

The NRA Severn-Thames Transfer Project: An Assessment of the Effect of Mixing of Source Waters on the Chemical Composition

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1. Introduction

The Severn-Thames Transfer Project is designed to abstract peak-flow water from the lower catchment of the River Severn and transport it via a pipeline to the upper reaches of the River Thames thus providing extra water resources for the Thames region as required. As a part of the overall assessment of the feasibility of this scheme the potential capacity for changes in chemical composition to occur during transfer and mixing of these waters was investigated using both theoretical calculations on analytical data and also using laboratory experiments. The eventual objective of this work is to advise the National Rivers Authority on the methods of handling and storage to ensure that the two water samples are chemically compatible.

2. Assessment of Water Types

The first part of these preliminary studies comprised a detailed critical assessment of the chemical nature of the two types of water as determined using data from two sites provided by the NRA regions concerned; one at Haw Bridge on the Severn is close to the abstraction site and the other at Buscot on the Thames. This is complicated by the fact that, to a certain extent, the two NRA regions have slightly different monitoring priorities and for certain parameters corresponding data was not available for both sites.

2.1. Data

Data was supplied in the form of ASCII files on disk. Supplied data sets were as follows:

- 1. Mean daily flow for R. Thames at Buscot for the period November 1993 to October 1995.
- 2. Mean daily flow for R. Severn at Haw Bridge for the period October 1994 to February 1996.
- 3. Field and laboratory determinands for R. Thames at Buscot for the period January 1994 to January 1996.
- 4. Field and laboratory determinands for R. Severn at Haw Bridge for the period January 1995 to January 1996.
- 5. Field and laboratory determinands for R. Severn at Ashleworth for the period January 1995 to January 1996
- 6. Field and laboratory determinands for R. Severn at Chaceley Stock for the period June 1995 to January 1996.

In cases where sufficient determinands were measured to make an assessment, ion balances were generally very good (<10% difference between total cations and total anions). In many cases, however, there was insufficient data to assess ion balances, or to carry out chemical speciation modelling:

1) Prior to June 1995 no measurements were made of major cations or alkalinity in the R. Thames at Buscot.

2) Until June 1995 approximately 50% of samples from the R. Severn at Haw Bridge were not measured for major cations, sulphate, phosphate, nitrate and iron.

In addition:

3) Measurements of chloride were missing from several of the post-June 1995 samples from the R. Thames at Buscot. This led to significant ion imbalance. Since chloride was found to vary only slightly during the relevant period, a mean of measured values was used to replace missing values. This estimate significantly improved ion balances, and since chloride does not usually interact to any large degree with other aquatic species this should not lead to significant errors in the modelling results in WATEQ.

4) Only four measurements of alkalinity were made in the R. Severn at Haw Bridge, so estimates had to be made on measurements from the nearest upstream and downstream sites (Chalcey Stock and Ashleworth). It was found that alkalinity values at Ashleworth were very close to those at Haw Bridge, so the Ashleworth data were used in ion balance and chemical speciation calculations for Haw Bridge. Where sampling dates were not coincident between the two sites, estimates for alkalinity at Haw Bridge were made by linear extrapolation from the Ashleworth data.

Seasonal trends and flow rate dependence are shown in Appendix A

2.2 Interpretation

The chemical composition of both waters is generally similar which is to be expected of the two rivers since a significant proportion of the dissolved minerals must derived from adjoining areas, as the catchments drain either side of the Cotswold watershed. There are however several determinands where there are quite marked dissimilarites. The essential difference is that, though they are both hard waters, the R. Severn at Haw Bridge is a lowland river and the R. Thames at Buscot is an upland chalk water course. This gives rise to certain characteristic differences in the two sets of data determinands. These are:

(i) Flow rate

The flow rate of the River Severn is approximately one order of magnitude greater than that of the River Thames. Both sets of data, however, exhibit the same approximately inverse relationship between flow rate and the parameters principally associated with water hardness, namely calcium and alkalinity. This suggests that at high flow rates (e.g. in the River Severn) the main effect of the increased water is that of a dilutant. Since the primary objective of the Severn-Thames transfer project is to abstract excess water from the Severn at high flow rates this implies that when the source waters are mixed the differences in calcium and alkalinity between the incoming Seven water and the recieving harder Thames would be greatest. It is expected therefore that chemical changes during mixing would be most pronounced during such episodes. Seasonal changes in flow rates are, as expected, broadly similar for the two sites, but relative decrease during the summer is greater in the R. Thames than in the River Severn. (ii) Suspended solids

The water from the R. Severn at Haw Bridge has significantly more suspended solids than the water from the R. Thames at Buscot which is relatively free of suspended material. Turbidity was measured in the R. Severn, but not in the R. Thames and it is not possible to estimate the proportion of suspended matter in colloidal form. An important question is whether the suspended material from the R. Severn, if not subject to settling processes when introduced, is demineralised or could desorb species of potential harm to the Thames ecology.

(iii) Relative hardness, dilution, conductivity, pH, temperature.

The water in the R. Thames is considerably harder than that from the R. Severn. This is borne out by the higher concentrations of calcium and alkalinity as mentioned previously. This was reinforced by the by the higher conductivity of the R. Thames sample recieved for mixing experiments which also had a pH closer to the theoretical level of pure saturated $CaCO_3$ in equilibrium with air of 8.3 when measured in the laboratory. The pH of the water in the NRA's data were otherwise broadly similar for the two rivers as was the temperature. The relatively lower level of the hard water ions in the R. Severn at Haw Bridge, though both rivers are saturated with calcite, is presumably the result of dilution and/or nucleation of mineral phases that could be more likely in a slow flowing lowland river than occurs in a chalk stream.

(iv) Other Ions.

A noticeable difference between the two waters was that although the water from the R. Thames is harder than that of the R. Severn, the concentration of the principal ions other than calcium and bicarbonate, i.e. magnesium and sulphate are noticiably higher in the R. Severn. The reason this should be so is unclear. For the other major anions there appears to be little difference in the levels of the 'soft water' ions sodium, potassium and chloride, nor for the nutrients phosphate or nitrite. Silicate and nitrate concentrations are slightly lower in the R. Severn, presumably as a result of dilution from the higher flow in that river, as observed for alkalinity and calcium. Concentration of other ions appears similar for both rivers.

(v) Biological Oxygen Demand and Dissolved Oxygen

There appears to be a significant increase in BOD in the R. Severn in the spring which is not reflected in the R. Thames data. This is possibly a sympton of increased biological activity in the Severn during this period but similarly depth may play a factor; in a slow flowing deep river like the Severn at Haw Bridge with higher levels of suspended material and organic carbon, BOD could be expected to vary to extent with sampling depth and sampled surface water may not be representative as a whole. Samples from the Thames at Buscot would not have this problem as the river is shallow enough so that water taken from the surface would represent the main bulk of the river.

(vi) Pesticides, PCB's and anionic detergents.

The levels of these man-made organic chemicals in the two waters are broadly similar. The levels of most pesticides is generally less than the EU maximum permissable limit of 0.5 μ g/l bulk pesticide and 0.1 μ g/l for any particular pesticide. The highest concentrations are

simazine (and for the Thames isoproturon - though this isn't measured in the R. Severn). Many of these compounds have limited aqueous phase affinity and since the R. Severn at Haw Bridge contains considerably more suspended material than does the R. Thames at Buscot the amount transferred by may depend on the exact partition between solution and sediment and would therefore be affected by the amount of settling of suspended material before transfer.

It is clear that the chemical characteristics of both water types - although both composed of hard water has some significant differences. An assessment of the effect of mixing of these waters must primarily be concerned with whether concerted interactions take place between the components of each water (dissolved, sediment or suspended) or whether the concentrations of species in the resultant solution are simply a result of inert or conservative mixing and is determined solely by the relative proportion of each species in the contributing source waters.

3. Theoretical Calculations on the Effect of Mixing (WATEQ)

The chemical speciation program WATEQ was used to calculate ion balances and all major thermodynamic equilibria for a comprehensive range of chemical species, both in solution and mineral phases. The version of WATEQ used at the IFE River Laboratory has been set up specifically for calcareous river waters and determines the potential stability of over one hundred chemical entities in waters using thermodynamic data of equilibria from the literature which is regularly updated. Input species were Total calcium, magnesium, sodium, potassium, alkalinity (as bicarbonate), sulphate, chloride, nitrate, dissolved oxygen, silica, phosphate and ammonia. In some cases measurements of iron, fluoride, manganese, borate and aluminium were also available.

Of specific interest to this project are the relative stability of the principal agents in hard water chemistry, carbon dioxide partial pressure (ρCO_2), Ca^{2+} & HCO_3^{-} concentrations, and the saturation index of calcite. Also important is the solubility of minerals involved in regulation of nutrients including phosphate minerals such as hydroxyapatite. Trace metals and trace organics such as pesticides are usually involved in surface processes on other minerals and therefore the stability of the bulk phases predicted by WATEQ cannot be easily applied to these minor components.

Samples were rejected as inputs to WATEQ if the main input species (calcium, magnesium, sodium, potassium, alkalinity (as bicarbonate), sulphate, chloride, nitrate, dissolved oxygen and silica had not been measured and if the ion balance was not within the range $\pm 10\%$. Thus model runs could only be carried out for Thames samples or for theoretical mixtures of R. Thames and R. Severn water for the period June 1995 to December 1995. Sufficient data was available from the R. Severn measurements to carry out runs covering the full study period January 1995 to December 1995. For both rivers, both the frequency of sampling and number of determinands measured noticeably increased after June 1995.

Theoretical mixing of the two waters was carried out by matching samples from the two rivers by date - in all cases the difference in sample dates were less than one week. This gave seven pairs of samples from the two rivers covering the period June 1995 to December 1995. Model runs were carried out at each of the paired sample dates at the following ratios: 1 part Severn water to 0.5 part Thames water, 1:1, 1:5 and 1:10.

The results of this are shown in Appendix B. The parent waters are generally saturated with the calcium or calcium/magnesium-containing minerals calcite, dolomite (carbonates) and the phosphate mineral hydroxyapatite. This is to expected with hard-water rivers such as the R. Severn and R. Thames; the values for the saturation of these minerals on mixing is in all cases intermediate between the that of the two rivers and since the saturation of the R. Thames in these minerals is usually larger, introducing Severn water should not have much effect on stimulating the precipitation of these minerals. WATEQ also shows that both rivers and consequently their mixtures are always in excess of CO₂ with respect to the atmosphere and that mixing calculations give values between the two waters as expected. The transfer of water between rivers in a pipeline where there will be limited access to atmospheric CO₂ may cause this imbalance to become more extreme. The other two graphs of Appendix B show that the common iron minerals haematite and pyrite are both highly supersaturated which is to be expected in the pH region 7.5-8.5 for an oxygen-rich environment and consequently virtually all iron in the system will be in insoluble form.

4. Mixing Experiments.

4.1 Experimental Methods

Chemical changes which occur on mixing of water from the two sites (Haw Bridge and Buscot) were investigated in a series of experiments at 20°C. This temperature was chosen as a temperature which could be encountered in river systems in which kinetics would be most stimulated thus providing a 'worst case scenario' for chemical changes. Samples were mixed in the following proportions, Severn:Thames - 1:0.5, 1:1, 1:5, 1:10 so as to provide a total volume of 0.6 dm⁻³.

For each ratio the conductivity and pH of the unfiltered stirred mixture was determined at hourly intervals from 0 to 8 hours. An aliquot was then taken and filtered for analysis of major ions and metals and the stirred mixture was left at 20°C for a further 10 hours representing the transfer time of the Severn-Thames pipeline, before the remainder was filtered and analysed in the same way as for the preceding aliquot. The solutions were analysed for the following

(i) Major Ions & Nutrients: Sodium, magnesium, potassium, calcium, iron, alkalinity, chloride, sulphate, nitrate, soluble reactive phosphate and silica. These are given in Table 1, (Appendix C) to $\pm 0.01 \text{ mg dm}^{-3}$, except for calcium ($\pm 0.1 \text{ mg dm}^{-3}$) and soluble reactive phosphate ($\pm 0.001 \text{ mg dm}^{-3}$). Iron was not detected above it minimum detectable limit of 0.02mg dm⁻³.

(ii) Trace Metals: lithium, magnesium, aluminium, calcium, titanium, vanadium, chromium, manganese, nickel, copper, zinc, strontium, molybdenum, cadmium and barium. These were determined by ICP-MS to a precision of approximately $\pm 1 \ \mu g \ dm^{-3}$ and are given in Table 2, (Appendix C). Lead was not detected at levels above $1 \ \mu g \ dm^{-3}$ in any sample.

The amount of any one chemical species that would be present during mixing, assuming no interaction, was also calculated using a mass balance. This was compared with the actual concentration for each chemical species and are given in Appendix C in diagrammatic form in terms of the percentage change.

WATEQ, was used to calculate the thermodynamically stable species in these solutions

from analytical chemical data and from the pH of the solution. Values for ρCO_2 and the saturation index (\log_{10} saturation) for calcite appeared to be principally dependant on the measured pH of the solution rather than on analytical determinands and since pH changed with time during the experiments it was not possible to deduce further information except that for all the principal soluble major ions the concentration was not dependant on other factors.

4.2 Interpretation

These experiments were performed on one sample from each river that were collected on the same day in March 1996. Therefore it is not possible to deduce any seasonal variability as was possible in section 3.2 and interpretation of this work must therefore be restricted simply to the chemical changes that occur occur when these two samples are mixed.

(a) pH, Conductivity

After mixing, a consistent pH change was observed with time. To enable direct comparison between mixing ratios this was converted to hydrogen activity, $a(H^+)$, since unlike pH this is a linear function. The change of $a(H^+)$ with time shows no obvious simple function with time other than a general downward trend but must be due to degassing of carbon dioxide as should be expected by the fact that all solutions possess a higher ρCO_2 value than atmospheric carbon dioxide. As was mentioned previously it is not clear whether degassing would occur during transfer of water from the R. Severn in the pipeline when exchange from the atmosphere would be limited.

(b) Major Ions

Three of the four metals that comprise the common cations in most waters, namely calcium, magnesium, sodium and potassium show conservative behaviour if the value of potassium in the 5:1 mixing ratio at 18 hours is discounted as unreliable - in that the measured concentrations are usually within $\pm 7\%$ of the value expected from the mass balance. The exception is sodium which shows a small increase in the mixed waters for all samples, and is presumably due to the need to maintain a balance of charge with released anions. WATEQ predicts that there should be little change concerning these mainly soluble species.

The change in anion concentrations, namely bicarbonate, chloride, sulphate, nitrate and phosphate show generally a higher level of scatter than that shown for cations but exhibit little discernable trend with the exception of alkalinity which is marginally increased after eighteen hours.

The expected changes in the soluble major ions as calculated by WATEQ were calculated. These are equilibrium values and in all cases show that changes in individual species are of the order of 3% or less. For the chemical species which are non-complexing and completely soluble such as chloride and nitrate this is to be expected. For the hard-water ions Ca^{2+} and HCO_3^- which are related to the solubility of calcite the amount of free ions should also remain fixed although the degree of saturation does not.

(c) Metals

Trace metals, unlike the major ions cannot be expected necessarily to form discrete phases, but are likely to be either soluble or distributed as minor components absorbed or contained in other materials. For these mixing experiments the relative changes in metal concentrations can be divided into the following groups and rationalised as follows:-

(i) Lithium, strontium, barium, titanium and chromium

These metals showed little change on mixing. They are all relatively redox stable in aqueous solution and at pH 7.5-8.5 are not subject to solution reactions which can alter the solubility of metal ions.

(ii) Aluminium and zinc

Aluminium and zinc are the two most common redox stable amphoteric metals. The Pourbaix diagrams (oxidation potential-pH plots) for these two metals are reproduced (copyright CRC press^{*}) in Appendix C. This shows that at the pH of interest (7.5-8.5) for both metals the stable phases are an insoluble one (oxide or hydroxide) in equilibrium with a soluble one. The role of organic complexing material on these equilibria is not however considered in these experiments and may be significant for aluminium.

(iii) Copper, nickel and vanadium.

These three metals all showed a definate increase when waters were mixed, markedly so for copper. It is interesting that the normal air-stable oxidation states for these three metals - Cu(II), Ni(II) and V(IV) are all mid-to-late transition metals with crystal field stabilisation energy and a preference for tetragonal/octahedral coordination. This suggests that these metals could be released by similar mechanisms but on the basis of one set of samples this cannot be conclusive.

(iv) Manganese, cadmium and molybdenum

These three metals all included determinations for the mixing experiments where the amount present was less than the lower limit of 1µmol dm⁻³. Therefore, although they appear to show fairly large changes with mixing in some cases it is not possible to discern whether changes are consistent. This is the reason why in Appendix C they are given as unshaded figures.

5 Conclusions

Changes in the chemistry of these waters during mixing are generally small for the major ions and this is predicted from theoretical calculations from WATEQ. For trace metals the effects appear to be greater for certain elements, noticeable for the amphoteric metals Al/Zn and for later transition metals Cu/Ni/V. It must be emphasised that these results only pertain to one set of mixing. One shortcoming of WATEQ in theoretical calculations for mixing experiments is that pH must be entered as a separate determinand - in other cases it can be measured - and a compromise value was used for these calculations. It is possible however to develop from first principles (mass balance, charge balance and equilibrium constants) a scheme to calculate pH values during mixing from total calcium and alkalinity in the mixed sample - neither of which appear to vary significantly with mixing - and this may improve further the utility of WATEQ in modelling such a system.

To summarise, the chemical changes which occur are either predicted by WATEQ to a fairly good degree or - for some of the metals - they can be rationalised from a knowledge of their inorganic chemistry. This work has looked at mixing of waters direct from the river and so the effect of storage of incoming waters before addition to the R. Thames - a postulated part of the Severn-Thames transfer project remains an unknown quantity.

Table 1 Major Ion Concentrations

(a) Cations

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Sample	Time /hr	Calcium /mg l ⁻¹	Magnesium /mg l ⁻¹	Sodium /mg l ⁻¹	Potassium /mg l ⁻¹
Unmixed Severn Water		68.5	12.1	28.2	3.78
Unmixed Thames Water		122	5,08	22.2	3.38
Severn/Thames 0.5:1	8	88.0	10.3	28.5	4.00
Severn/Thames 0.5:1	18	94.0	10.5	30.8	4.10
Severn/Thames 1 :1	8	97.8	8.73	27.4	3,75
Severn/Thames 1 :1	18	103	9.30	29.0	3.88
Severn/Thames 1 :5	8	113	6.23	25.4	3.53
Severn/Thames 1 :5	18	119	6.11	26.6	2.32
Severn/Thames 1 :10	8	117	5.47	24.0	3.75
Severn/Thames 1 :10	18	117	5.40	24.1	3.69

(b) Cations

Sample	Time /hr	Alkalinity /meg 1 ⁻¹	Chloride /mg l ⁻¹	Sulphate /mg l ⁻¹
	. /111	·	0	•
Unmixed Severn Water		2.22	54.6	61.0
Unmixed Thames Water		4.38	37.6	49.7
Severn/Thames 0.5:1	8	2.97	39.0	64.4
Severn/Thames 0.5:1	18	3.16	48.2	68.2
Severn/Thames 1 :1	8	3.30	42.2	58.6
Severn/Thames 1 :1	18	3.47	46.8	55.7
Severn/Thames 1 :5	8	4.06	33.0	55.7
Severn/Thames 1 :5	18	4.25	42.6	59.6
Severn/Thames 1 :10	8	4.22	37.6	55.7
Severn/Thames 1 :10	18	4.25	48.6	49.0

Sample	Time	Nitrate N	Phosphate P	Silica
	/hr	/mg 1 ⁻¹	/µg 1 ⁻¹	/mg 1 ⁻¹
Unmixed Severn Water		8.03	359	2.43
Unmixed Thames Water		9.90	420	1.97
Severn/Thames 0.5:1	8	8.61	365	2.26
Severn/Thames 0.5:1	18	7.50	382	2.45
Severn/Thames 1 :1	8	8.80	394	2.19
Severn/Thames 1 :1	18	9.70	402	2.37
Severn/Thames 1 :5	8	10.0	401	2.00
Severn/Thames 1 :5	18	10.2	390	2.13
Severn/Thames 1 :10	8	9.70	412	2.79
Severn/Thames 1 :10	18	8.65	408	2.00

Table 2 Metal Concentrations

Sample	Time /hr	Lithium /µg l ⁻¹	Aluminium /µg l ⁻¹	Titanium /µg l ⁻¹	Vanadium /µg I ⁻¹
Unmixed Severn Water		7,49	20.1	3.67	3.71
Unmixed Thames Water		4.93	11.5	4.21	5.11
Severn/Thames 0.5:1	8	6.50	7.86	3.33	4.35
Severn/Thames 0.5:1	18	7.58	8.09	3.49	4.82
Severn/Thames 1 :1	8	6.25	9.81	3.95	5.21
Severn/Thames 1 :1	18	6.28	8.98	3.44	5.43
Severn/Thames 1 :5	8	5.33	8.79	3.76	5.49
Severn/Thames 1 :5	18	5.66	11.1	4.09	5.15
Severn/Thames 1 :10	8	5.03	7.85	3.96	5.31
Severn/Thames 1 :10	18	5.00	10.2	4.09	5.01

Sample	Time /hr	Chromium /µg l ⁻¹	Manganese /µg I ^{.1}	Nickel /µg l ⁻¹	Copper /µg l ⁻¹
Unmixed Severn Water		22.1	2.06	7.49	3.56
Unmixed Thames Water		45.9	1.64	12.4	2.98
Severn/Thames 0.5:1	8	27.7	1.35	9.1	6.94
Severn/Thames 0.5:1	18	34.5	1.10	14.2	11.0
Severn/Thames 1 :1	8	35.1	1,68	11.2	4.31
Severn/Thames 1 :1	18	33.7	<1.0	10.8	3.94
Severn/Thames 1 :5	8	44.3	1.43	12.0	3.46
Severn/Thames 1 :5	18	41.8	<1.0	11.8	3.79
Severn/Thames 1 :10	8	46.2	1.35	14.1	5.01
Severn/Thames 1 :10	18	45.7	<1.0	14.4	4.40

Sample	Time	Zinc	Strontium	Molybdenum
	/hr	/µg l-1	/µg 1 ⁻¹	/µg 1 ⁻¹
Unmixed Severn Water		50.6	295	0.96
Unmixed Thames Water		40.1	365	<1.0
Severn/Thames 0.5:1	8	35.9	319	1.10
Severn/Thames 0.5:1	18	43.4	346	1.35
Severn/Thames 1 :1	8	41.0	340	<1.0
Severn/Thames 1 :1	18	44.4	336	<1.0
Severn/Thames 1 :5	8	31.9	359	<1.0
Severn/Thames 1 :5	18	31.3	373	<1.0
Severn/Thames 1 :10	8	35.9	363	1.53
Severn/Thames 1 :10	18	15.8	354	1.46

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Sample	Time	Cadmium	Barium	Lead
	/hr	/µg 1 ⁻¹	/µg l ⁻¹	/μg l ⁻¹
Unmixed Severn Water		<1.0	169	<1.0
Unmixed Thames Water		<1.0	122	<1.0
Severn/Thames 0.5:1	8	5.37	155	<1.0
Severn/Thames 0.5:1	18	18.73	184	<1.0
Severn/Thames 1 :1	8	1.06	136	<1.0
Severn/Thames 1 :1	18	<1.0	175	<1.0
Severn/Thames 1 :5	8	<1.0	128	<1.0
Severn/Thames 1 :5	18	<1.0	162	<1.0
Severn/Thames 1 :10	8	3.03	138	<1.0
Severn/Thames 1 :10	18	2.84	90.0	<1.0

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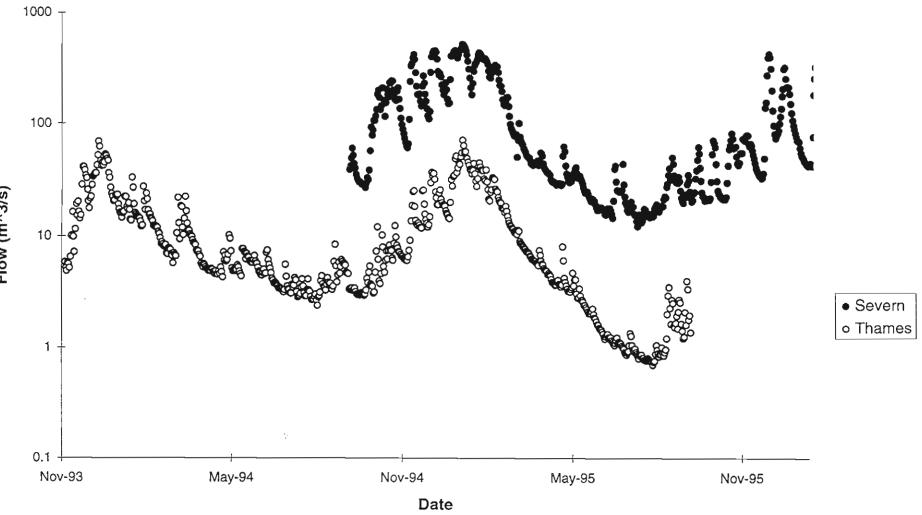
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Appendix A

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Source water - trends and differences



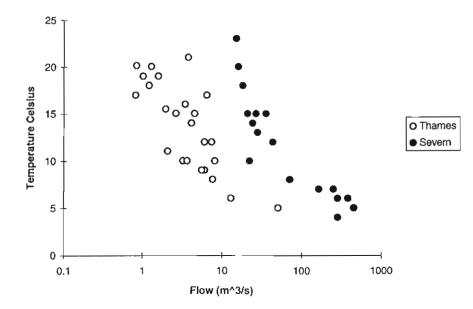
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Flow (m^3/s)

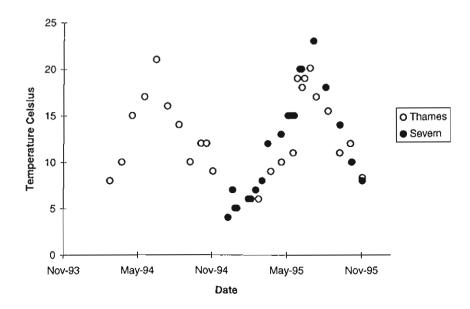
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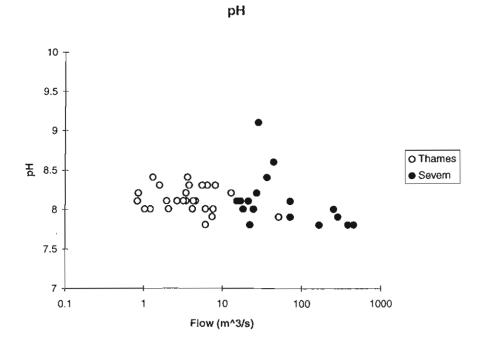
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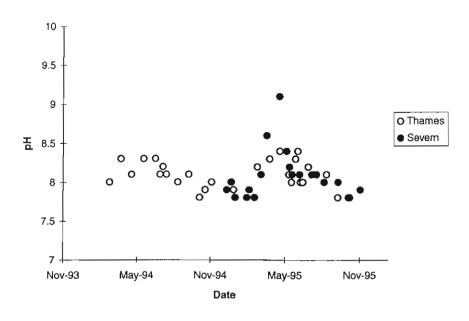


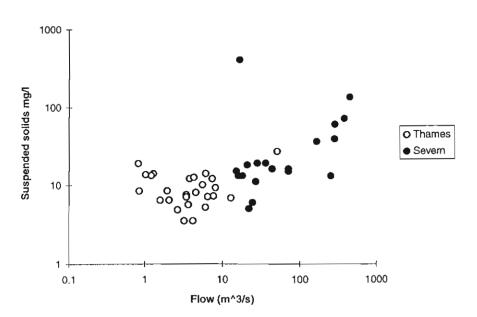
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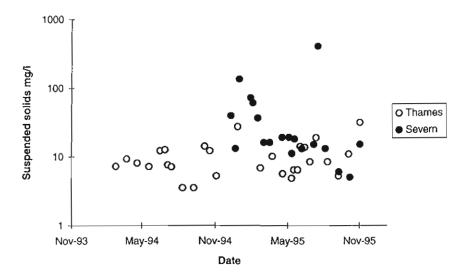


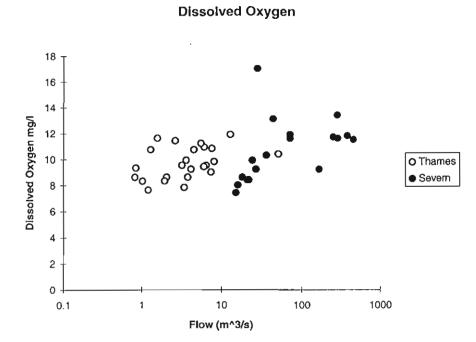
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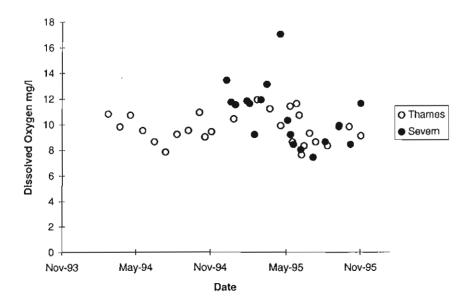
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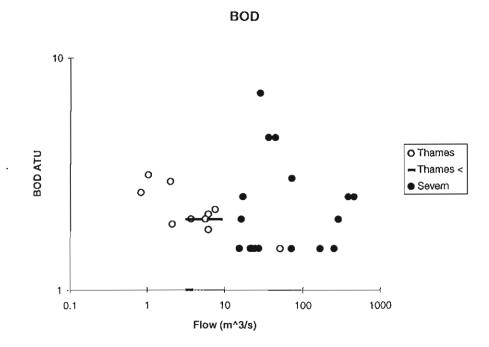
Suspended solids

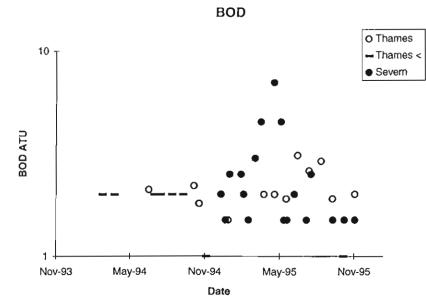


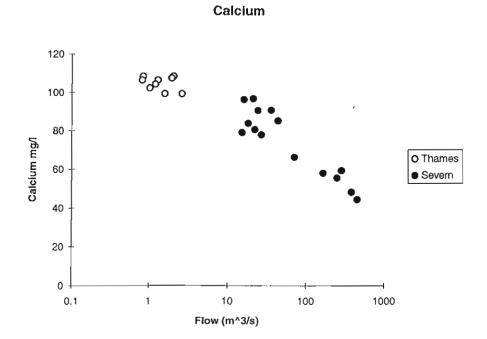


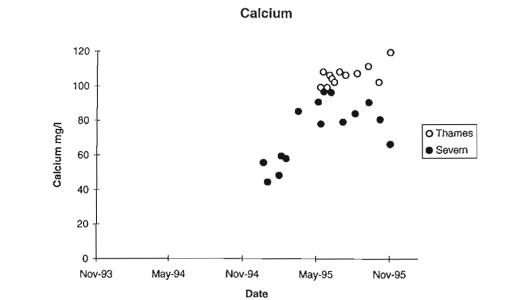
Dissolved Oxygen

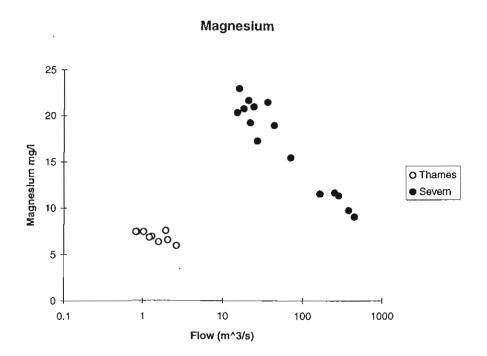


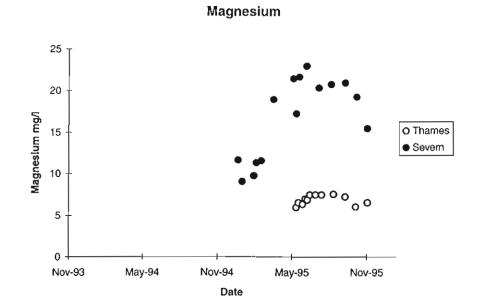


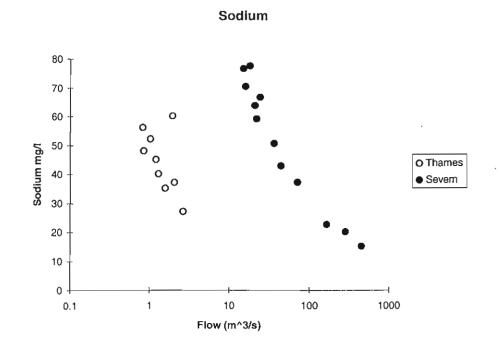




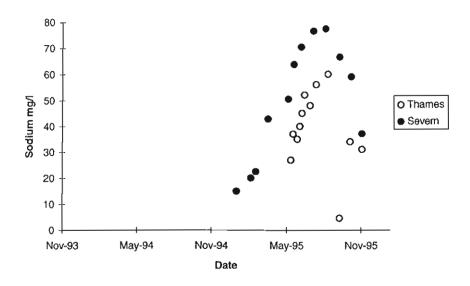


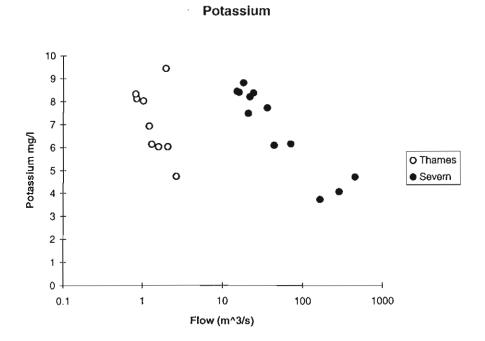


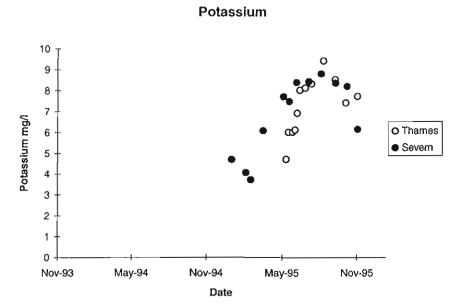




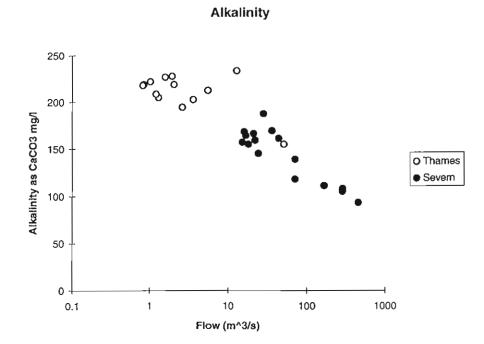








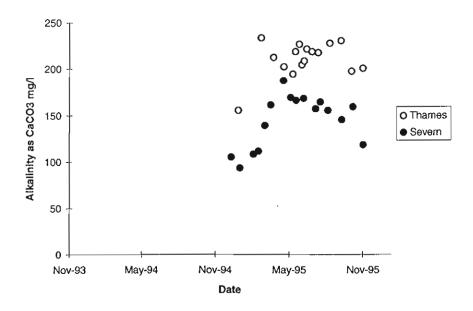
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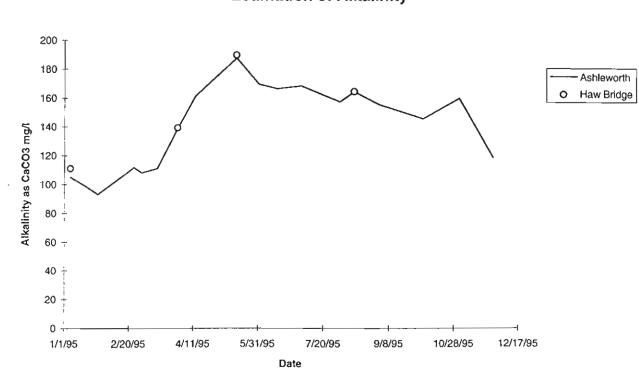


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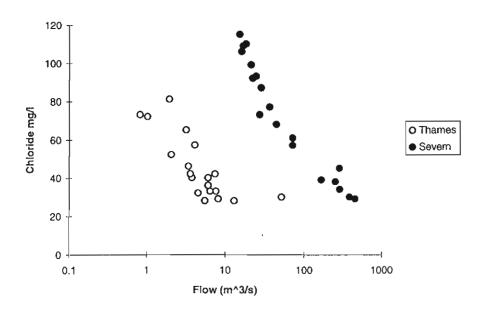
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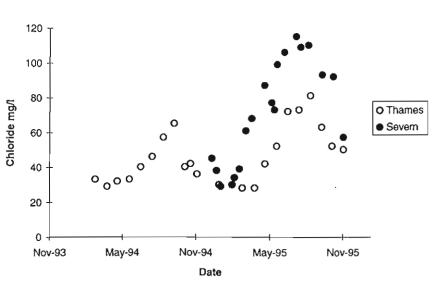




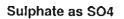
Estimation of Alkalinity

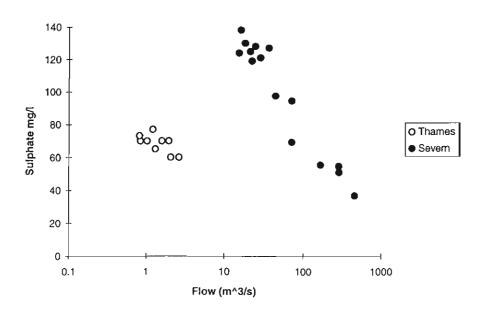


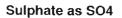


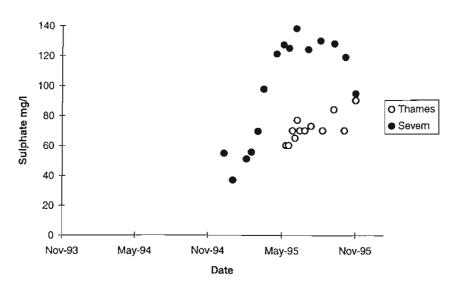


Chloride as CI

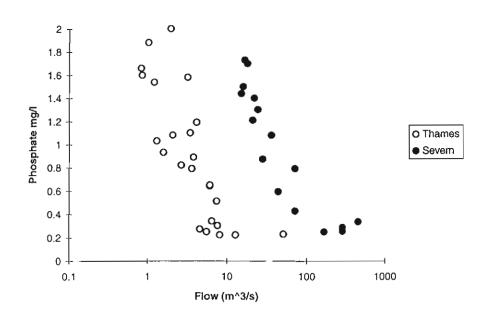


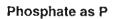


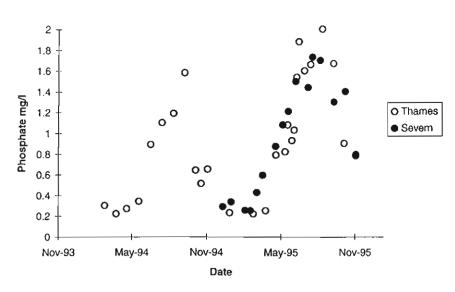


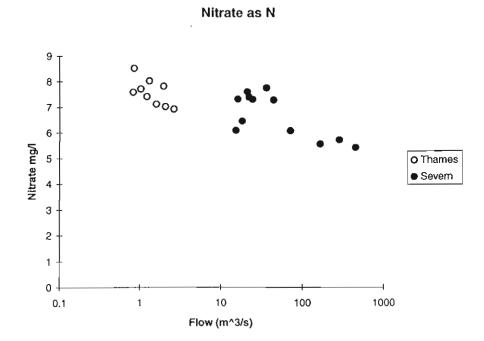










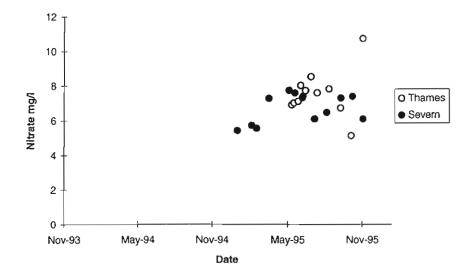


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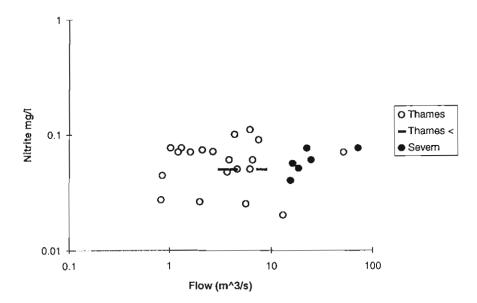
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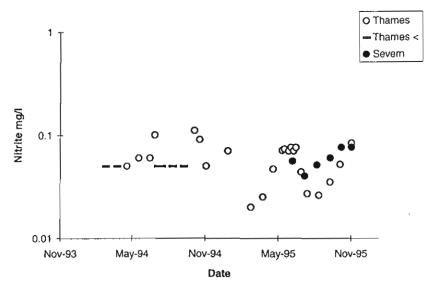
Nitrate as N

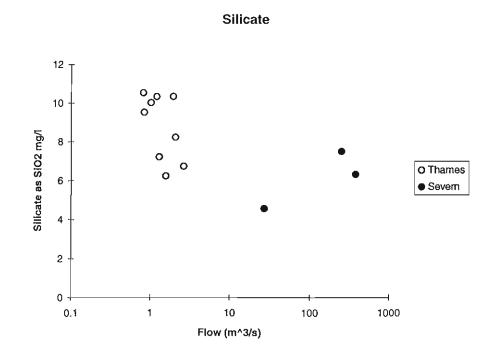




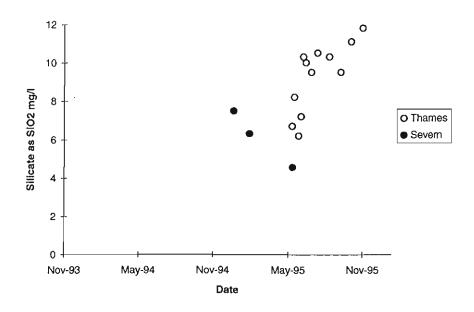


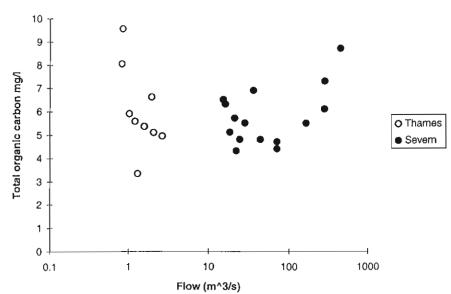
Nitrite as N





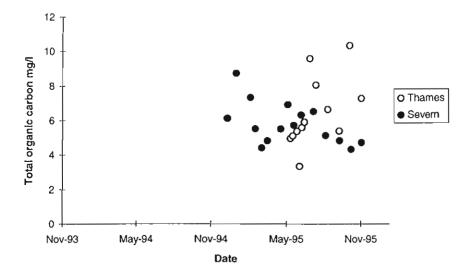






Total organic carbon

Total organic carbon

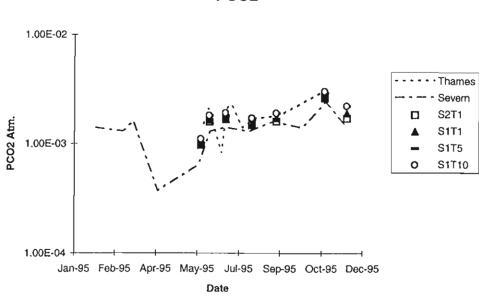


Appendix B

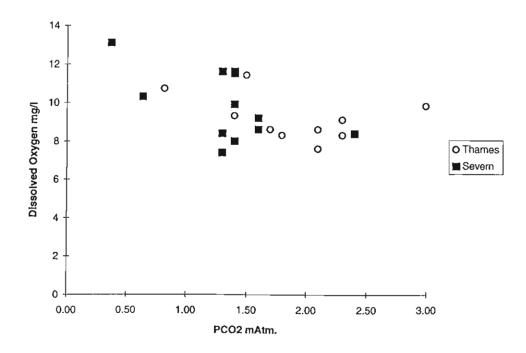
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Theoretical modelling of mixing

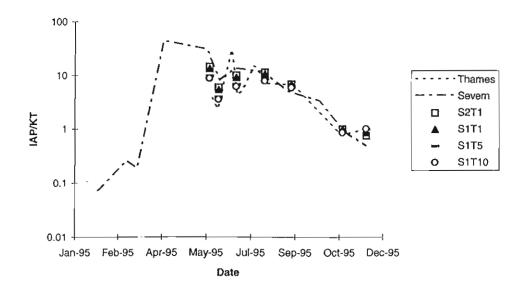


DO vs PCO2

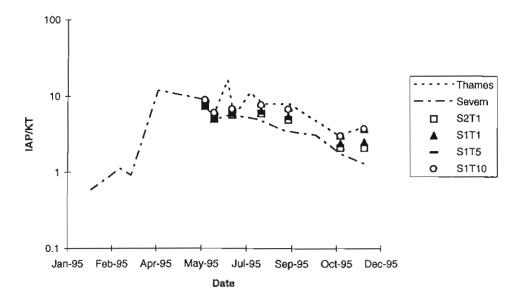


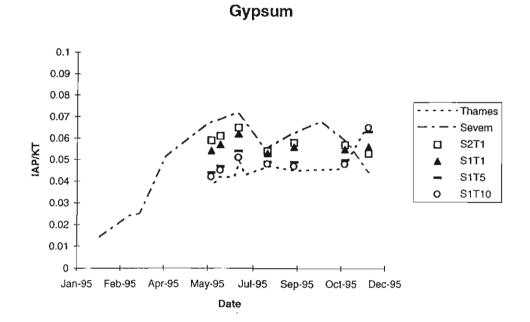
PCO2



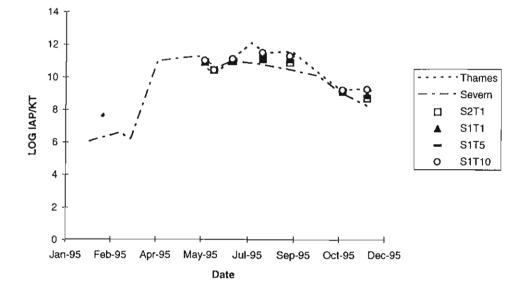


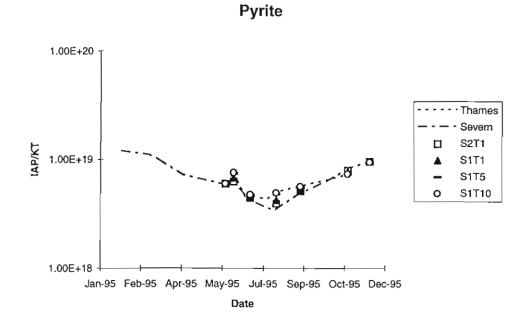
Calcite





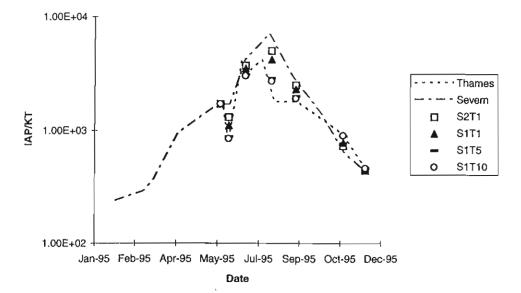
Hydroxylapatite





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Haematite



Appendix C

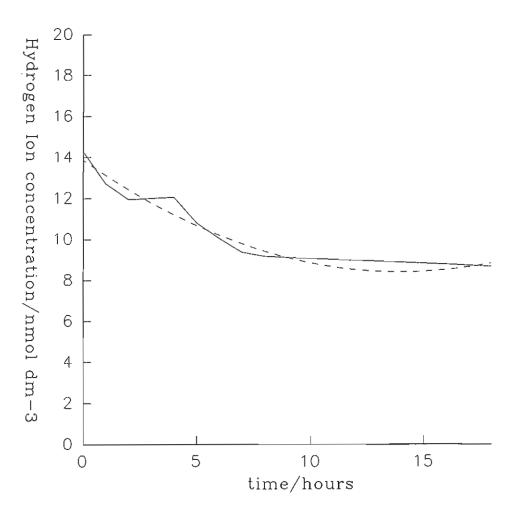
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Experimental mixing of source waters

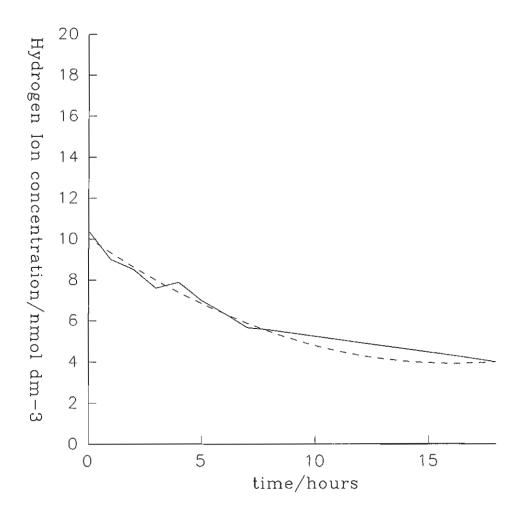


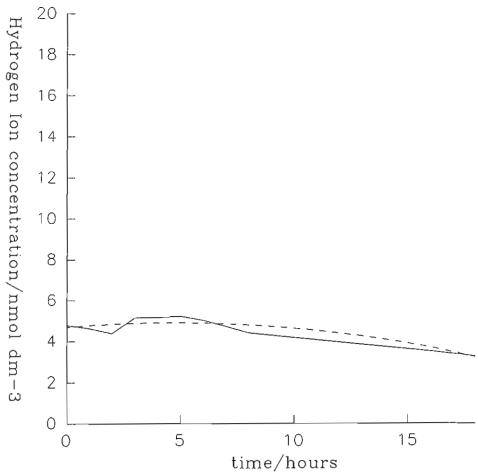
Severn/Thames 1:0.5

Severn/Thames 1:1

11

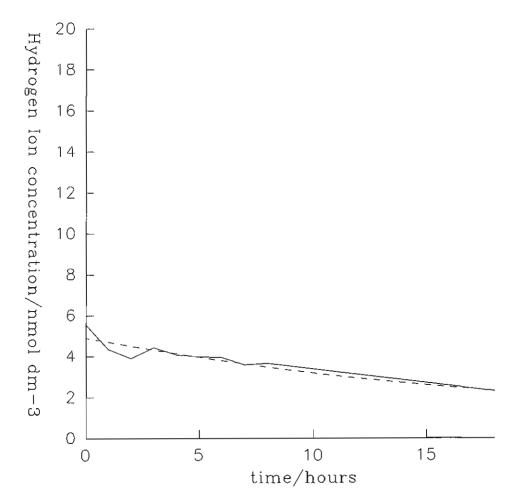
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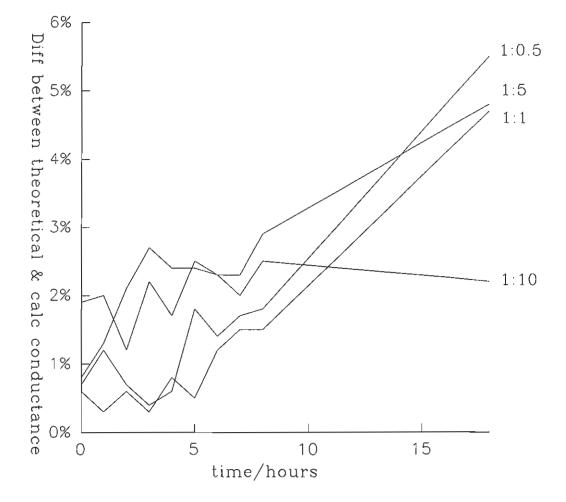
Severn/Thames 1:5

(



Severn/Thames 1:10

П

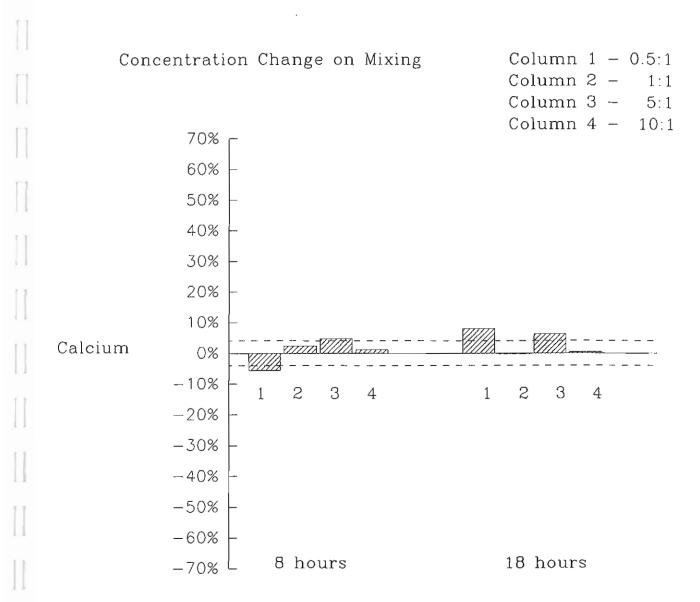


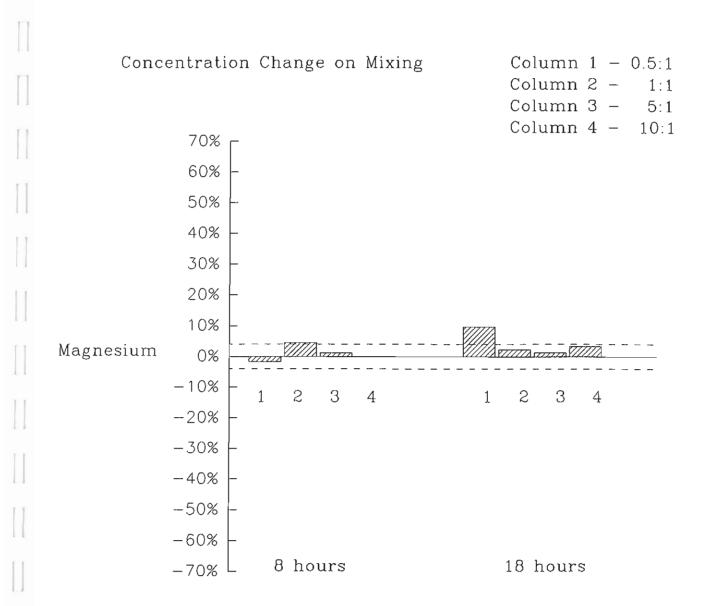
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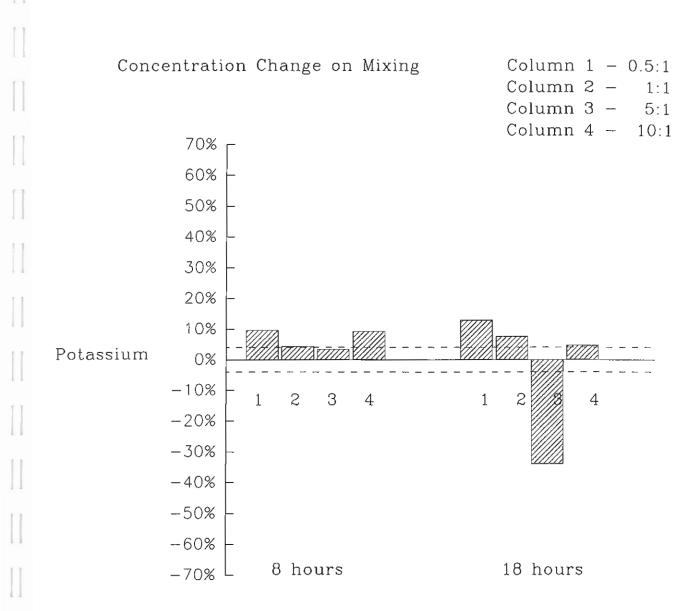
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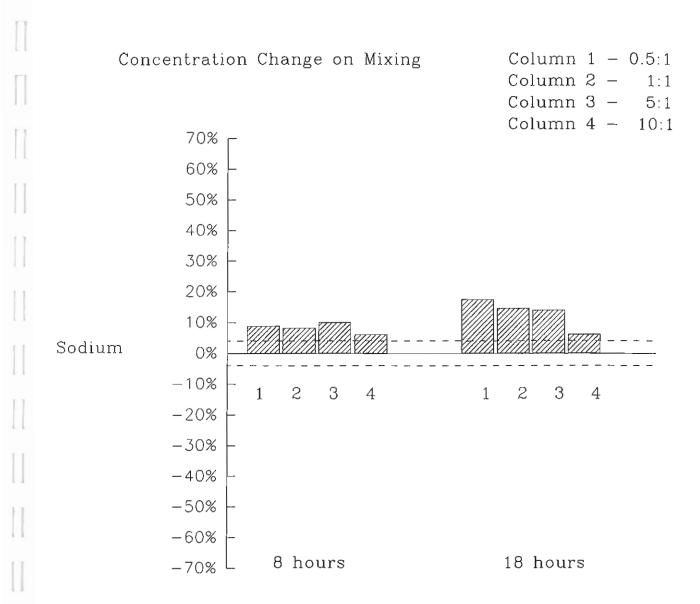
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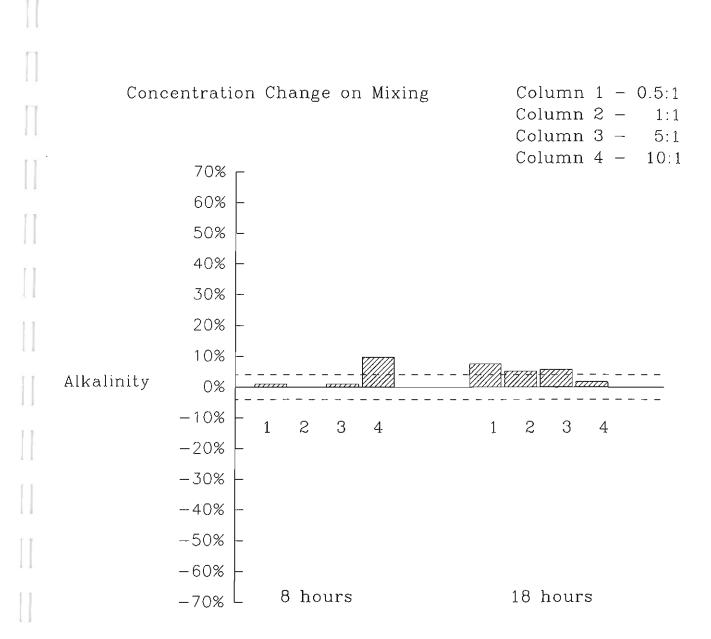
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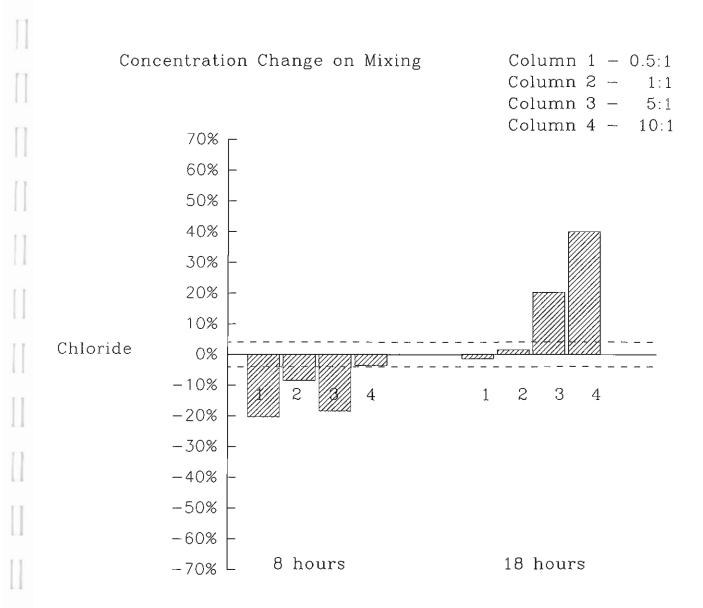


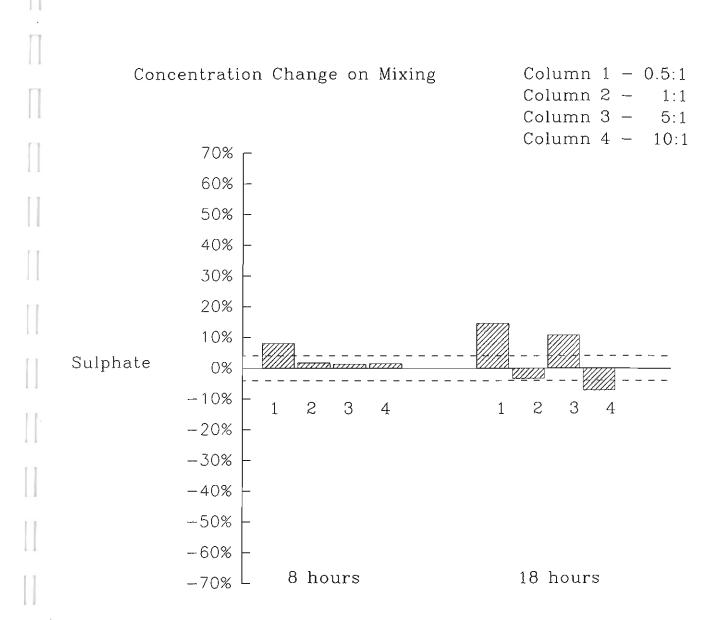


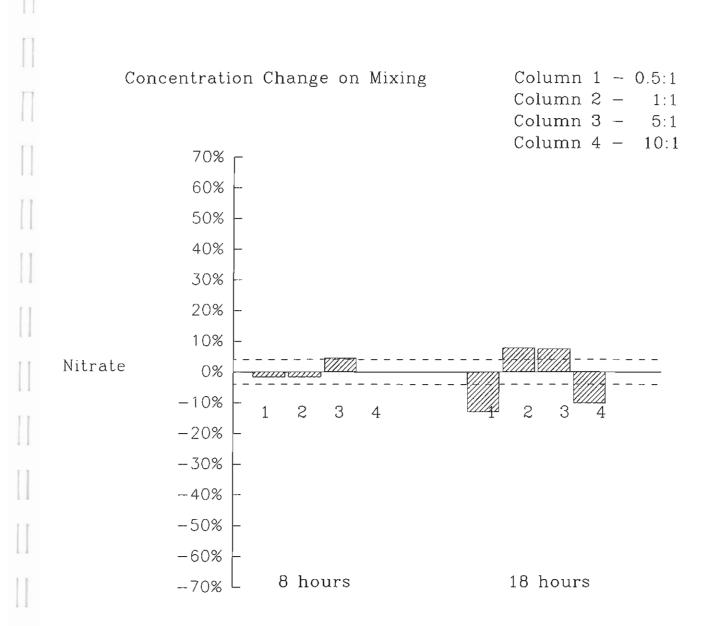




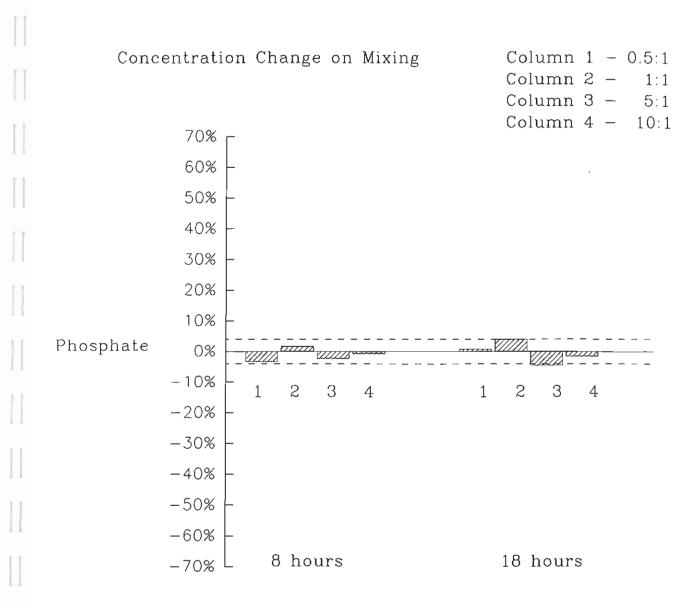


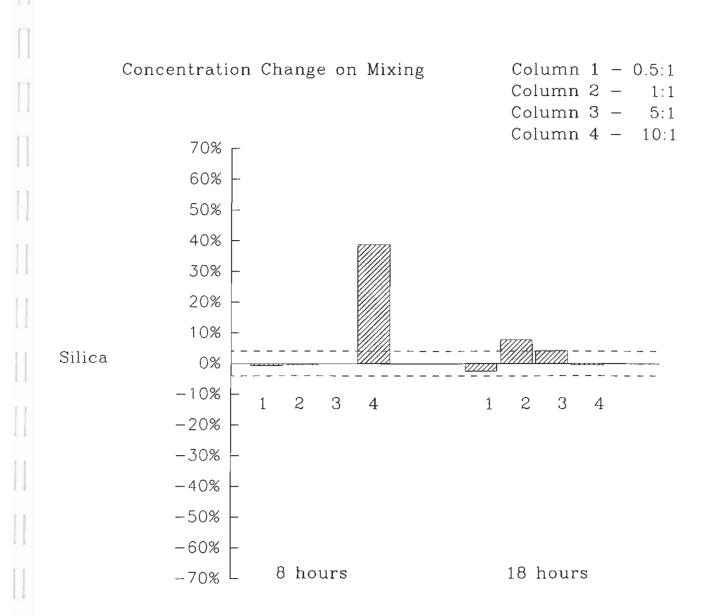


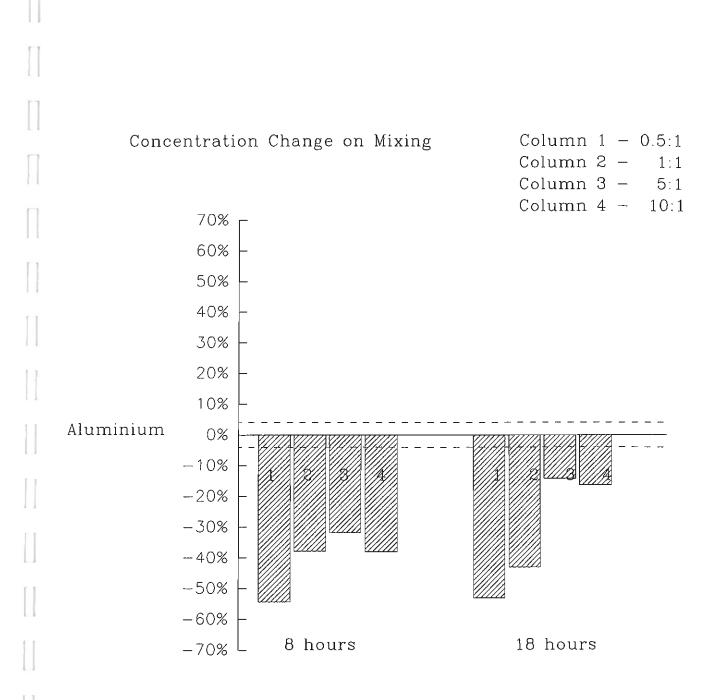


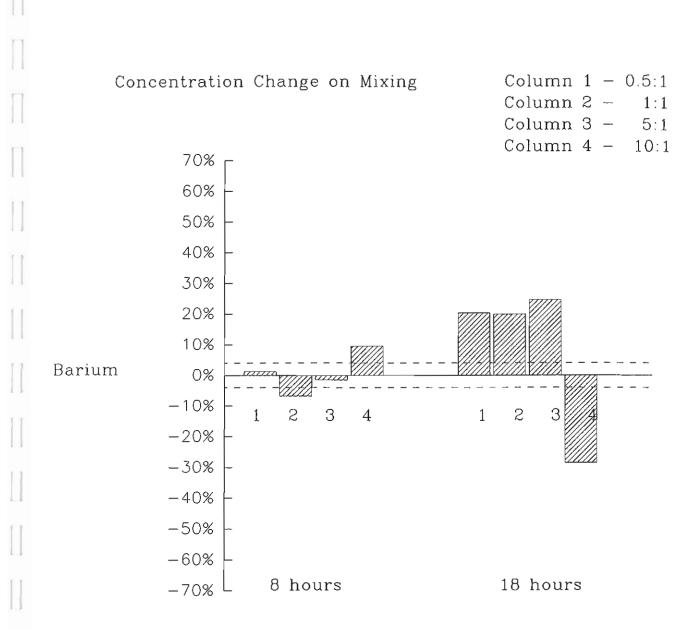


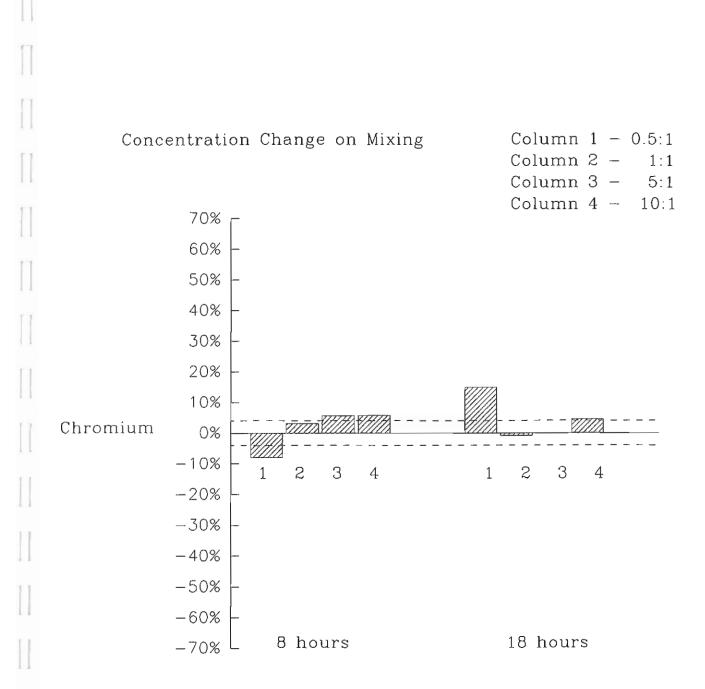
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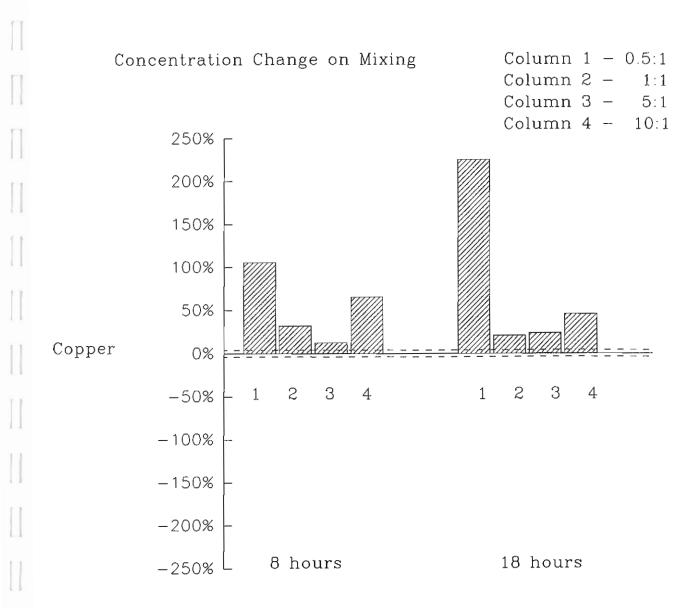


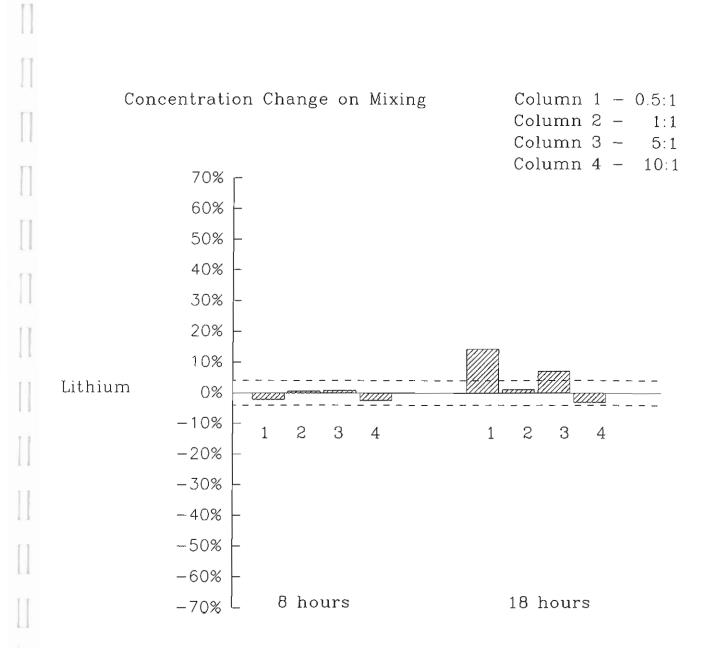


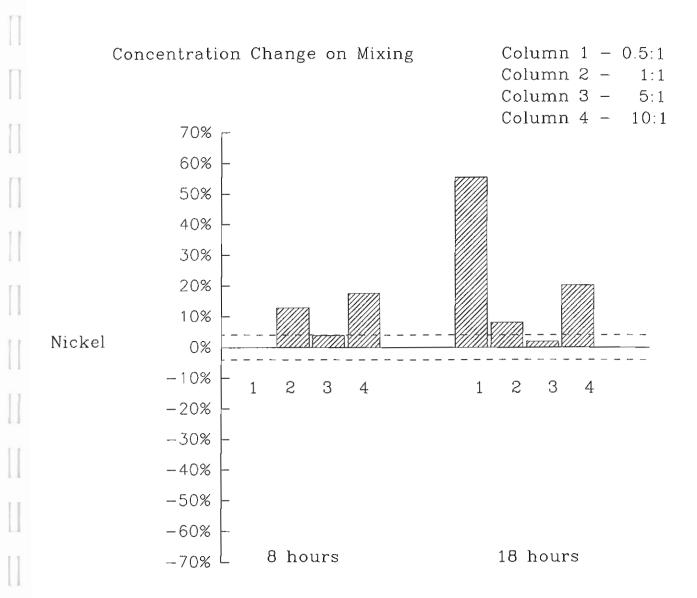


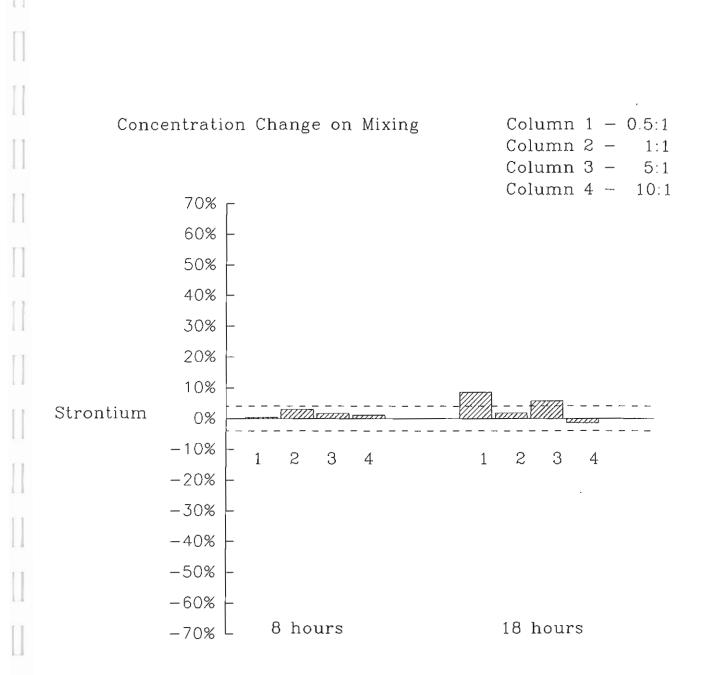


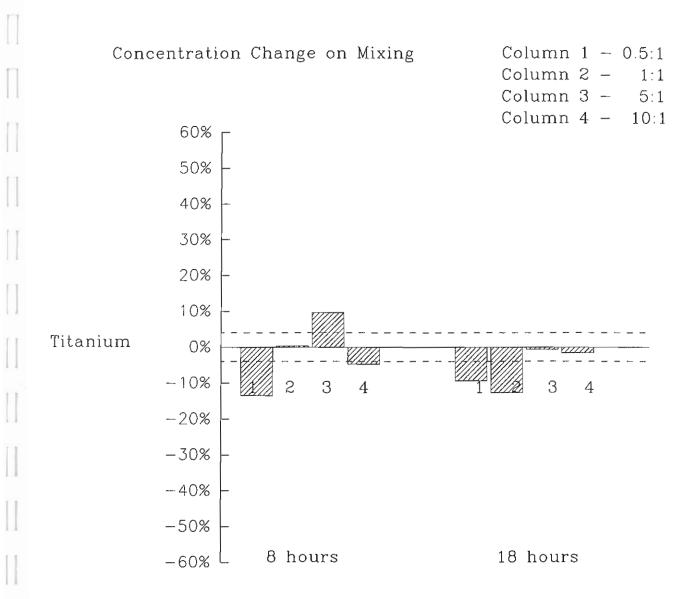


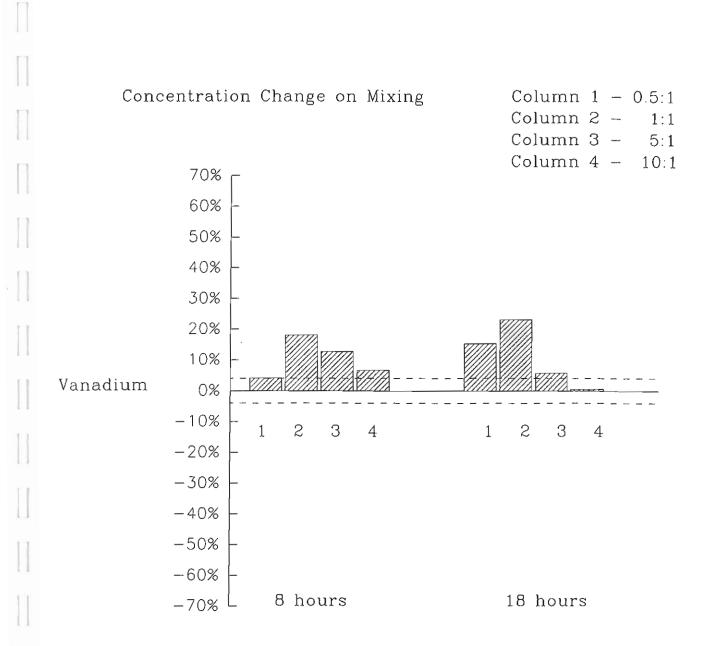


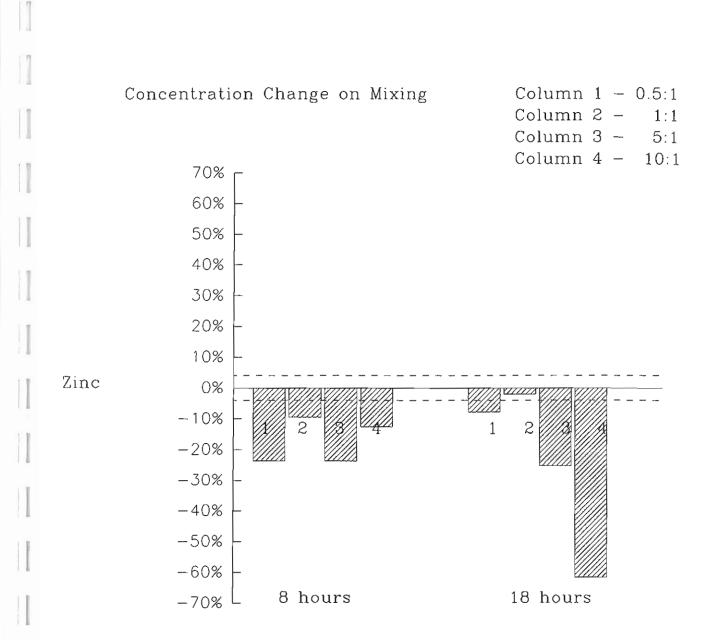


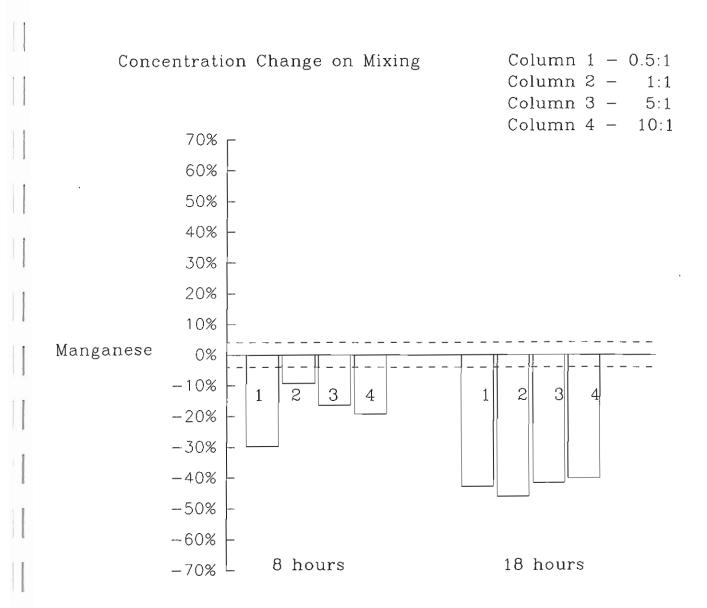


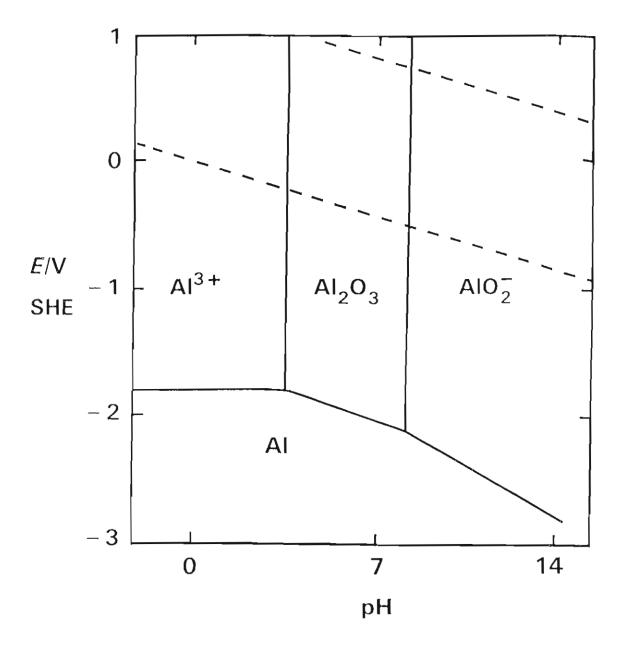














Pourbaix diagram for the aluminum-water system at 25 °C. $\partial_{AI}^{3+} = \partial_{AIO_2^{-}} = 10^{-6}$

Domain for the stability of water shown by dotted lines.

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