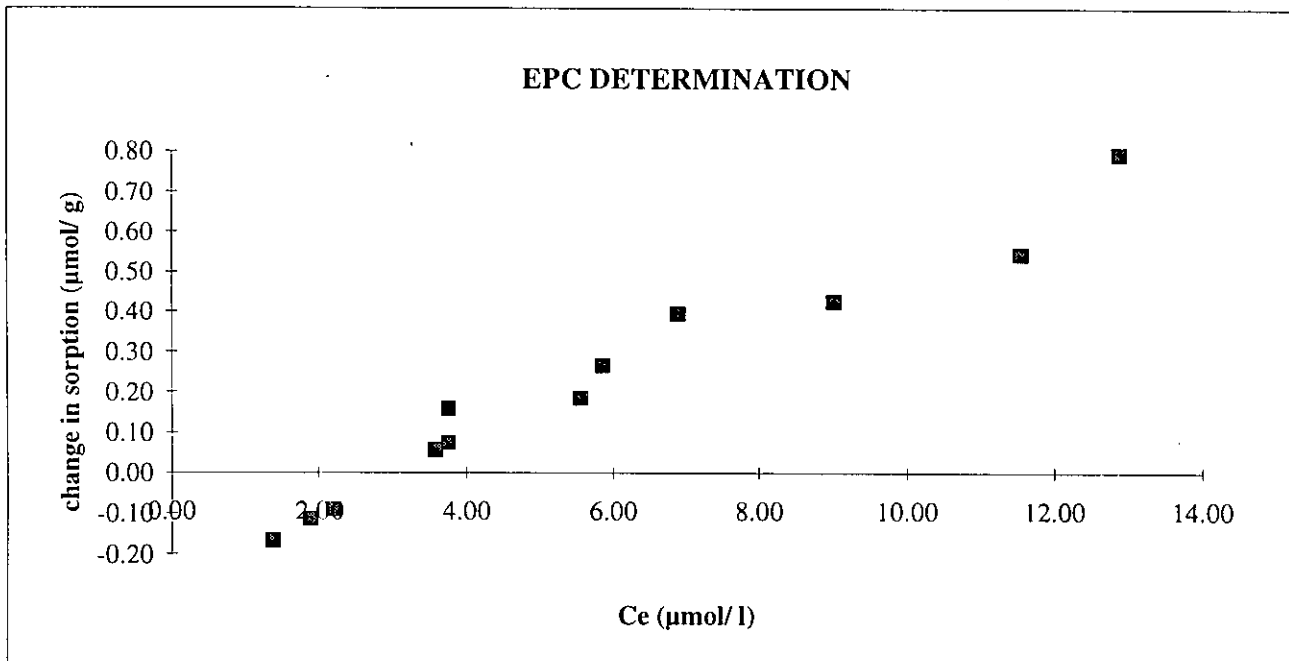


TABLE 15

SITE 4 GREAT OUSE: BRACKLEY STW. SEDIMENT & WATER COLLECTED 25/5/94

EPCo DETERMINATION: ANALYSIS 2/6/94				
weight of wet sediment/ g	weight of dry sediment/ g	initial [P] (μM)	[P] at 24 h (μM)	dN ($\mu\text{mol/g dry wt}$)
2.46	1.95	0	1.72	-0.18
2.47	1.96	5	4.04	0.10
2.03	1.61	10	7.30	0.34
2.69	2.13	20	13.51	0.61
4.05	3.21	0	2.22	-0.14
4.07	3.23	5	4.08	0.06
4.05	3.21	10	6.32	0.23
4.43	3.52	20	11.87	0.46
6.22	4.93	0	2.46	-0.10
6.17	4.90	5	4.12	0.04
6.06	4.81	10	5.37	0.19
6.17	4.90	20	10.28	0.40

% WATER OF SEDIMENT = 20.61

ORGANIC MATTER OF SEDIMENT AS % OF DRY MASS = 2.10%

TOTAL PHOSPHORUS OF SEDIMENT = 39.38 $\mu\text{mol/g}$

SRP OF WATER = 15.07 $\mu\text{mol/l}$

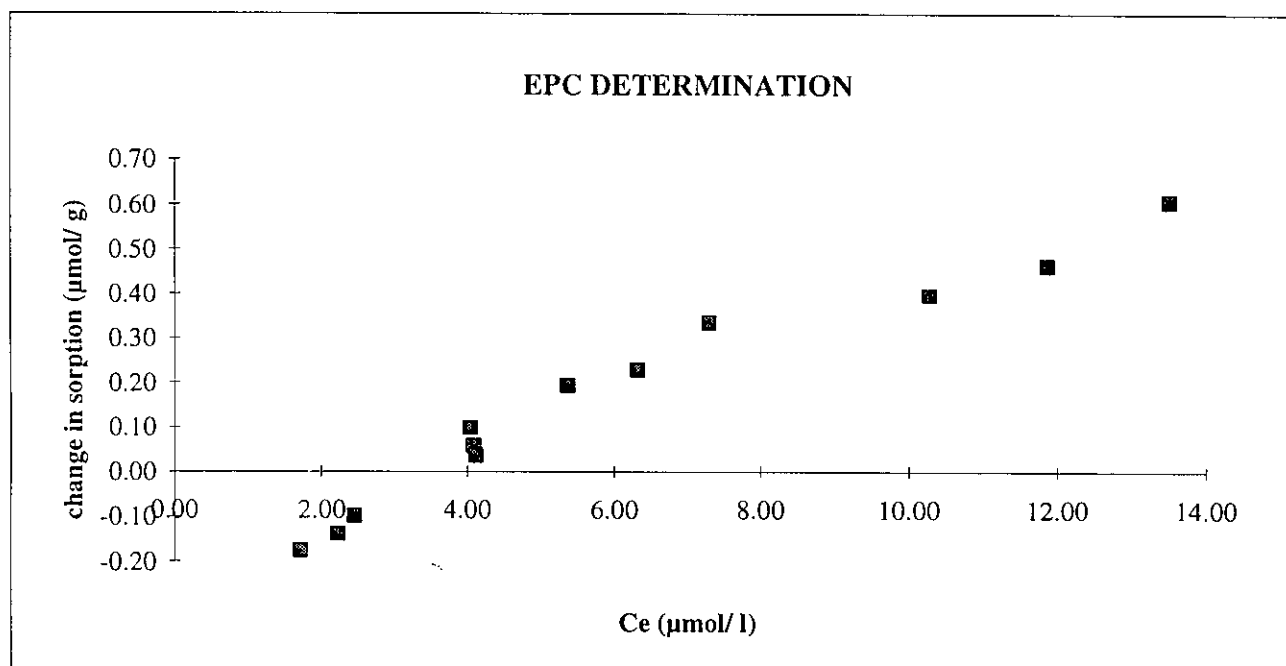
TDP OF WATER = 19.42 $\mu\text{mol/l}$

TP OF WATER = 19.89 $\mu\text{mol/l}$

EPCo = 3.53 μM

Kd = 924.4 l/kg

ni = 0.33 $\mu\text{mol/g}$



5. Fluvarium channel; design and progress

A new channel has been constructed following the revision of a prototype used last autumn on another project. The design is shown in Fig 1. The sediment depth is about 5 cm with a 4 cm depth of water above the sediment. The system is recirculating permitting slow chemical changes to be monitored.

The modified version 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 conductivity are logged using a Hunter portable computer.

Further developments in progress include:

1. Automatic measurement of oxygen with data collection.
 2. Incorporation of a transducer for automatic flow measurements.
 3. Automatic sampling and water filtration on-site during long experimental runs.
- Of these, the third is near completion and the other developments are in progress and should be complete within a month.

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.

6. SCHEDULE

It is planned to continue the pilot studies with a more detailed survey of the R. Wey. The BAP method will also be reexamined prior to this visit. Discussion with DoE and the NRA will continue with the purpose of selecting a STW at which P reduction can be expected between March and September 1995. In addition, the development of the fluvarium channel will continue as outlined above in readiness for experiments with bed-sediments from selected pilot study sites.

REFERENCES

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- House, W.A., Denison, F.H. and Armitage, P.D. (1994) Comparison of the uptake of inorganic phosphorus to a suspended and stream bed-sediment. *Wat. Res.* (in press).
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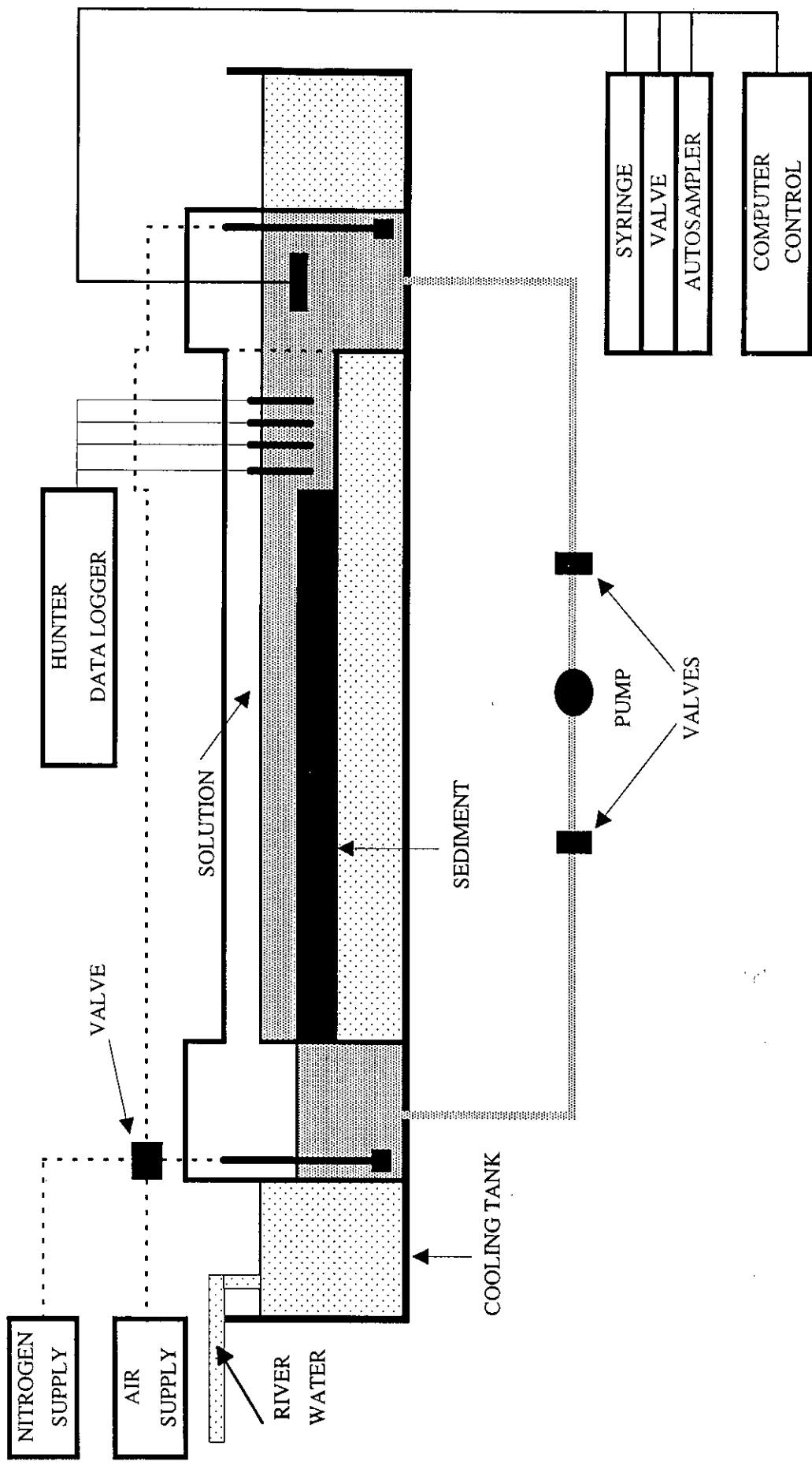
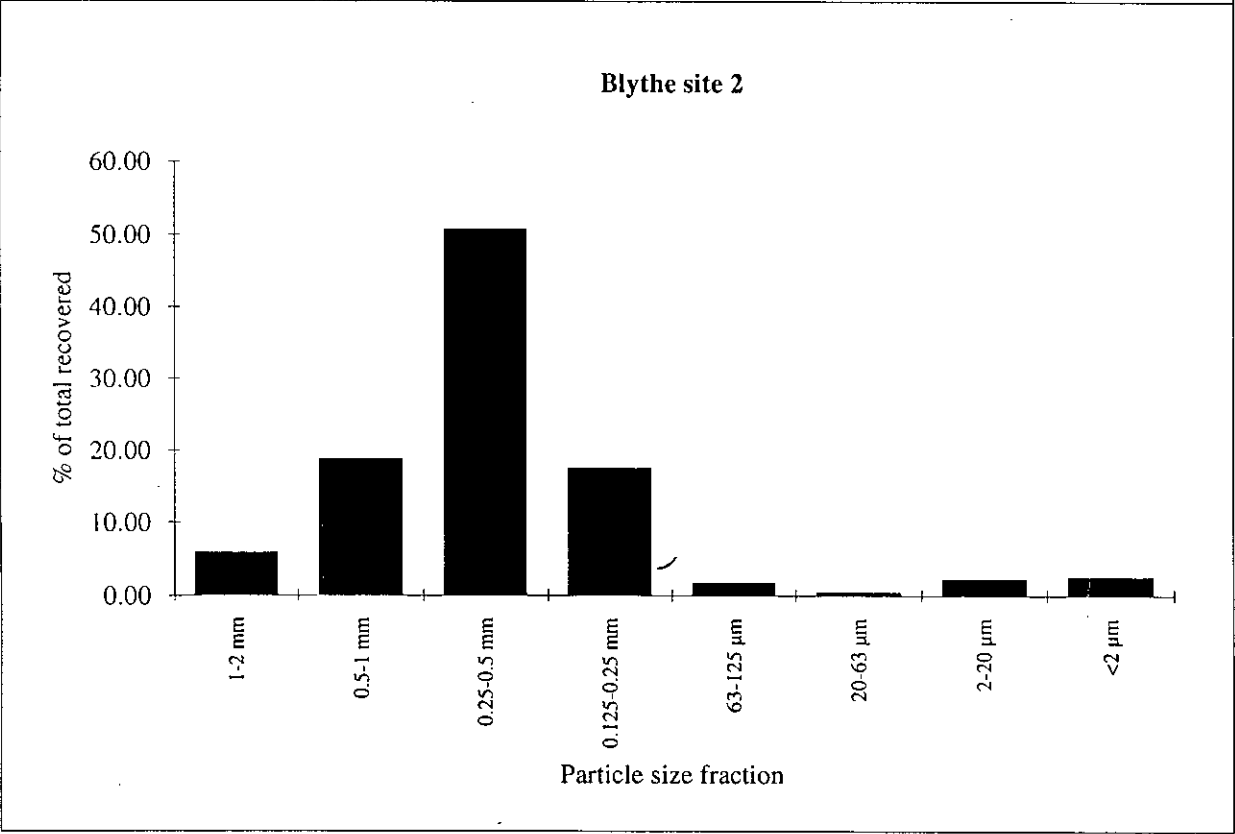
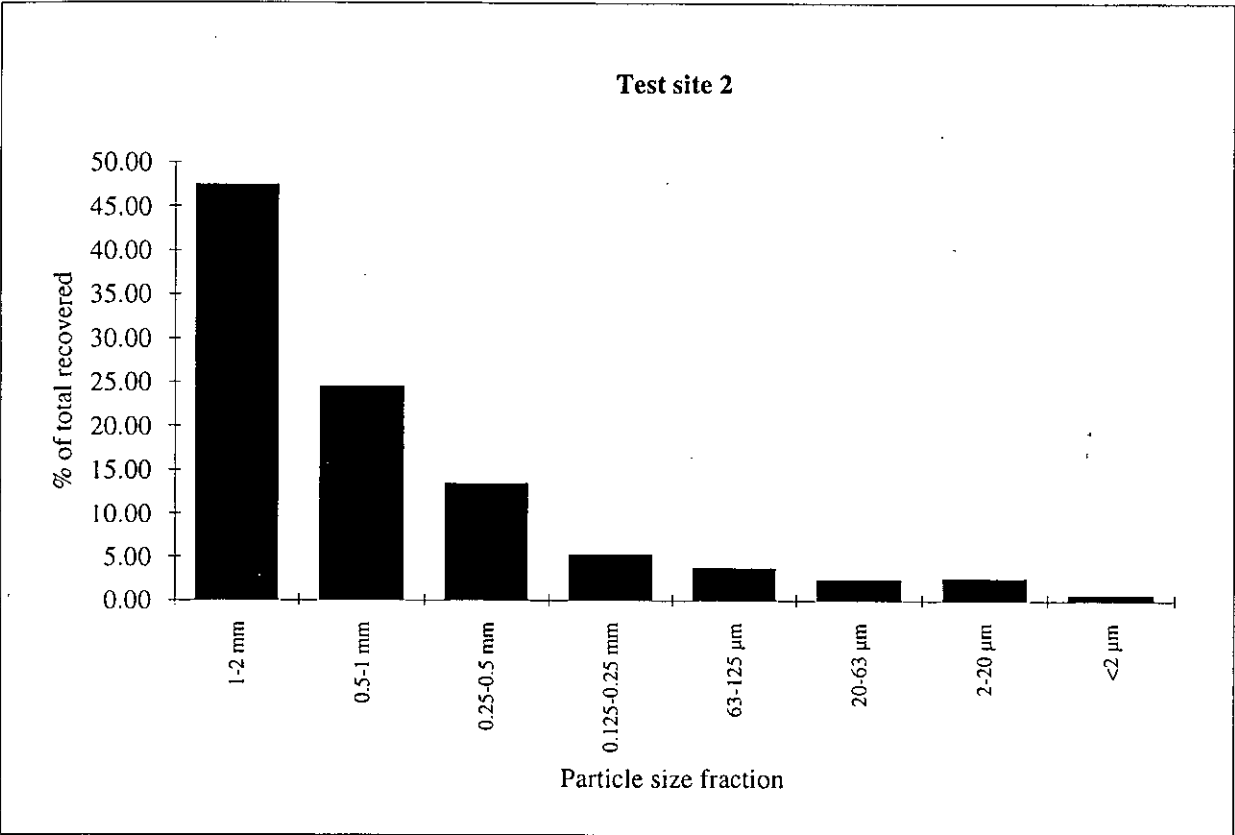
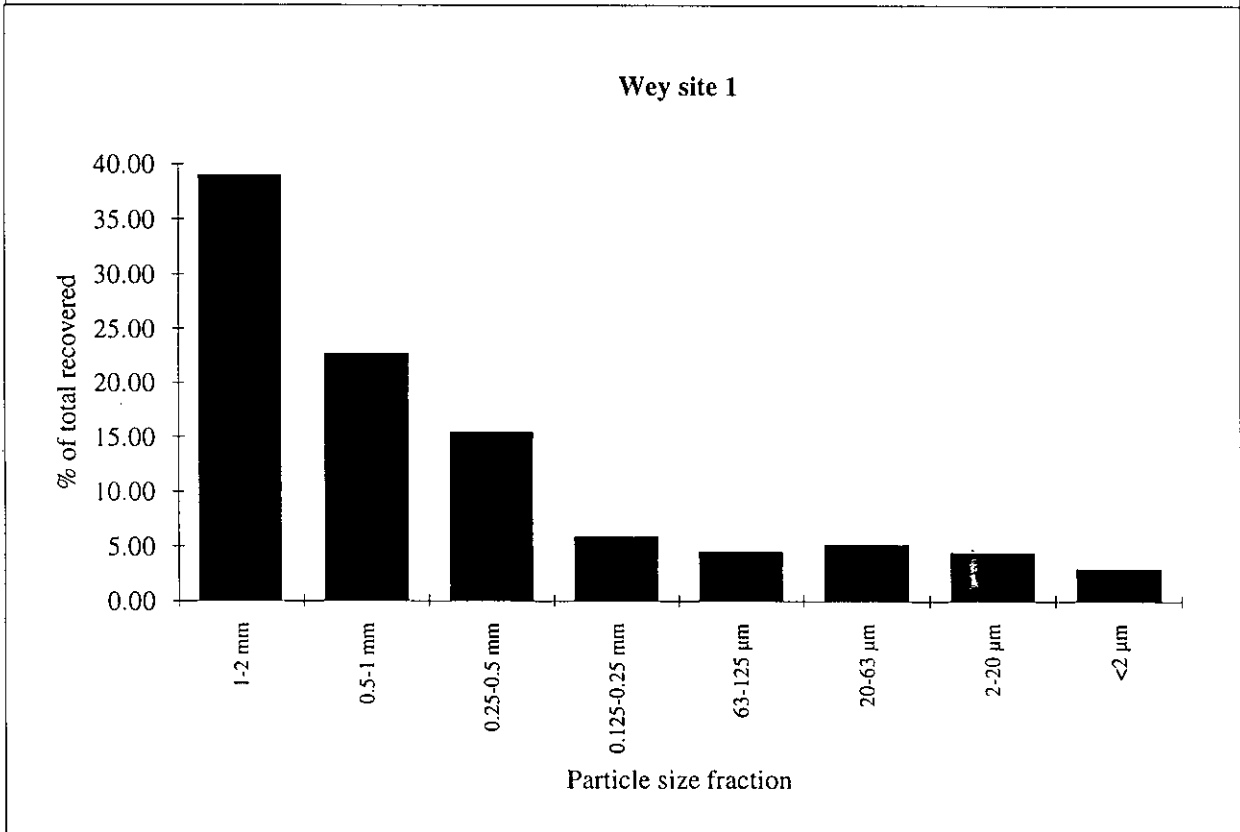
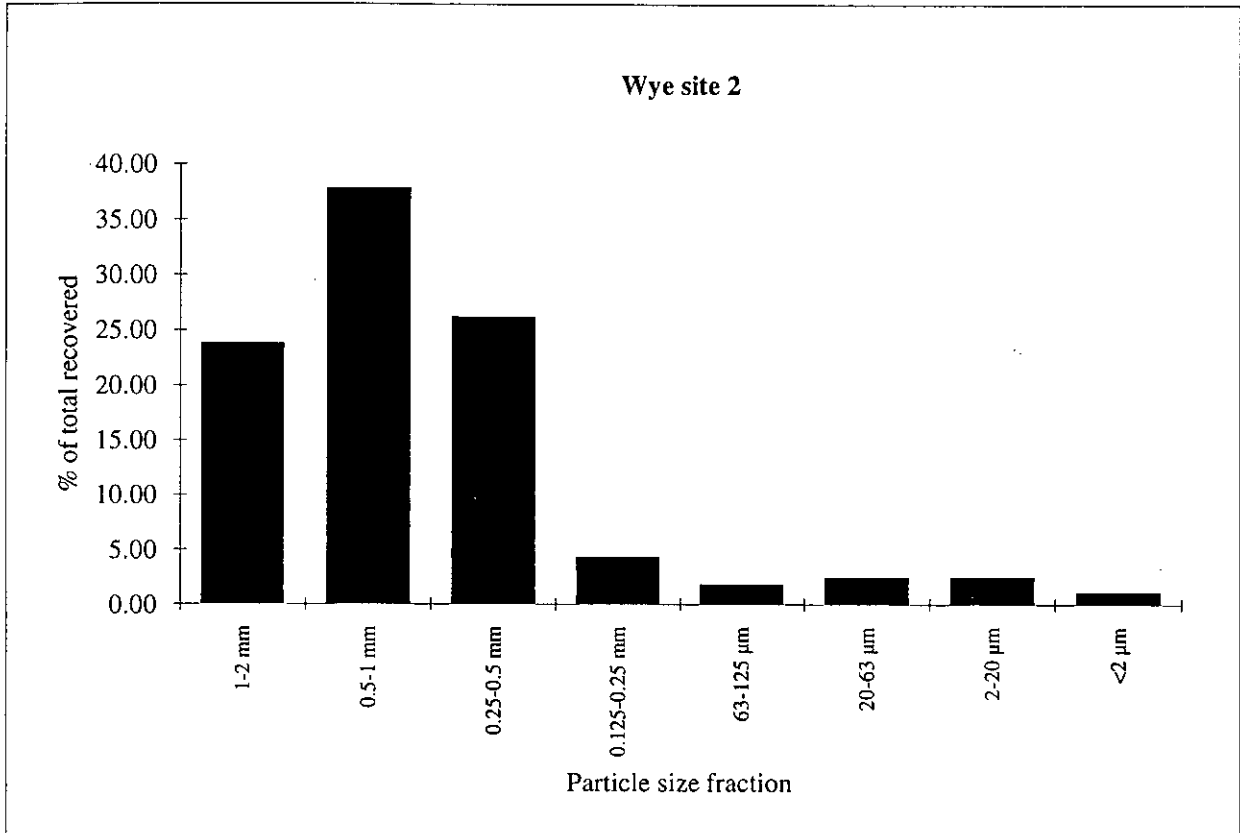


FIGURE 1.
Fluvarium channel for bed-sediment flux studies.

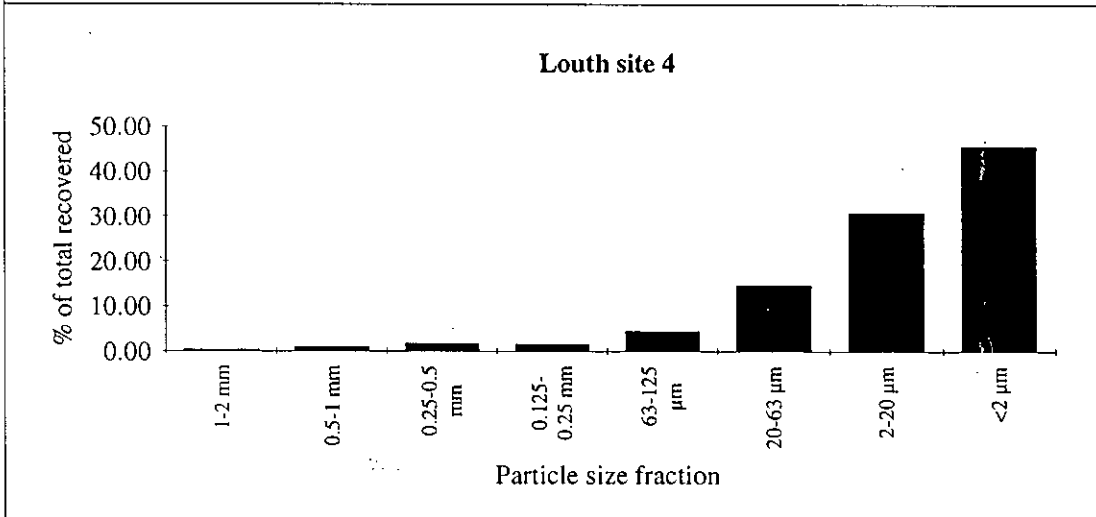
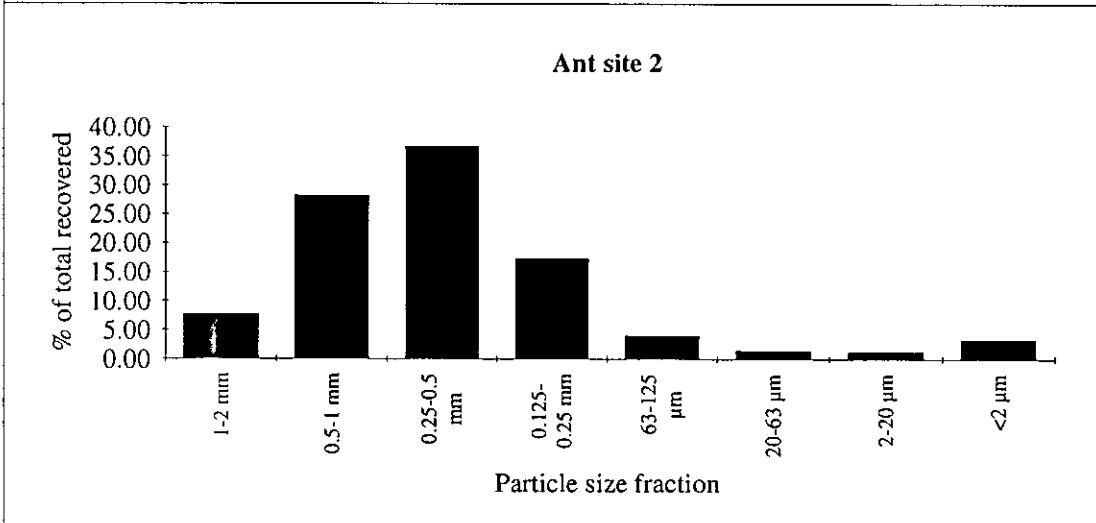
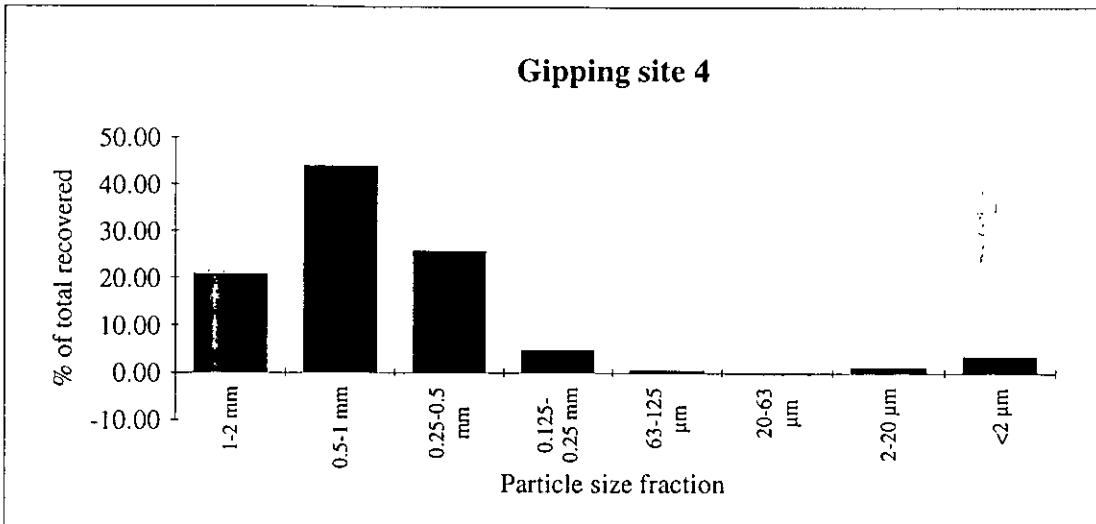
**PARTICLE SIZE DISTRIBUTION
OF PILOT STUDY SEDIMENTS**



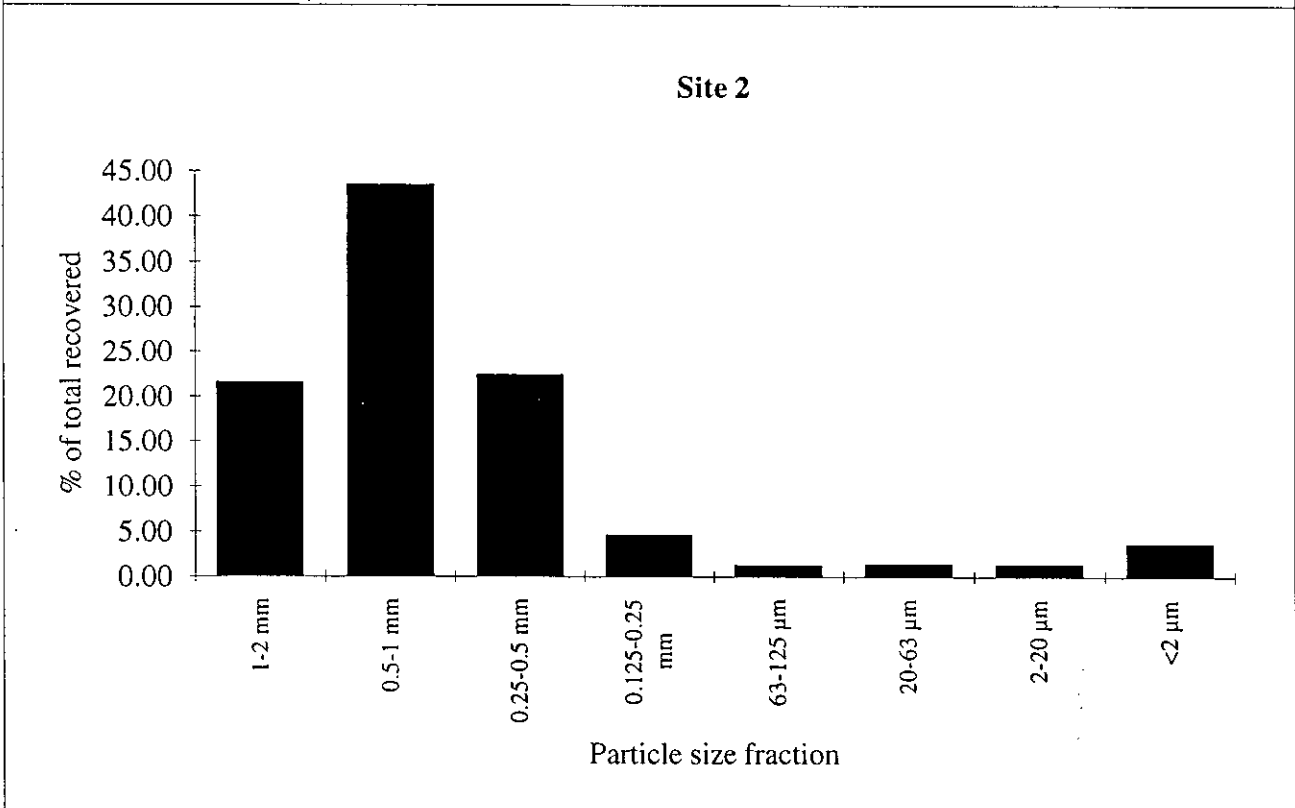
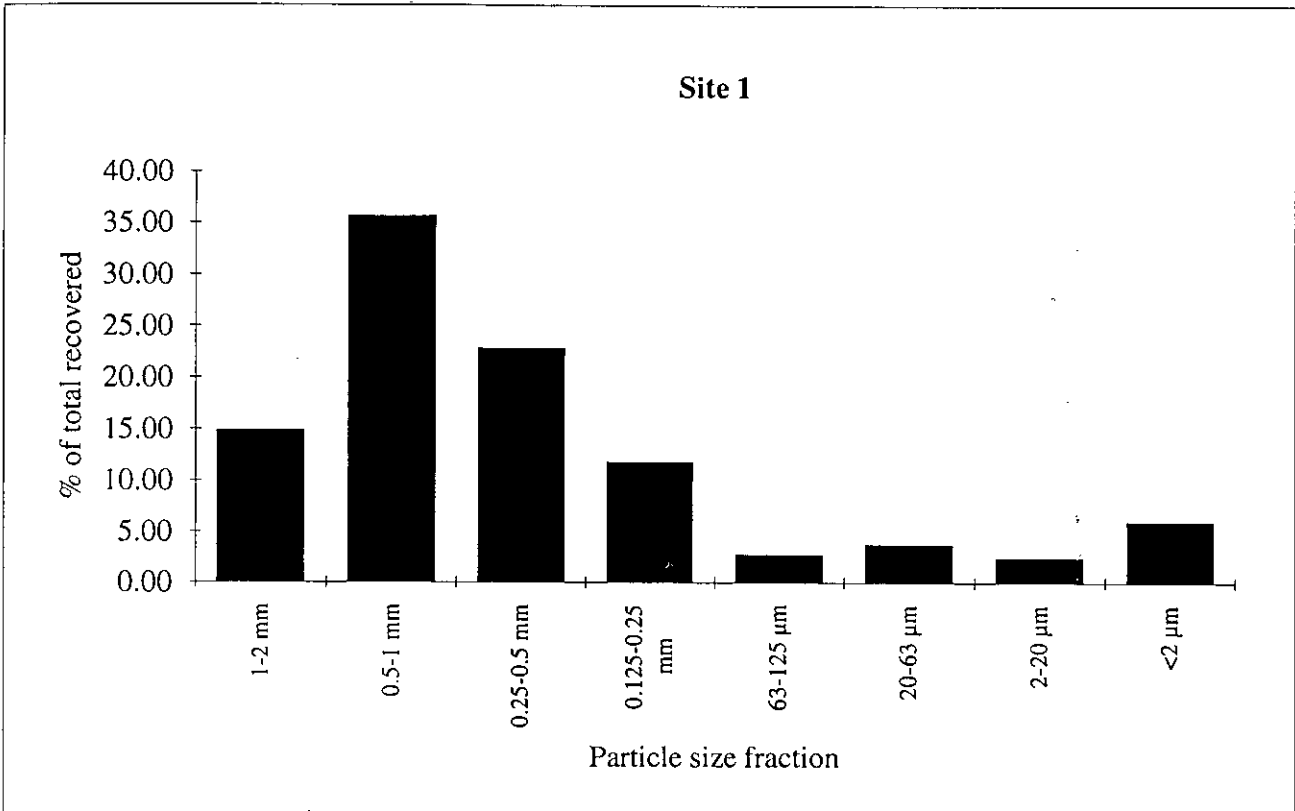
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APPENDIX 2

**PARTICLE SIZE DISTRIBUTION
OF GREAT OUSE SEDIMENTS**

