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The Severn-Thames Transfer Project: Phase II - Chemical Interactions of Transferred Sediment with the Host Water.

Final Report

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1.1 Executive Summary

The primary purpose of the work carried out at the IFE River Laboratory on behalf of the Environmental Agency (formally the NRA) Thames Region was to investigate the potential effects of sediment involved during the transfer by pipeline of water from the lower reaches of the River Severn into the upper Thames. As part of this project samples and *in situ* measurements were taken at sites from either end of the proposed pipeline, namely at Haw Bridge on the R. Severn (the extraction site) and at Buscot on the R. Thames (the host site for the transfer). This was done for each of four seasons in the year 1996-7 and experiments were carried out to determine the potential effect of sediment influx during transfer on aqueous chemistry of the host water. This comprised adding sediment extracted from Severn water to unfiltered Thames water and monitoring changes in chemical composition over a period of 24 hours. The relative volumes of water from which the sediment to host water was 50:1 to magnify changes in solution composition.

Parameters considered in this work include 10 major ions, 13 metals, the particle size, mineral components and biological composition of the sediment and the organic content of the solution. From this, together with the previous work carried out on the mixing of Severn and Thames water (IFE Report No.T04073o7/1), it has been possible to predict potential changes in the concentrations of chemical species which may occur once water is transferred and this is summarised in Table 1 on page 13. This predicts that, if complete mixing of incoming water occurs and adequate dispersal of transferred sediment is achieved, the concentrations of most species should be similar to that in the unmixed River Thames assuming the defining chemical equilibria are relatively unaffected. Exceptions to this may be barium which could be expected to increase on transfer and certain other trace metals e.g. copper, nickel, manganese and zinc which may exhibit unpredictable behaviour.

The complexity of the chemistry involved in these solutions, comprising many different species, combined with the lack of information regarding previous inter-riverine transfer projects, has also required that predictions have been primarily based on an interpretation of the underlying aqueous chemistry - specifically concerning the equilibrium speciation of solutions with respect to pH and oxygenation (strictly redox potential) - rather than on direct comparisons with other schemes. Prediction of the rate at which solutions approach equilibrium is more difficult. This is because information on the mechanisms involved in many important chemical reactions in natural waters - for example on iron(II) oxidation by atmospheric oxygen - is limited and extrapolation of rate orders derived from experiments on pure laboratory solutions may not be justified. This therefore precludes accurate prediction of chemical kinetics including estimations for the time for equilibrium to be achieved.

Changes in solution concentrations immediately after mixing depend on the pH and degree of oxygenation of the water - both of which decrease presumably as a result of respiration due to the organic content in the sediment; however in the experiments pH and oxygen concentration

appeared to re-establish a more equilibrium value within 24 hours. Considering that in the real situation of water mixing after pipeline transfer the sediment content of the water will be of the order of 1/50 of that of these experiments, changes in pH and oxygenation after mixing would be considerably smaller and the time for re-equilibrium correspondingly less.

The rôle of micro-organic species in each river was also considered in this work using information supplied by both EA regions. Both rivers appear to be relatively free from micro-organic contamination with no species recorded in more than a minority of samples. The most commonly found anthropogenic contaminants in the source water (Severn), such as simazine, atrazine and lindane also tended to be found in the host Thames water. Therefore the injection of high levels of such material as a result of transfer appears unlikely on the evidence considered. It is recommended however that those compounds at present determined in the R. Severn but not in the R. Thames should be included in the future monitoring of the R. Thames. This will provide useful background information to assess future water quality changes.

The chemical nature of the two waters appear largely similar (as discussed in the previous report - T04073o7/1), with a possible exception during winter months, when high flow rates may cause the R. Severn to lose some of its hardwater character because of dilution with softer water from the headwaters - unfortunately it has proved impossible to investigate this during the study because of the lack of rainfall in the winter of 1996-7. The experimental work carried out during this period did however show a high release of some metals which cannot be explained from the aqueous solution chemistry, especially manganese, copper, cadmium, & zinc. This is mirrored to a certain rxtent by a change in some amphoteric metals - compare aluminium & titanium - but not for 'conservative' metals (e.g. strontium and lithium) or the major ions, and the strange behaviour of this sample may be due to accumulated particulate debris of anthropogenic nature washed in by heavy rains after a long dry spell and which may also explain the high biodiversity (see electron micrographs) in the sediment. Therefore the observed changes in the chemistry of these metals in this sample may be anomalous and have not been included in the discussion.

It was found that sediment collected from Haw Bridge achieved a constant value for suspended solids (3-4 mg/l) after about 4-6 hours; most of the remaining material was still in suspension after 5 days and is presumably colloidal material which may be explained by the high clay content of the sediment. Given that the addition of sediment to the host water appears to have little permanent effect on the solution chemistry, the question of provision of settlement ponds is likely to be dictated by other factors and any benefit to water chemistry would be accomplished with a relatively small settlement time.

In conclusion, there is a general similarity in chemical composition of the two rivers, as described by parameters such as mineral saturation, pH and dissolved oxygen concentration of the solutions investigated. This infers that interactions with the sediment from the R. Severn - whether equilibrium is achieved or a more complex situation exists between sediment and water - should also be similar whether the bulk water is Severn or Thames water. Therefore permanent changes in the inorganic chemistry as a result of water transfer should be expected to be relatively small except for the few species outlined in Table 1.; the reasons for these changes are explained more elsewhere in this text. An exception to this may be during conditions which temporarily perturb the solution chemistry away from equilibrium such as occurs in storm episodes or pollution incidents.

1.2 Introduction

Investigations into the chemical changes involved during mixing of source (Severn) and host (Thames) waters has been investigated and described in some detail in IFE report RL/T04073o7/1. The general conclusions of this were that changes of major ions (calcium, alkalinity, sulphate, sodium, phosphate, nitrate, etc.) were relatively minor - the concentrations in the mixed water being in line with that expected from the relative volumes added. For metals a similar behaviour was largely observed except for the two common amphoteric (i.e. capable of acting as both acidic or basic) metals aluminium and zinc which exhibited a significant decrease, and for a few transition metals (i.e. d-block elements), e.g. nickel and copper which exhibited a small increase.

The purpose of phase II of this work was to examine the behaviour and effect of sediment from incoming Severn water into the River Thames with special relevance to release/absorption and solubilisation/precipitation of material from the introduced solid material into the aqueous phase.

1.3 System Controls

The chemistry of aqueous solutions is a complex and demanding subject This is especially so when the chemistry of the aqueous media is as complicated as a natural water where numerous phases and dissolved species can be present - all influenced by biological and geological factors; the situation is often conducive to a semi-empirical approach. For many systems this is facilitated by the prevalence of watercourses which can be observed, monitored and the results compared to other water bodies of similar type. This comparitive approach is useful in many instances but is of only moderate utility as a predictive tool for artificially induced chemical interactions for natural waters. Prediction of the chemistry of sediment-solution interactions involved during Severn-Thames transfer must therefore rely to a large extent on a knowledge of the basic physical-inorganic and geochemical principles and not on a wealth of experimental data on previous projects.

For any stable aqueous system concentrations of chemical species are controlled by solution equilibria and for a system not at equilibria, the kinetics involved as a solution tries to reach equilibria is also important. A complicating factor in the interpretation of the chemistry of natural waters is that whilst for chemical components which are present to an appreciable extent, the constants which control equilibria (solubility products, ion-pair formation constants etc.) have been usually determined in laboratory measurements on pure systems, for many of the lesser species (e.g. trace minerals) there is the additional possibility that in solid form they may not exist primarily as pure phases but may be dispersed, isomorphically substituted or adsorbed onto substrates composed primarily of other minerals.

One feature of the aqueous chemistry of natural waters - except for very concentrated solutions (brines and the like) which often allows a simplification of the interpretation of solution speciation is that the solvent, water, is generally present in a very large excess, usually greater than 99.5%. Therefore two of the most ubiquitous chemical properties of water which influence the chemical speciation of aqueous solutions and solid phases in equilibrium with it can be used to assess the stability of dissolved species.

These are, firstly pH (the propensity for water to self-dissociate into hydrogen and hydroxyl ions and the rapid mobility of these ions through solution dictates that pH-influenced reactions are often close to equilibrium) and secondly redox (i.e. electrical) potential, also called E_H (the high dielectric constant of water confers the ability of water to dissolve and stabilise charged species such as ions - it also facilitates ready changes in the redox potential of dissolved species by electron transfer between such species). A useful tool in predicting the behaviour of chemical species in water is to examine the relative stability of species containing a common element - for example a metal - with respect to pH and E_H. This approach which is embodied in the use of E_H-pH plots (often called Pourbaix diagrams) is a common instrument in metallurgy, materials science and geology.

The behaviour of certain species can be influenced by other factors. For example unlike many metals, which in the the forms of ions are readilly disposed to spherical geometry because of electrostatic considerations, metals from the transition series (scandium-zinc, yttrium-cadmium & lanthanum-mercury) when in a suitable oxidation state can exert a tendency to certain favoured geometries because of partially filled inner electron shells (d-orbitals) and which have directional symmetries. This and the consequent energetics of this effect is at least partially responsible for the behaviour of these metals to form many different oxidation states and - except for species with 5 or 10 d-electrons: manganese(II), iron(III), zinc(II), cadmium(II), and molybdenum(VI) - and confers properties of colour, directly bonded strong complexes, and influences kinetic reactions of these metals. For this reason copper(II), molybdenum(V) and to a much lesser extent nickel(II) are predisposed to non-spherical geometry in compounds and when solvated, they can slow high preferences to bonding to certain functional groups depending on the metal - copper(II) with ammonia and amines for example. The kinetic inertness of many reactions involving direct substitution of groups bonded to chromium(III) - the reduced form of chromium, found in anoxic sediments - and cobalt(III) is also due to this effect.

The interpretation of the measurements in this work have therefore been performed *primarily using four criteria.:-*

(a) For the most abundant species - calcium, magnesium, sodium, potassium, bicarbonate/carbonate (alkalinity), chloride, sulphate, nitrate + nitrite, phosphate and silicate conventional solution equilibria were used to explain the solution chemistry of the water in a manner akin to the use of WATEQ in the previous report. The principal difference was that for sediment-water interactions local conditions in pH and redox potential may be different to that which can be measured in the bulk solution and emphasis during interpretation of results was therefore on the role of chemical equilibria in affecting relative change of composition over time rather than with absolute concentrations.

(b) For minor species (aluminium, barium, cadmium, copper, lithium, manganese, molybdenum, nickel, lead, strontium, titanium and zinc) changes in chemistry were primarily considered in terms of interactions with solvent water and derived solid phases (soluble ions, oxides and hydroxides) and the relative stability of each species under the projected changes in pH and redox potential of the Thames water with Severn sediment during mixing.

(c) For certain minor species changes in some major components can have a profound influence if they give rise to minerals of low solubility. Therefore relative changes in concentrations of bicarbonate, sulphate and calcium magnesium and the potential for removal of, for example, barium (by sulphate), molybdenum, and titanium (as mixed oxides) or strontium, lead and lithium (as carbonates) were considered amongst other species.

(d) The later transition metals, specifically the copper and nickel were observed to exhibit unusual behaviour during the experiments on the mixing of host Thames and source Severn waters. This was explained as a result of the peculiarity of these metals, when as the oxidatively stable divalent cations, in exhibiting preferences for certain geometrical environments, their predisposition for absorption onto various surface-active substrates and ability to form complexes with certain ligands.

(e) Finally certain species are known to be able to exist in natural waters in non-equilibrium forms. For example manganese is unstable in oxygenated freshwaters but has been detected using such techniques as electron spin resonance at pH of upto 8.5. Where the non-equilibrium behaviour of individual species was well documented it was taken into account in the interpretation of the changes in chemistry during mixing experiments.

2.1 Field Measurements

Measurements were made during sampling trips at Haw Bridge on the River Severn and at Buscot on the River Thames on the same day (within four hours) in each season on the following days; spring : 28th May 1996, summer : 4th July 1996, autumn : 3rd October 1996 and winter: 6th February 1997. At each site the following parameters were determined: temperature, pH, dissolved oxygen, conductivity and redox potential.

As far as possible measurements were taken in mid-stream at approximately 0.5m depths from the surface. For the site at Haw Bridge this usually enabled four measurements to be made and similar measurements were also taken at 5 metres to either side of the mid point. For the site at Buscot measurements were made at either the north or south weir - depending on which was most free of weed, however measurements could only be made at the mid-point at two or three depths (one in winter) owing to the shallowness and the narrowness of the channel.

The results of these measurements on-site are given in Table 2 and show that, as far as can be determined, at both sites the rivers seem relatively homogenous; for the Severn site this is allows the assumption to be made that sampled water should be relatively similar to that which may be eventually abstracted irrespective of the surface depth or the distance from mid-channel of abstraction point.

At both sites water samples were then taken close to the mid point of the channel and about 0.5 m from the water surface. Sample volumes collected were 50 litres of unfiltered water at Haw Bridge and 10 litres of unfiltered water at Buscot (from which 1 litre of water would be taken for the mixing experiments). At the same time filtered samples were taken for analysis.

2.2 Laboratory Measurements

Experiments were conducted each season within two days of sampling. The sediment from the 50 litres of Severn water collected from Haw Bridge was removed (within 24 hours of collection) by continuous-flow centrifugation together with a residual amount of water (300 ml) to keep the sediment wet. This sediment was stored overnight in the dark at 5°C. Owing to practical difficulties the centrifuged sediment for the autumn sample was stored for 36 hours under the same conditions.

The sediment was transferred (without storage water) to a thermostated mixing vessel at 10°C to which one litre of Thames water taken from the 10 litres collected at Buscot (also equilibrated to 10°C) was added. The solution was stirred sufficiently to keep the sediment suspended and a controlled gas mixture (0.6 ml/minute carbon dioxide in 1 litre/minute oxygen free nitrogen) applied to the top of the mixing vessel. After 1 hour, 3 hours, 6 hours and 24 hours approximately 250 ml of solution was extracted, filtered using a 0.45 μm Whatman GF/F filter under negative pressure.

The filtrate was divided into two portions - a fraction of about 180 ml was analysed for major ions:- calcium, magnesium, sodium, potassium, iron, alkalinity, chloride, nitrate, phosphate, sulphate and silica by standard analytical methods. The remainder was analysed for metals by Inductively Coupled Plasma Mass Spectrometry (ICPMS). The sensitivity is quoted as 1 μg/l except for aluminium which had a minimum detection limit of 5 μg/l.

Vanadium and chromium were not determined because of interference from chloride in the samples for ICPMS analysis from added hydrochloric acid used to keep metals in solution. This was used because it was desired to use a non-oxidising acid so as not to influence the redox chemistry of the solution at any stage, especially since all filters were acid-washed and filtration of the sediment laden aliquots required prolonged contact with the filter.

In the presence of aqueous solutions the stable form of vanadium is as insoluble vanadates (V) or - under anoxic conditions as the insoluble vanadium (IV) dioxide. Chromium in the reducing environment of river sediment is in the form of the kinetically inert insoluble chromium (III) phases, usually in mixed compounds with iron, e.g in the mineral chromite, or as hydroxides. For both these metals significant release from sediment over the timescale of 24 hours - the duration of mixing experiments - is unlikely and they can usually be regarded as 'conservative' species.

3. Results

3.1 Sediment Analysis

3.1.1 Mineralogical Determination

The mineral species of centrifuged River Severn sediment samples were qualitatively analysed using the X-ray Diffraction facility at the Postgraduate Research Institute for Sedimentology at Reading University. Using the sample collected during the spring as an example the minerals detected in the sediment were

Mineral	Classification of Mineral	Abundance
Mica	Clay Mineral Aluminosilicate	Present
Chlorite	Clay Mineral Aluminosilicate	Dominant
Quartz	Silica, SiO_2	Dominant
Potassium Feldspar	Framework Aluminosilicate	Trace
Plagioclase Feldspar	Framework Aluminosilicate	Present
Siderite	Iron(II) Carbonate	Trace

The particle size distribution was as follows:

Clay fraction (less than 2 μm)	11.9%
Silt fraction (2 - 63 μm)	81.4%
Sand fraction(63 - 900 μm)	6.7%

and the majority (52%) of particles were in the range 5 - 25μm. Semi-quantitative analysis of the clay fraction by X-ray diffraction revealed that it was composed of :-

Illite	39%
Expandable (e.g. smectites, montmorillionite)	40%
Chlorites	21%

It is interesting to note the absence of the common aluminosilicate mineral, kaolinite (china clay) which is often presumed to be one of the minerals controlling aluminium solubility. The absence of calcite (calcium carbonate) and dolomite (calcium-magnesium carbonate) as distinct solid phases is interesting considering that the previous work (IFE Report RL/T04073o7/1) predicts, using WATEQ, that the water is supersaturated with both these minerals. This would suggest that there is relatively little tendency for calcite to precipitate from solution.

Another unusual feature about the mineral composition of the sediment is the presence of siderite - iron(II) carbonate - which requires deoxygenated conditions and concentrations of dissolved carbon dioxide above that encountered in waters in equilibrium with the atmosphere. The lack of the normal iron mineral for aerated surface waters - haematite (α-iron(III) oxide) or amorphous ferric hydroxide further reinforces the suggestion that the water in direct contact with the sediment is oxygen-poor and carbon dioxide-rich compared to water in equilibrium with the atmosphere.

3.1.2 Scanning Electron Microscopy

Scanning electron microscopy has been carried out, at magnifications in the range 1200x - 4500x, on the sediment from samples collected during each season and the results from the spring and summer, autumn and winter samples have been examined. The morphology of the geochemical matrix of the sediment for all samples appear similar and identifiable mineral phases of the sediment comprises mainly of clay mineral platelets with a very small amount of crystals of possibly rhombohedral symmetry which may be consistent with the carbonate minerals calcite, dolomite or siderite.

The biological material is principally composed of the silica shells of large numbers of centric (cylindrical) and pennate (elongated) diatoms but also included specimens of scales from chrysophytes synura petersenii & mallomonas cratis (spring samples) and scales from the heliozoon pinaciophora (summer sample). There were also possibly present microfossils and faecal pellets. It is interesting to note that the winter sediment sample showed the most diversity in biological remains with filamentous diatoms, amoebal remains, green algae and fungal filaments identified as well as the more usual centric and pennate diatom remains. Photomicrographs are reproduced in appendix A.

3.2 Mixing Experiments

Results of the mixing experiments are given in Tables 3, 4, 5 & 6 and appendices B to E. In each Table the concentration of a particular chemical species is given in order of mixing time in hours with the value at time zero being the unmixed host Thames water. The concentration of each species in the filtered Severn water is given for comparison. Measurements below the limit of detection are given as the "less than" that value, e.g <1mg/l, etc. and are plotted as open circles. Measured concentrations for iron were all below the minimum detection limit of 0.1mg/l.

4.1 Discussion

The changes in the concentration of the various chemical species can be broadly classified as follows.

(a) Ions which are comparatively abundant and exist primarily as soluble species

Magnesium, sodium, potassium, chloride, nitrate, phosphate, sulphate and silica generally show little discernible trend with time compared to that observed with trace minerals. This is also the case for calcium and alkalinity except for the autumn sample where there is a gradual rise over the first six hours until a new apparent equilibrium is reached; presumably this was due to degassing carbon dioxide generated by the extra length of storage of this sample (36 hours)

(b) Conservative trace metals

Lithium and strontium show little change in concentration with time. They are redox stable under normal conditions.

(c) Reducible metals

There are two metals, excluding iron which was below detection limit in all measurements, which can be potentially reduced in waters to species of lower oxidation state under mildly anoxic conditions. These are manganese, and molybdenum. In these experiments manganese is usually at first released and then removed from solution. Molybdenum generally shows much smaller changes in concentration.

(d) Amphoteric metals

Amphoteric metals exhibit solubility in acidic solution (usually as a free cation) and also in alkaline solution (usually as an oxy or hydroxy anion). At intermediate pH these metals are usually present as insoluble oxides or hydroxides. The pH at which these metals become soluble depends on the individual metal and can be complicated by the presence of organic material and certain ions such as bicarbonate and sulphate but it is characteristic that solubility is very pH dependent. Metals which come into this catagory of amphoteric behaviour are aluminium, zinc, lead, cadmium and titanium; these all show to a greater or lesser extent a release of dissolved species into solution followed be a reprecipitation into the colloidal phase.

The principal metal in this class is aluminium the solubility of which is often controlled by the solubility of the minerals, gibbsite (aluminum hydroxide), kaolinite and magnesium-montmorilionite; the latter two minerals are aluminosilicates and, since the mineral with the lowest solubility controls the concentration of soluble aluminium the concentration of silica can also important although like other amphoteric metals pH is the dominant factor.

(e) Late transition metals.

As mentioned previously, certain transition metals are characterised by the presense of underlying electronic d-orbitals which can profoundly influence the chemistry of these metals. The exact nature of this behaviour is rather complicated but the most important two metals which fall into this catagory when in their water-stable oxidation states are copper and nickel. Both metals tend to exhibit a mild release with the copper concentration then falling back with time to a value similar to introduction of sediment. With nickel this is much less pronounced.

(f) Barium

The concentrations of barium in the River Severn are much higher than in the Thames and when the sediment was added there is a quick release to a relatively high value.

The Severn sediment contains an appreciable amount of organic matter. This can influence the rate of deoxygenation of solid material and its effect can be determined from the biological oxygen demand or BOD. From data supplied by the EA Severn-Trent Region the River Severn at Haw Bridge has a 5-day BOD typically in the region of up to 3-5 mg/l. For mixing experiments the amount of sediment extracted by centrifugation was concentrated by approximately 170 times prior to dispersion in the host (Thames) water from which it can be estimated that dissolved oxygen (normal saturation 10-12 mg/l) present will be locally deplected around sediment particles in a relatively short time (approx 2-8 hours). Since the time taken for centrifugation was approximately 4-6 hours deoxygenation of the sediment during extraction prior to mixing experiments was likely.

Consumed oxygen is converted to carbon dioxide by respiration so the local pH in the sediment pore water should also decrease. Deoxygenation of the sediment is also suggested by the presence of siderite instead of haematite as mentioned in section 3.1.1. Mixing of oxygen depleted sediment by dilution with oxygen abundant well stirred water from the River Thames as happened during the mixing experiments should therefore tend to re-establish similar conditions of pH and redox potential of aerated waters.

Measurement of the bulk solution pH and dissolved oxygen concentrations during mixing experiments confirmed this was the case: the magnitude of the drop in pH after mixing was about 1-2 pH units and had not re-adjusted completely at the end of the experiment - however the effect of the controlled atmosphere (carbon dioxide/nitrogen) on the pH is not clear under these conditions. Complete deoxygenation occurred within about 2 hours, however reoxygenation occurred within 24 hours. These changes in pH and redox potential explain the following observations in the categories described above.

(a) The major ions show generally little change due to the large change in pH or redox which would be needed to affect a large concentration. This is because many of them are thermodynamically stable or kinetically resistant to changes in pH and redox potential. The only exception to this is that the curves for calcium (+magnesium) and alkalinity in the autumn sample show increases to a new higher equilibrium value consistent with carbon dioxide production dissolving calcite and/or dolomite material in the sedimentt. Since this sample was left to become anoxic for 36 hours owing to practical difficulties the amount of carbon dioxide from respiration and consequent change in pH may explain this. One final point is that one of the major ions, nitrate, could be expected to be at least partly reduced to nitrite under these conditions but the standard method of analysis of nitrate used in its measurement actually determines nitrate + nitrite so changes in nitrate levels would not be observed.

(b) The conservative metals lithium and strontium have little solubility dependence with pH and redox potential and so the lack of change in concentration can be expected. These metals have a tendency to form insoluble, redox stable, carbonates like calcium and magnesium and therefore the free metal concentration tends to be buffered by equilibrium with carbonate phases.

(c) The two metals manganese and molybdenum can change form with changing redox potential. The simplest way of showing the effect of this is to consider a typical common species for each metal in oxidised and reduced (i.e. oxygen depleted) conditions and then to correlate this with the solubility of the metal in each form.

Metal	possible oxidised form	possible reduced form
Manganese	manganese dioxide (insoluble)	manganese(II) cation (soluble)
Molybdenum	calcium molybdate (insoluble)	molybdenum(V) oxyhydroxide (insoluble)

It is evident that deoxygenation should release manganese as manganese(II) ions but that for molybdenum this effect should be much less than for manganese due to the limited solubility of the products of reaction. Subsequent reoxygenation will then eventually reprecipitate release minerals, unless as may be the case for the autumn sample if the water is not sufficiently re-aerated to completely re-establish equilibrium in which case some of the released manganese may still be in solution. It is thought, however that metals such as manganese can exist to an extent in non-equilibrium forms, e.g. as manganese(II) or manganese(II)-hydrogencarbonate ion-pair in aerated waters.

(d) Amphoteric metals become more soluble in acid pH. Production of carbon dioxide around sediment particles lowers the local pH and therefore these metals should be released to varying degrees once the sediment in deoxygenated and subsequent addition of the sediment to the Thames water should then precipitate them once the solutions are fully mixed and in equilibrium. This release-reprecipitation behaviour is observed for the amphoteric metals: aluminium, zinc, titanium, lead and cadmium.

Aluminium concentrations are controlled largely by the solubility of minerals such as gibbsite, kaolinite (china clay) and magnesium montmorillionite all of which are strongly pH sensitive; since the latter two minerals are aluminosilicates the role of silica can play a role. Aluminum from feldspathoid minerals is generally less mobile.

Titanium minerals exhibit the pH sensitive behaviour characteristic of the amphoteric metals; however titanium as well as forming the dioxide, rutile as a primary mineral is also found as a mixed oxide with calcium in the mineral perovskite and the slight net decrease of titanium levels during the mixing of the autumn experiments may be due to interaction with increased calcium concentrations.

The mobility of zinc, cadmium and lead to and from solution is also affected by the degree of absorption onto other substrates. This is itself pH dependent due to competition of the metal cations with hydrogen ions - confirming the general amphoteric nature of these metals - but the nature of the substrate (i.e. aluminosilicate, amount of organic acids etc.) is also important.

(e) The late transition metals, copper and nickel show unusual behaviour - possibly because the chemistry of these metals is often determined by geometry around the ions. The unusual behaviour of these metals was also noted in phase I of the Severn-Thames project.

Both copper(II) and nickel(II) form a large number of stable soluble complexes with organic acids with can therefore promote solubility and mobility of these metals even though they both form insoluble phases at neutral pH (copper oxides, nickel hydroxide) and are strongly absorbed onto other phases such as manganese dioxide and iron oxides as the pH sensitive copper(II)-hydroxy and nickel(II)-hydroxy ion-pairs. Removal of precipitated manganese dioxide by conversion to manganese(II) may be responsible for the slight increase in copper and nickel concentrations during sediment mixing but this cannot be conclusive since the behaviour of these metals is very environment dependent.

(f) Barium can be expected to be determined by the solubility of the sulphate and carbonate - the precipitations of which exhibit relatively fast precipitation/dissolution kinetics. Calculations show that for these waters the River Severn is generally saturated in barium sulphate whereas the water from the River Thames is not. Therefore the observed trend in increasing barium concentrations is probably caused simply by dissolution of barium sulphate into the host water.

As part of this work the role of micro-organic materials during transfer was to be considered. This is complicated by the fact that both regions of the Environmental Agency involved - Thames region and Severn-Trent region - may have different priorities concerning the pesticides of special interest and this is a influenced by the different land uses, primarily agricultural, in each catchments. The assessment of micro-organic materials in this work was purely from data supplied from the two EA regions involved and forms a piece of work separate to the main inorganic measurements. It is therefore given in Appendix F.

To confirm the hypothethis that the interactions of sediment in the concentrated phase with host water proceeds through an anoxic interval the system was modelled by the speciation PHREEQC, a development of WATEQ, as an organic material in contact with an equilibrium mixture of calcite (calcium carbonate) and atmospheric carbon dioxide, fixed at the same proportion to that of the mixing experiments. The re-aeration of this solution was then modelled by equilibrating with fixed portions of air. The model predicted that the conditions of the sediment (redox, pH & carbon dioxide) would be sufficient to favour the formation of siderite as was found. This supports the assumption that E_H and pH are controlling parameters and the system is thermodynamically well-behaved.

5.1 Conclusions

It can be seen from the preceding section that changes observed during the experiments can be explained in terms of sediment concentration followed by re-dispertion. The net effect of this process is that after a certain period (significantly within 24 hours for most species) the *status quo* in the chemical speciation of the host water is restored. The only noticeable exception to this is barium. Other changes may possibly occur during a rapid natural build-up of sediment but may be expected to be rectified - according to these results - on adequate dispersal and/or aeration of the solid material. Such changes may be induced by an accumulation of sediment in pipework during transit or storage in settlement ponds. In the latter it is important to ensure that the residence time and aeration are such that adverse reducing conditions do not develop.

Tables

Table 1: General Summary: Prediction in Potential Chemical Changes Induced in Transfer of Sediment from the River Severn to the River Thames.

Species	Change after Initial Transfer (effect on Thames water)	Net Change after Dispersal in Host Water (effect on Thames water)
Alkalinity	Little Change or Small Increase	Little Change
Calcium	Little Change or Small Increase	Little Change
Chloride	Little Change	Little Change
Magnesium	Little Change or Small Increase	Little Change
Potassium	Little Change	Little Change
Phosphate	Little Change	Little Change
Nitrate	Possible reduction to nitrite	Little Change
Sodium	Little Change	Little Change
Silicon	Little Change	Little Change
Sulphate	Little Change	Little Change
Iron	Below Detection	Below Detection
Aluminium	Increase	Little Change
Barium	Increase	Increase
Cadmium	Small Increase	Little Change
Chromium	Little Change	Little Change
Copper	Small Increase ?	Small Increase?
Lithium	Little Change	Little Change
Manganese	Increase	Little Change/Small Increase?
Molybdenum	Small Increase/Little Change?	Little Change?
Nickel	Small Increase?	Small Increase?
Lead	Small Increase	Little Change
Strontium	Little Change	Little Change
Titanium	Small Increase	Little Change
Vanadium	Little Change	Little Change
Zinc	Increase	Little Change/Small Increase?

Table 2: Field Measurements

Spring - 28/5/96

	Haw Bridge (2 pm)			Buscot(6 pm)
	mid span	5m north	5m south	mid span
Depth/m	0.05	0.09	0.05	0.05
Temperature/°C	13.1	13.1	13.1	12.6
Diss. Oxygen/%sat	97.1	93.7	95.3	98.3
pH	7.90	8.01	8.03	8.25
Conductivity/μScm^{-1}	492	491	491	724
Redox/mV	336	347	360	322
Depth/m	0.44	0.42	0.40	0.52
Temperature/°C	13.1	13.1	13.1	12.6
Diss. Oxygen/%sat	94.8	94.2	94.6	98.3
pH	8.03	8.03	8.03	8.18
Conductivity/μScm^{-1}	493	491	492	723
Redox/mV	343	348	360	326
Depth/m	0.92	1.03	0.88	
Temperature/°C	13.1	13.1	13.1	
Diss. Oxygen/%sat	95.9	93.7	94.6	
pH	8.02	8.02	8.03	
Conductivity/μScm^{-1}	493	491	492	
Redox/mV	342	348	359	
Depth/m	1.52	1.48	1.04	
Temperature/°C	13.1	13.1	13.1	
Diss. Oxygen/%sat	94.8	93.6	94.7	
pH	8.00	8.02	8.05	
Conductivity/μScm^{-1}	492	491	493	
Redox/mV	341	349	359	

Summer - 4/7/96

	Haw Bridge (12 pm)			Buscot (3 pm)
	mid span	5m north	5m south	mid span
Depth/m	0.13	0.19	0.09	0.16
Temperature/°C	17.0	17.1	17.1	15.7
Diss. Oxygen/%sat	81.1	85.3	79.2	82.6
pH	8.17	8.18	8.19	8.07
Conductivity/μScm^{-1}	941	932	942	807
Redox/mV	316	350	345	347

Depth/m	0.57	0.51	0.45	0.78
Temperature/°C	17.1	17.1	17.1	15.7
Diss. Oxygen/%sat	79.6	80.2	79.2	81.0
pH	8.14	8.16	8.19	8.00
Conductivity/μScm^{-1}	942	943	941	805
Redox/mV	315	349	344	339

Depth/m	1.03	1.07	0.95	1.52
Temperature/°C	17.0	17.1	17.0	15.6
Diss. Oxygen/%sat	79.2	78.8	78.6	81.4
pH	8.10	8.17	8.20	8.06
Conductivity/μScm^{-1}	943	944	943	805
Redox/mV	315	347	344	337

Depth/m	1.43	1.55	1.47	
Temperature/°C	17.0	17.0	17.0	
Diss. Oxygen/%sat	78.4	78.1	78.9	
pH	8.12	8.17	8.19	
Conductivity/μScm^{-1}	945	943	945	
Redox/mV	315	347	362	

Autumn - 3/10/96

		Haw Bridge (1pm)		Buscot (4pm)
	mid span	5m north	5m south	mid span
Depth/m	0.53	0.62	0.50	0.54
Temperature/°C	13.6	13.6	13.6	13.1
Diss. Oxygen/%sat	83.1	84.2	83.1	75.5
pH	7.97	7.95	7.95	7.87
Conductivity/μScm^{-1}	873	868	859	907
Redox/mV	346	366	376	350
Depth/m	0.97	0.94	1.12	0.88
Temperature/°C	13.6	13.5	13.6	13.05
Diss. Oxygen/%sat	81.5	81.6	80.8	75.5
pH	7.94	7.95	7.94	7.85
Conductivity/μScm^{-1}	871	866	863	914
Redox/mV	347	360	368	350
Depth/m	1.42	1.37	1.51	
Temperature/°C	13.6	13.6	13.6	
Diss. Oxygen/%sat	82.0	82.1	81.6	
pH	7.94	7.94	7.94	
Conductivity/μScm^{-1}	871	867	861	
Redox/mV	347	363	373	

Depth/m	1.84	1.92	1.83
Temperature/°C	13.5	13.6	13.6
Diss. Oxygen/%sat	80.9	81.5	80.9
pH	7.92	7.91	7.94
Conductivity/μScm^{-1}	872	866	863
Redox/mV	347	353	370

Winter - 6/7/96

	Haw Bridge (1pm)			Buscot (12.40pm)
	mid span	5m north	5m south	mid span
Depth/m	0.41	0.46	0.20	0.07
Temperature/°C	5.41	5.42	5.42	6.59
Diss. Oxygen/%sat	87.8	89.0	89.0	82.0
pH	7.93	7.91	7.94	7.85
Conductivity/μScm^{-1}	793	817	818	895
Redox/mV	335	333	327	304

Depth/m	0.73	1.23	0.96
Temperature/°C	5.41	5.42	5.41
Diss. Oxygen/%sat	88.3	88.4	88.4
pH	7.93	7.91	7.92
Conductivity/μScm^{-1}	824	817	818
Redox/mV	334	332	327

Depth/m	1.10	1.62	1.26
Temperature/°C	5.41	5.41	5.42
Diss. Oxygen/%sat	88.6	88.3	88.4
pH	7.93	7.90	7.91
Conductivity/μScm^{-1}	822	818	819
Redox/mV	333	332	328

Depth/m	2.15	--	0.52
Temperature/°C	5.41	--	5.41
Diss. Oxygen/%sat	88.7	--	89.0
pH	7.93	--	7.92
Conductivity/μScm^{-1}	821	--	819
Redox/mV	330	--	327

Depth/m	1.74	--	1.48
Temperature/°C	5.41	--	5.41
Diss. Oxygen/%sat	88.7	--	88.2
pH	7.93	--	7.91
Conductivity/μScm^{-1}	820	--	818
Redox/mV	332	--	326

Depth/m	2.90	--	2.31
Temperature/°C	5.41	--	5.41
Diss. Oxygen/%sat	88.6	--	88.2
pH	7.93	--	7.91
Conductivity/μScm^{-1}	819	--	817
Redox/mV	330	--	326

Table 3 Chemical Analysis - Spring (28/5/96)

Sample	Alkalinity meq	Calcium mg/1	Chloride mg/l	Magnesium mg/l	Potassium mg/l	Nitrate mg/l N	Phosphate mg/l P	Sodium mg/l
Thames (0 hr)	4.26	86.8	37.5	5.12	4.19	5.48	0.62	24.4
1 hour	4.17	86.5	34.0	5.27	4.12	5.26	0.64	27.4
3hour	4.23	85.8	38.1	5.26	4.05	5.43	0.66	26.6
6hour	4.28	85.8	41.8	5.29	4.12	5.42	0.65	24.4
24 hour	4.24	84.7	37.6	5.24	3.83	5.28	0.71	25.2
Severn	1.81	39.0	38.0	9.76	4.19	3.78	0.49	24.5

Sample	Silica mg/l Si	Sulphate mg/l	DOC mg/l	Aluminium µg/l	Barium µg/l	Cadmium µg/l	Copper µg/l	Lead µg/l
Thames (0 hr)	3.14	88.8	7.48	38.7	<1.0	<1.0	<1.0	<1.0
1 hour	3.19	77.3	5.32	218	32.0	8.10	4.83	3.46
3 hour	3.21	77.8	4.35	18.4	27.9	<1.0	2.68	<1.0
6 hour	3.17	76.4	4.05	16.5	32.7	<1.0	2.37	<1.0
24 hour	3.30	77.3	5.92	<5.0	31.2	<1.0	1.84	<1.0
Severn	2.59	77.3	11.2	81.9	31.2	<1.0	2.35	1.32

Sample	Lithium µg/l	Manganese µg/l	Molybdenum µg/l	Nickel µg/l	Strontium µg/l	Titanium µg/l	Zinc µg/l
Thames (0hr)	6.90	12.3	1.11	7.54	124	5.77	6.27
1 hour	6.52	162	1.56	13.1	125	13.3	136
3 hour	5.89	148	1.08	11.8	127	4.48	10.2
6 hour	5.81	59.3	1.10	11.6	127	3.87	8.72
24 hour	5.71	69.0	1.24	13.4	128	3.46	6.13
Severn	8.36	20.8	1.40	7.29	100	6.09	12.5

Table 4 Chemical Analysis - Summer (4/7/96)

Sample	Alkalinity meq	Calcium mg/1	Chloride mg/l	Magnesium mg/l	Potassium mg/l	Nitrate mg/l N	Phosphate mg/l P	Sodium mg/l
Thames (0 hr)	4.26	116	54.6	8.09	5.97	7.23	1.20	45.0
1 hour	4.12	110	61.0	6.10	6.15	7.33	1.20	43.7
3hour	4.39	113	48.9	6.14	6.34	7.30	1.20	43.8
6hour	4.40	112	52.5	6.20	6.12	7.36	1.20	41.2
24 hour	4.41	119	53.2	6.25	6.29	7.28	1.20	45.0
Severn	3.51	95.8	89.7	17.8	7.50	6.60	1.40	60.1

Sample	Silica mg/l Si	Sulphate mg/l	DOC mg/l	Aluminium µg/l	Barium µg/l	Cadmium µg/l	Copper µg/l	Lead µg/l
Thames (0 hr)	4.95	80.4	7.48	13.2	11.2	<1.0	5.01	3.14
1 hour	5.00	70.0	5.32	<5.0	44.2	<1.0	7.68	<1.0
3 hour	4.34	68.1	4.35	121	45.4	<1.0	27.9	8.56
6 hour	4.99	67.9	5.05	40.3	44.4	<1.0	10.7	4.79
24 hour	5.01	68.2	5.92	<5.0	45.3	<1.0	8.44	<1.0
Severn	4.20	119	11.2	6.40	73.6	<1.0	4.47	<1.0

Sample	Lithium µg/l	Manganese µg/l	Molybdenum µg/l	Nickel µg/l	Strontium µg/l	Titanium µg/l	Zinc µg/l
Thames (0hr)	8.45	9.68	4.31	11.4	147	7.66	8.45
1 hour	7.05	12.1	7.77	13.3	136	8.51	15.1
3 hour	7.39	26.3	9.35	17.1	139	20.0	23.1
6 hour	7.13	23.5	8.51	14.2	140	10.7	17.4
24 hour	7.22	17.1	7.55	14.4	137	9.59	8.44
Severn	16.3	14.2	5.38	9.97	215	8.33	8.68

Table 5 Chemical Analysis - Autumn (4/10/96)

Sample	Alkalinity meq	Calcium mg/1	Chloride mg/l	Magnesium mg/l	Potassium mg/l	Nitrate mg/l N	Phosphate mg/l P	Sodium mg/l
Thames(0 hr)	4.66	110	74.8	2.82	9.23	7.91	1.70	60.3
1 hour	5.44	126	---	2.72	8.92	7.80	1.70	60.3
3 hour	6.06	136	74.1	2.98	9.31	8.00	1.80	61.6
6 hour	6.26	141	75.5	3.43	9.28	7.94	1.80	63.4
24 hour	6.54	147	79.1	3.50	9.41	8.66	1.80	62.5
Severn	2.96	79.8	86.5	7.92	7.49	7.55	1.70	61.9

Sample	Silica mg/l Si	Sulphate mg/l	DOC mg/l	Aluminium µg/l	Barium µg/l	Cadmium µg/l	Copper µg/l	Lead µg/l
Thames (0 hr)	6.20	107	---	<5.0	88.0	4.80	<1.0	2.70
1 hour	6.30	---	---	<5.0	281	2.30	2.20	1.70
3 hour	6.20	110	---	<5.0	225	2.30	2.60	1.40
6 hour	6.35	108	---	<5.0	299	2.20	2.10	2.30
24 hour	6.20	109	---	<5.0	237	1.80	2.30	2.50
Severn	4.67	135	---	<5.0	170	1.50	<1.0	2.50

Sample	Lithium µg/l	Manganese µg/l	Molybdenum µg/l	Nickel µg/l	Strontium µg/l	Titanium µg/l	Zinc µg/l
Thames (0hr)	1.20	11.6	2.50	7.40	218	3.96	22.7
1 hour	<1.0	102	2.70	14.0	314	3.34	93.9
3 hour	<1.0	136	3.30	15.4	336	3.27	85.2
6 hour	<1.0	72.2	2.40	12.1	283	2.34	107
24 hour	<1.0	97.4	2.50	13.8	321	2.10	81.6
Severn	10.8	17.6	2.70	7.30	316	4.17	29.4

Table 6 Chemical Analysis - Winter (6/2/96)

Sample	Alkalinity meq	Calcium mg/l	Chloride mg/l	Magnesium mg/l	Potassium mg/l	Nitrate mg/l N	Phosphate mg/l P	Sodium mg/l
Thames(0 hr)	3.59	117	75.2	6.50	7.78	5.48	2.00	53.0
1 hour	3.44	120	78.4	6.80	7.76	5.40	1.80	54.0
3hour	3.62	124	82.6	6,85	7.98	5.23	2.30	53.9
6hour	3.51	129	84.4	6.95	7.71	5.10	2.90	54.3
24 hour	3.41	127	86.2	7.15	8.18	5.07	2.70	55.7
Severn	2.03	80.0	76.6	15.3	6.16	5.83	1.70	57.1

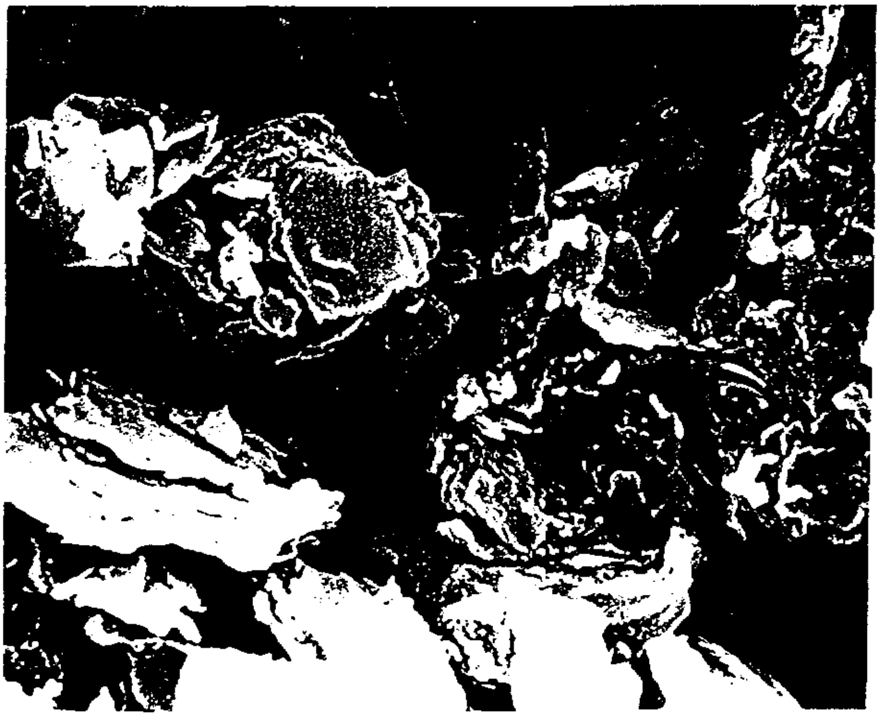
Sample	Silica mg/l Si	Sulphate mg/l	DOC mg/l	Aluminium µg/l	Barium µg/l	Cadmium µg/l	Copper µg/l	Lead µg/l
Thames(0 hr)	4.71	94.6	5.20	<5.0	11.5	<1.0	5.8	1.32
1 hour	4.33	95.3	5.03	<5.0	243	<1.0	12.9	1.53
3 hour	5.16	91.0	4.43	14.9	302	<1.0	15.6	1.88
6 hour	5.53	90.1	6.00	13.8	247	1.50	18.4	3.26
24 hour	5.46	94.0	6.40	35.2	207	3.08	19.6	2.75
Severn	4.59	107	4.44	12.7	95.6	2.60	6.3	<1.0

Sample	Lithium µg/l	Manganese µg/l	Molybdenum µg/l	Nickel µg/l	Strontium µg/l	Titanium µg/l	Zinc µg/l
Thames (0hr)	6.52	6.5	2.73	35.6	136	34.8	11.4
1 hour	7.06	32.1	2.90	40.8	143	39.3	107
3 hour	7.14	145	2.84	47.4	152	48.3	276
6 hour	6.95	192	2.96	49.1	150	49.3	292
24 hour	6.65	262	3.11	59.7	154	55.2	293
Severn	10.7	31.3	1.93	26.8	146	25.2	15.0

Appendix A

Electron Micrographs of Severn Sediment Collected from Haw Bridge

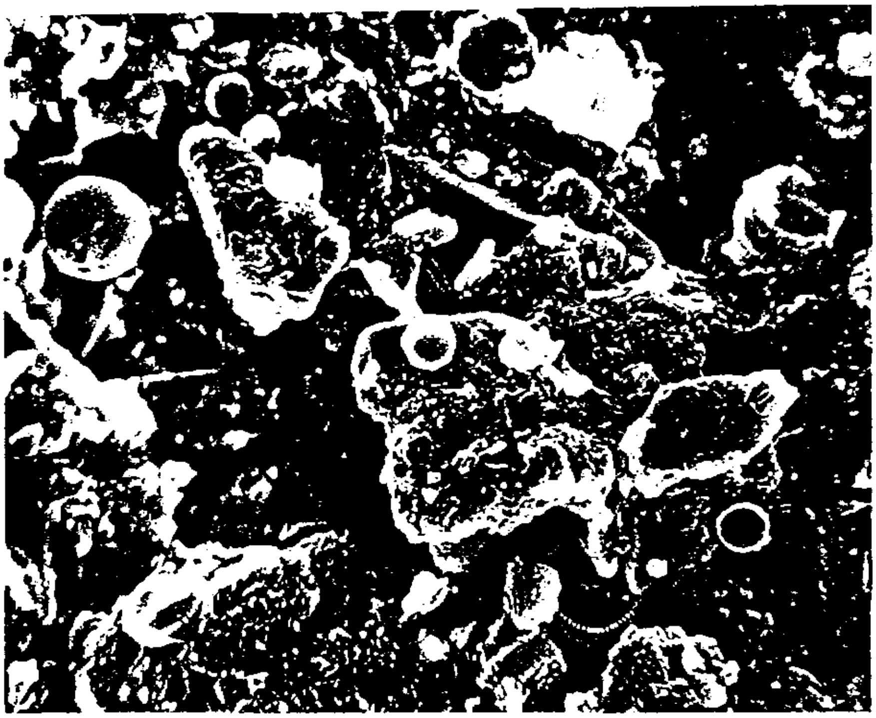
Spring (May1996)



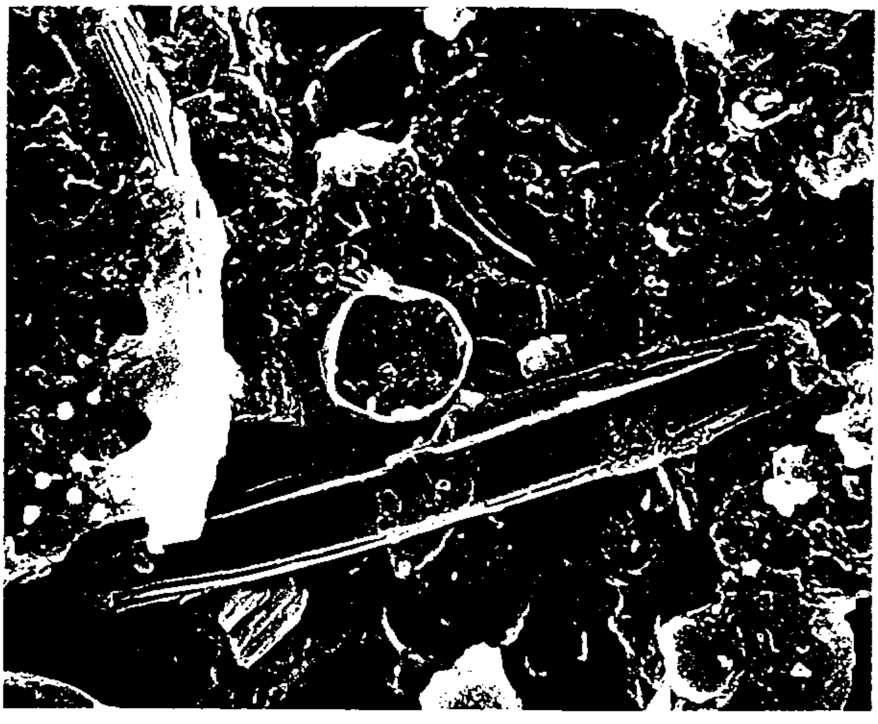
1. Undiluted Sediment. Clay Particles: 12,000x magnification

2. Undiluted Sediment: Biological Remains Include Centric & Pennate Diatom Frustules. Scale of Heliozoon Genus Pinaciophora (Arrowed): 3,600x magnification

Summer (July 1997)

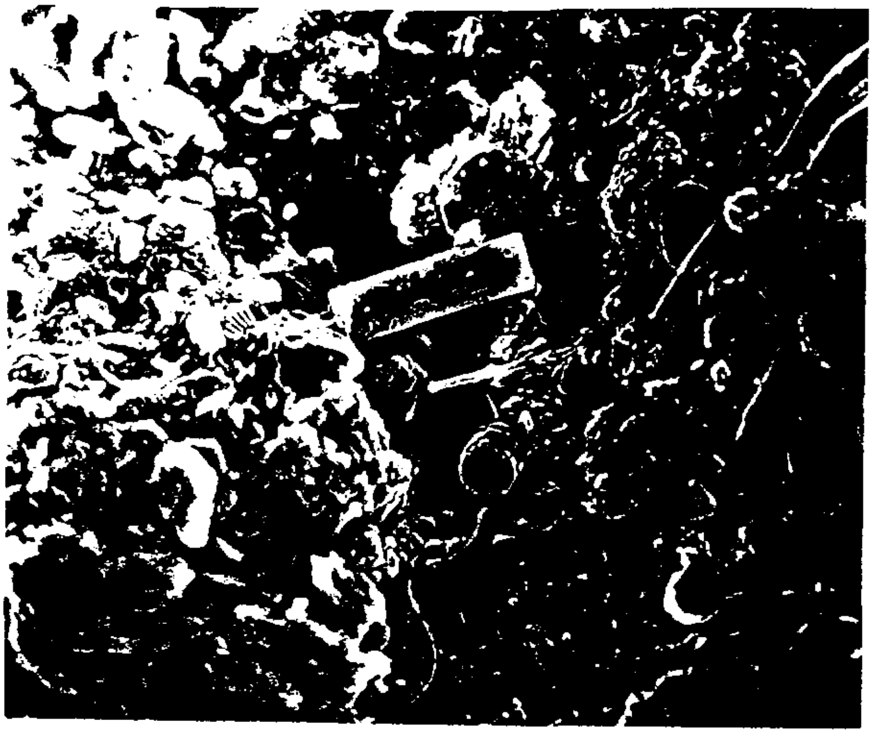


1. Undiluted Sediment. Biological Remains include Frustules of Centric and Pennate Diatoms: 1,200x magnification

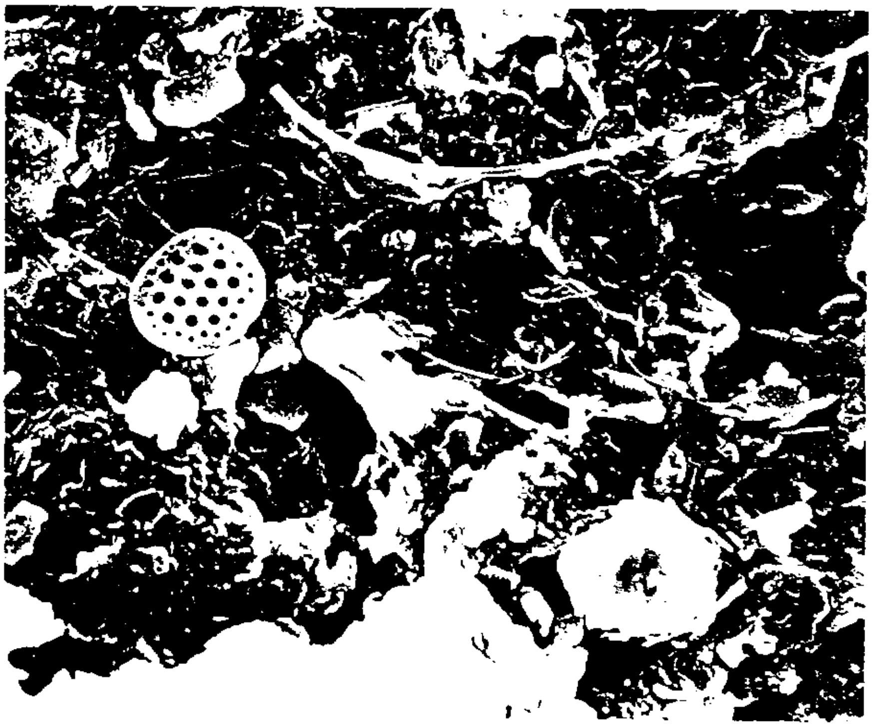


2. Undiluted Sediment. Biological Remains Include Frustules of Centric and Pennate Diatoms. Possible Remains of a Micro-Fossil at Left-Hand Edge of Micrograph: 3,600x magnification

Autumn (October 1996)



1. Undiluted Sediment. Biological Content; Centric and Filamentous Diatom Remains: 1,200x magnification



2. Undiluted Sediment. Pennate Diatom Remains, Possible Invertebrate Remains. Scale From Heliozoon Pinaciophora: 3,600x magnification.

Winter (February 1997)

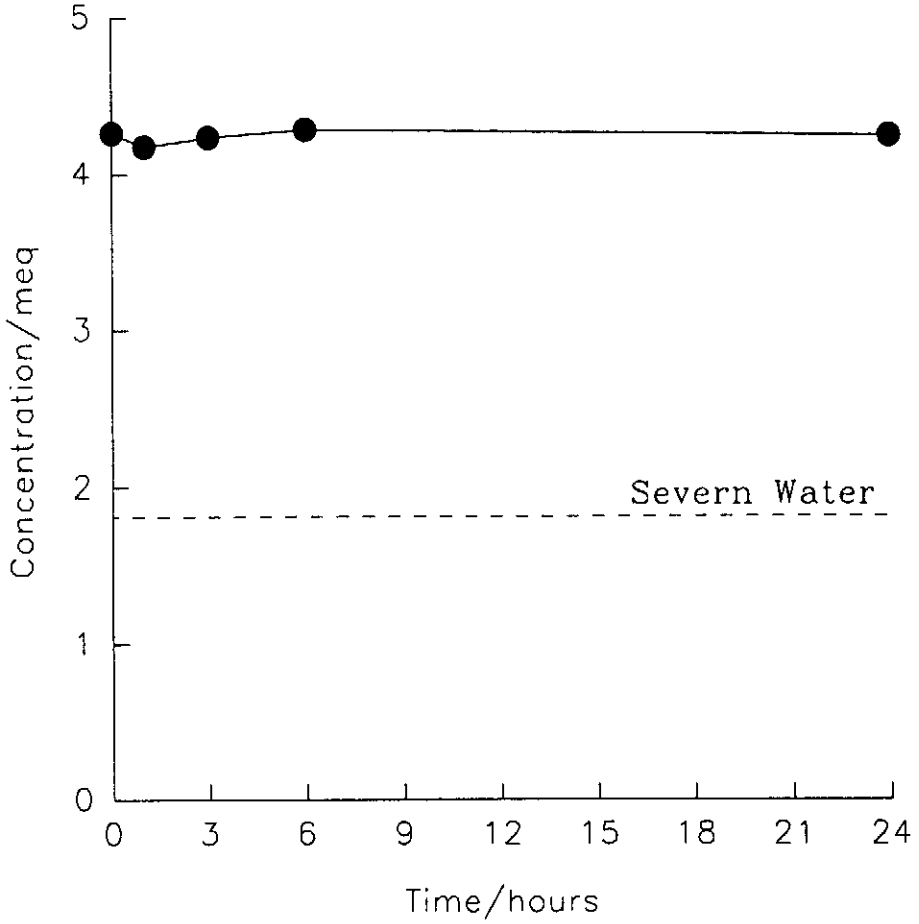
1. Undiluted Sediment. Pennate and Centric Diatoms, Fungal Filaments, Remains of Green Alga: 3,600x magnification.

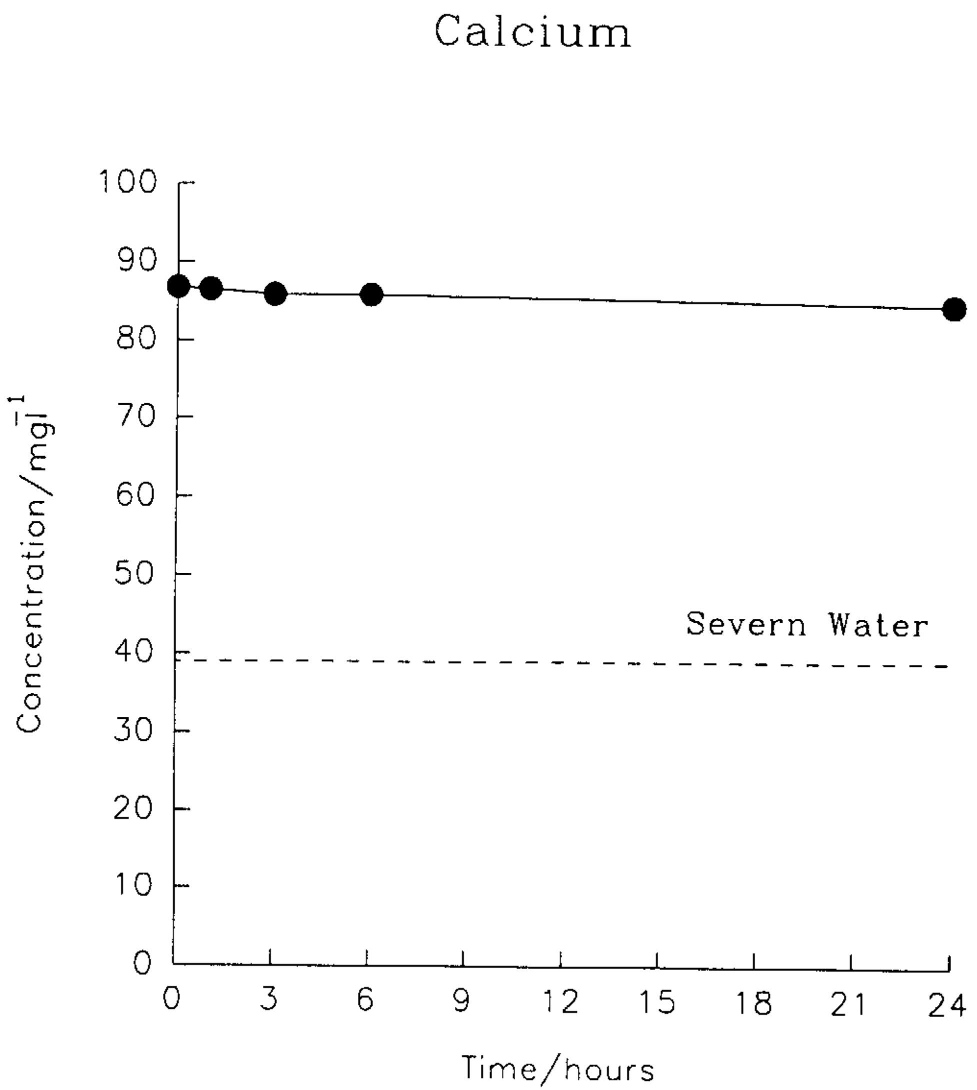
2. Undiluted Sediment. Biological Remains. Scaled Test of Testate Amoeba. 1,800x magnification.

Appendix B

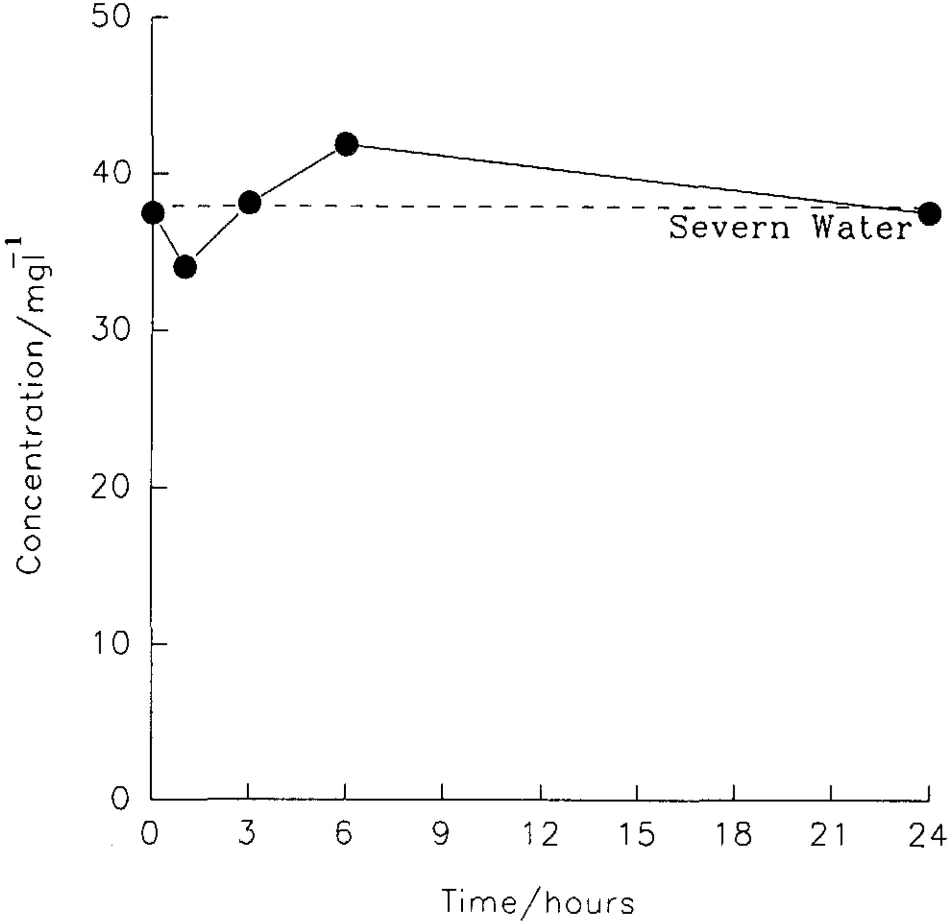
Chemical Changes in Sediment Water Mixing Experiments - Spring

Alkalinity

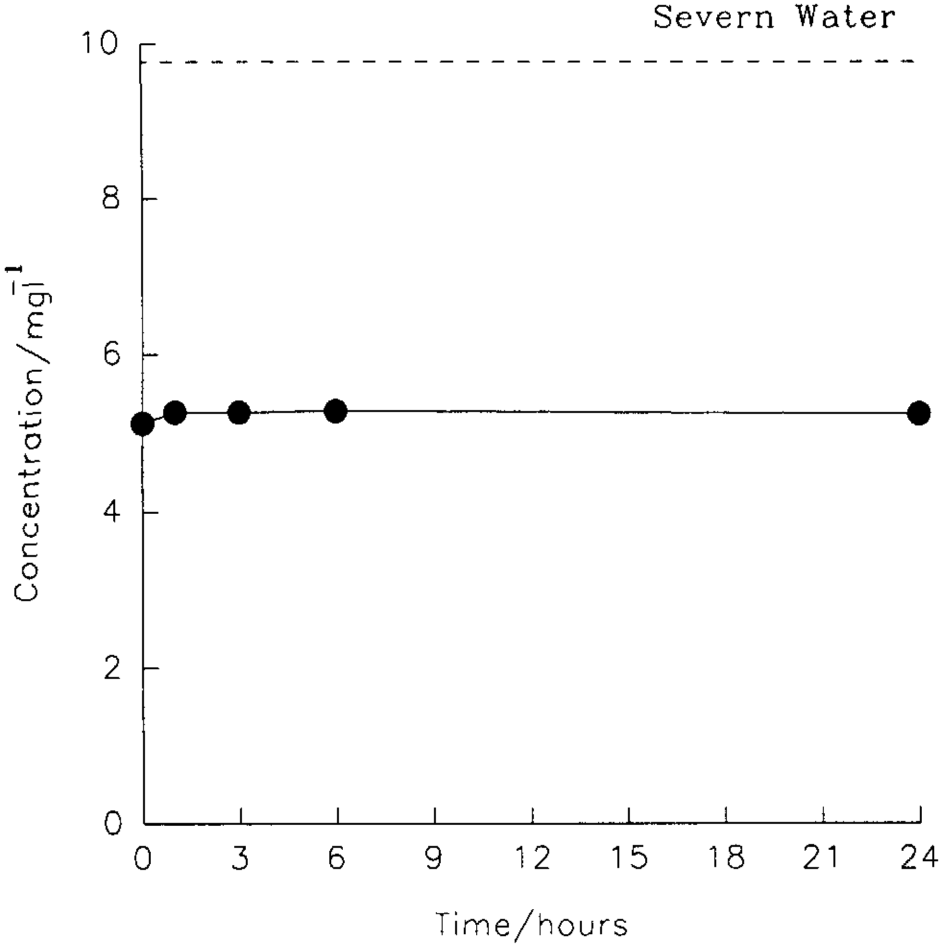

5
4
3
2
1
0
Concentration/meq
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

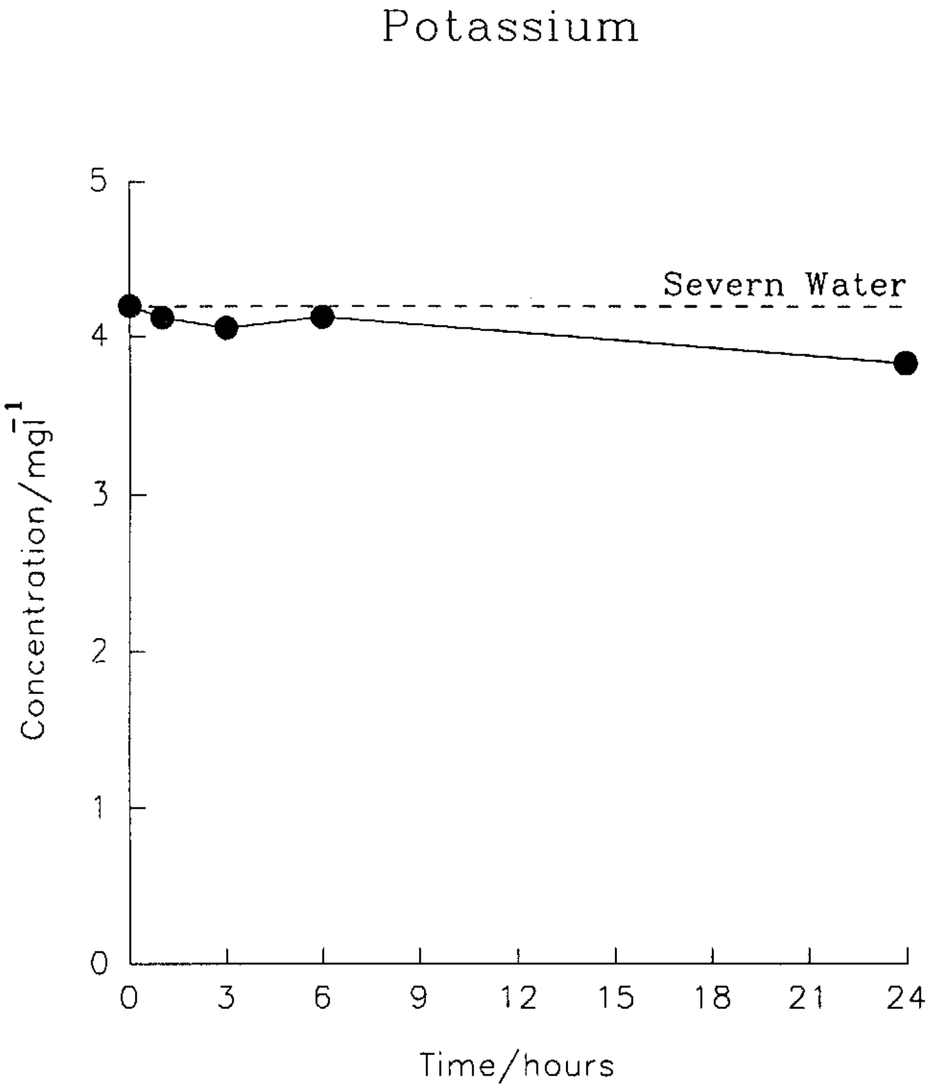

Calcium
100
90
80
70
60
50
40
30
20
10
0
Concentration/mgl^{-1}
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

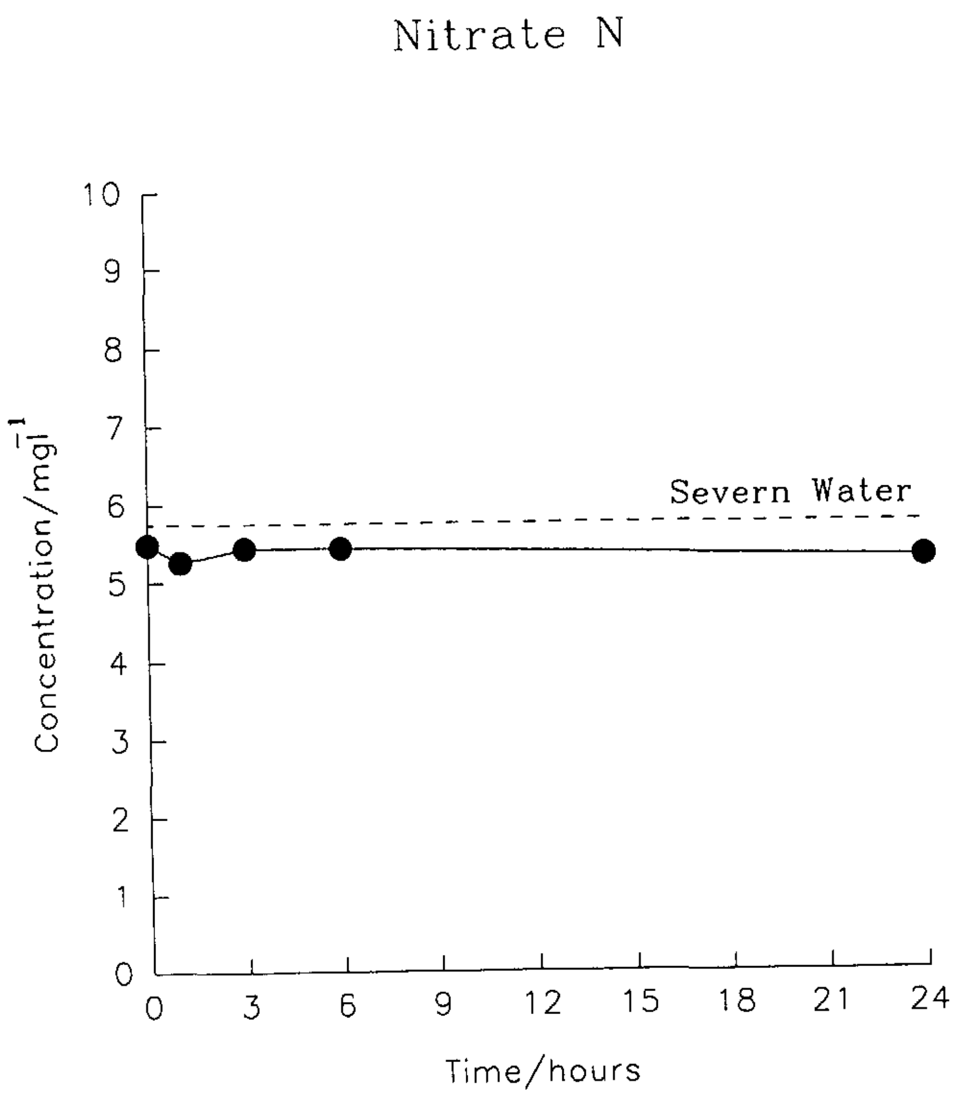
Chloride


Concentration/mgl^{-1}
50
40
30
20
10
0
0
3
6
9
12
15
18
21
24
Time/hours
Severn Water

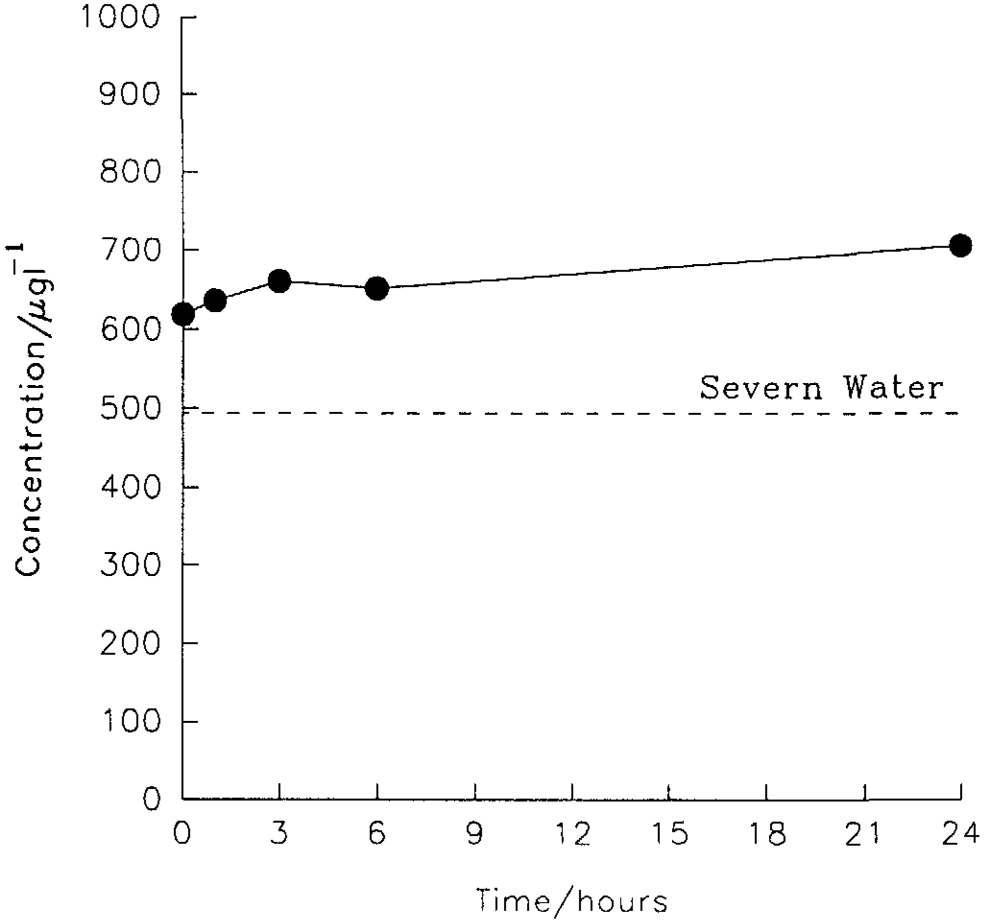
Magnesium


Severn Water
10
8
6
4
2
0
Concentration/mgl^{-1}
0
3
6
9
12
15
18
21
24
Time/hours

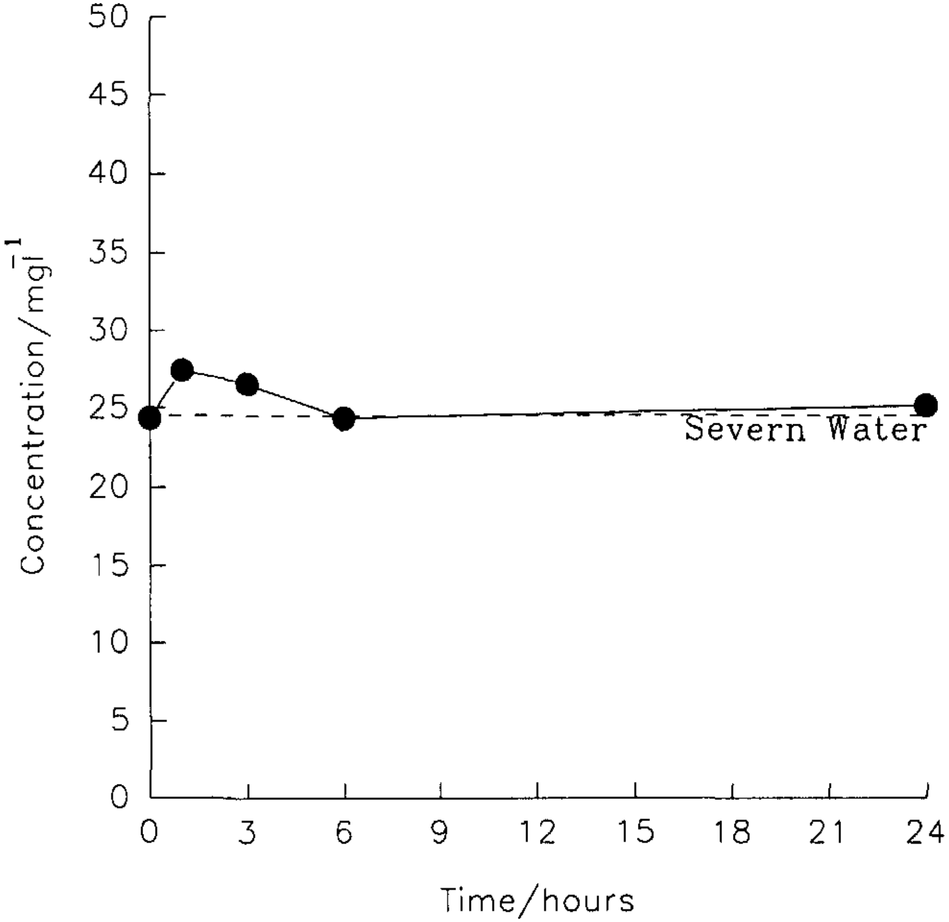

Potassium
Severn Water
Concentration/mgl^{-1}
0
1
2
3
4
5
Time/hours
0
3
6
9
12
15
18
21
24


Nitrate N
Concentration/mgl^{-1}
10
9
8
7
6
5
4
3
2
1
0
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

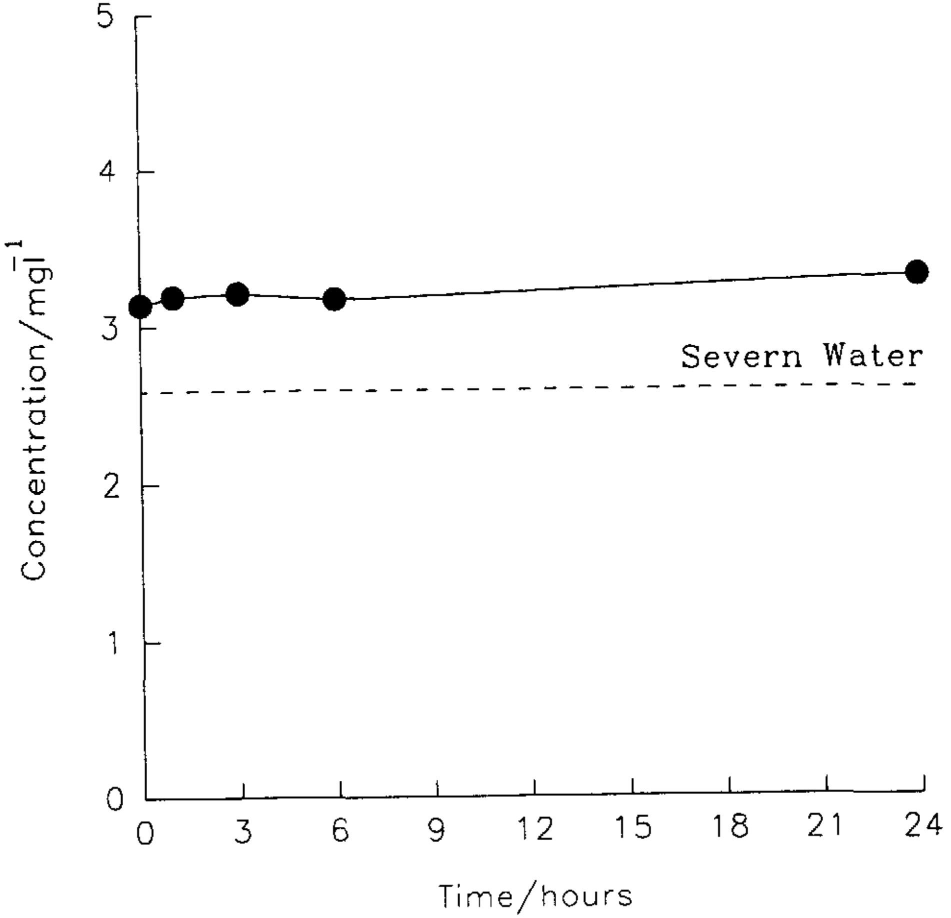
Phosphate P

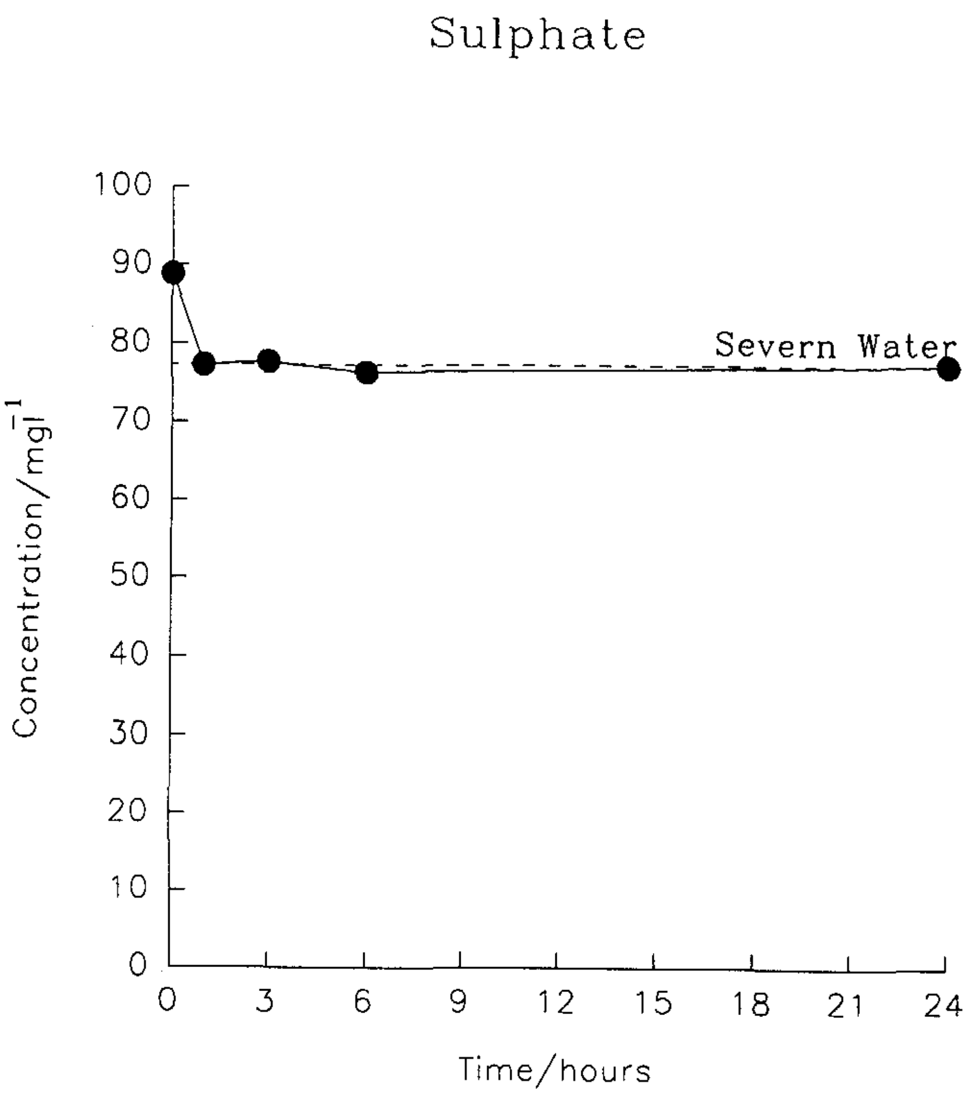

Concentration/$\mu g l^{-1}$
1000
900
800
700
600
500
400
300
200
100
0
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

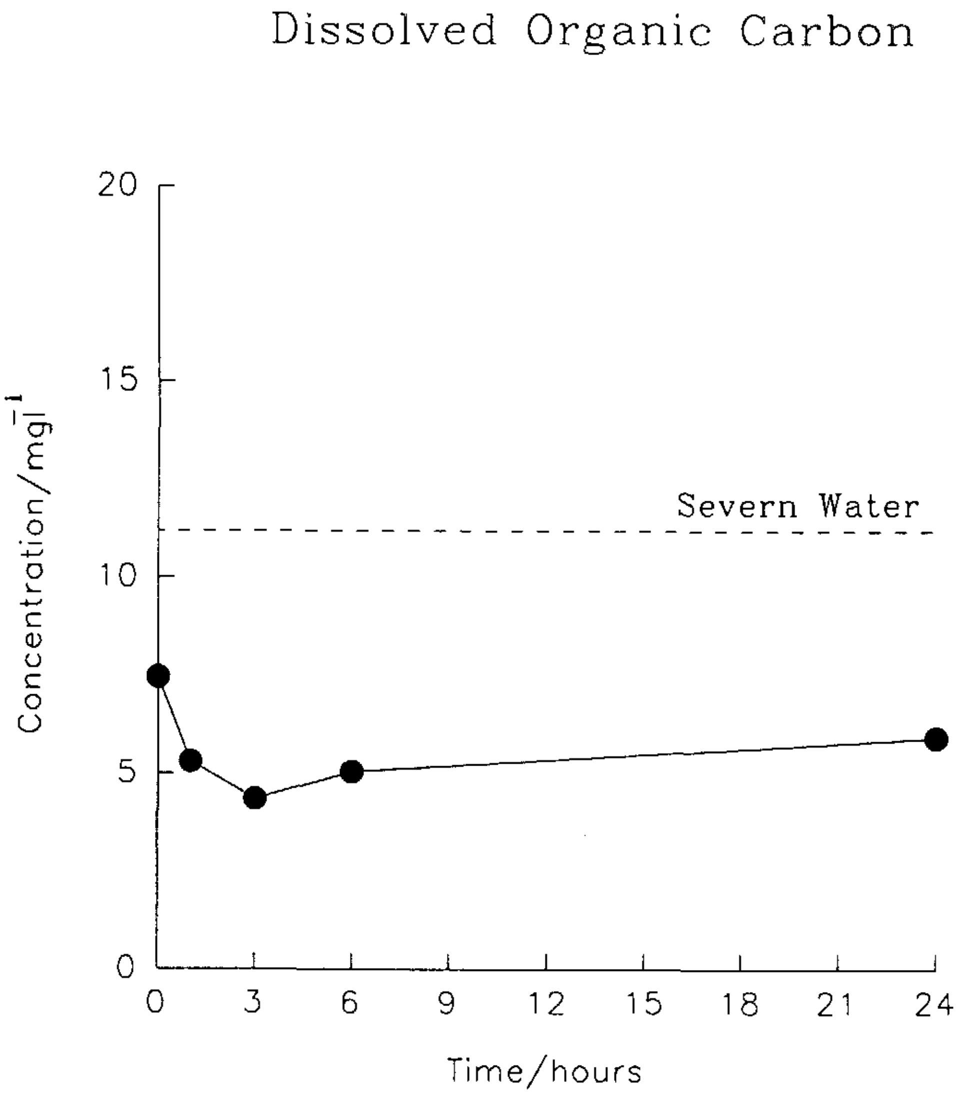
Sodium


Concentration/mgl^{-1}
50
45
40
35
30
25
20
15
10
5
0
0
3
6
9
12
15
18
21
24
Time/hours
Severn Water

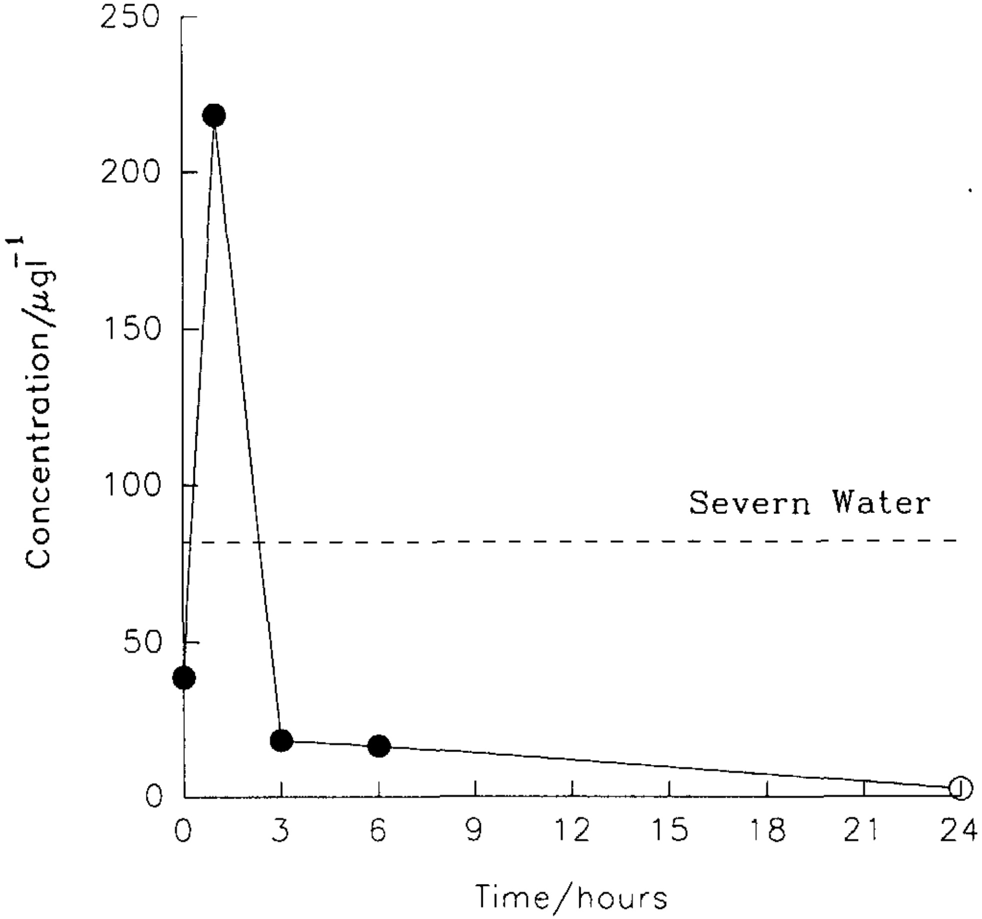
Silica Si


Concentration/mgl^{-1}
5
4
3
2
1
0
0
3
6
9
12
15
18
21
24
Time/hours
Severn Water

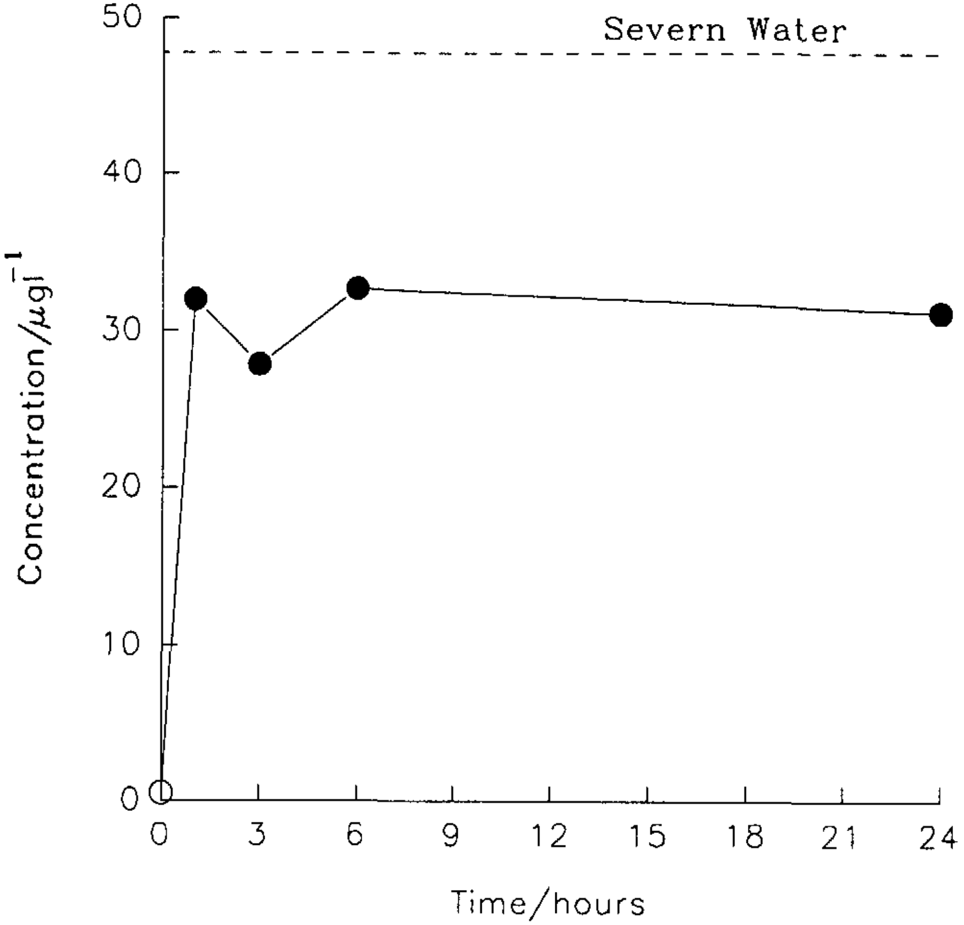

Sulphate
Concentration/mgl^{-1}
100
90
80
70
60
50
40
30
20
10
0
0
3
6
9
12
15
18
21
24
Time/hours
Severn Water


Dissolved Organic Carbon
Concentration/mgl^{-1}
20
15
10
5
0
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

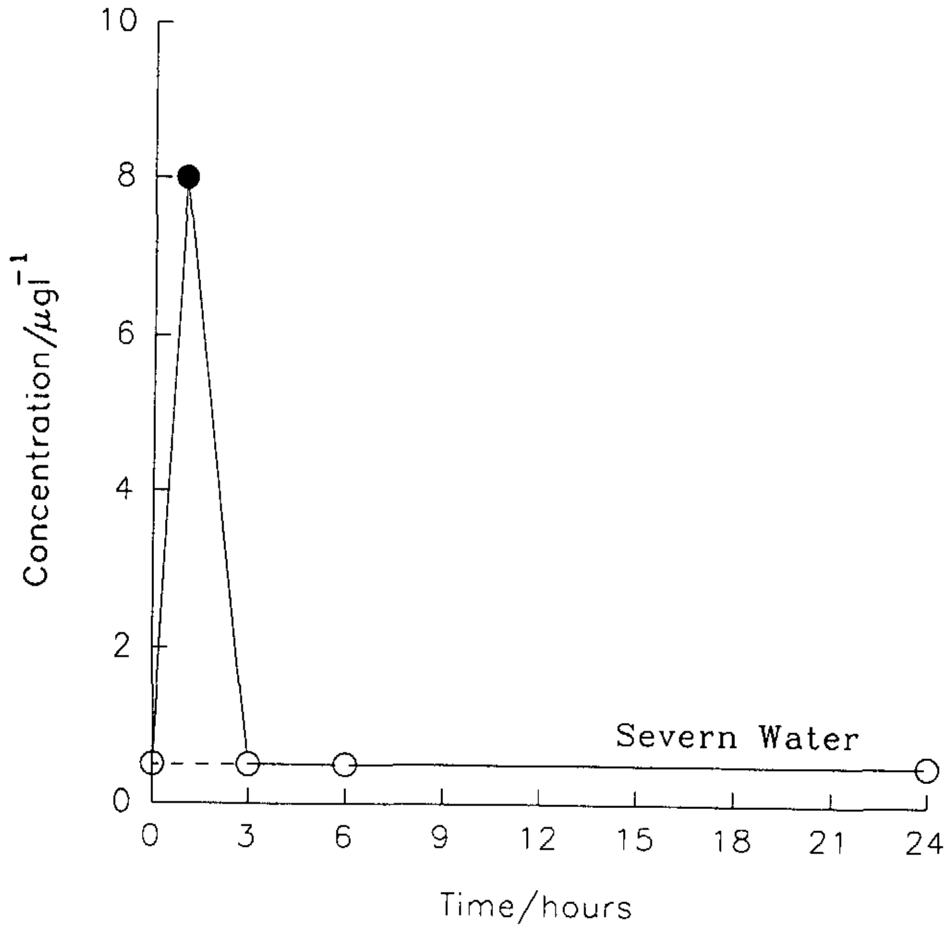
Aluminium


Concentration/μgl^{-1}
250
200
150
100
50
0
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

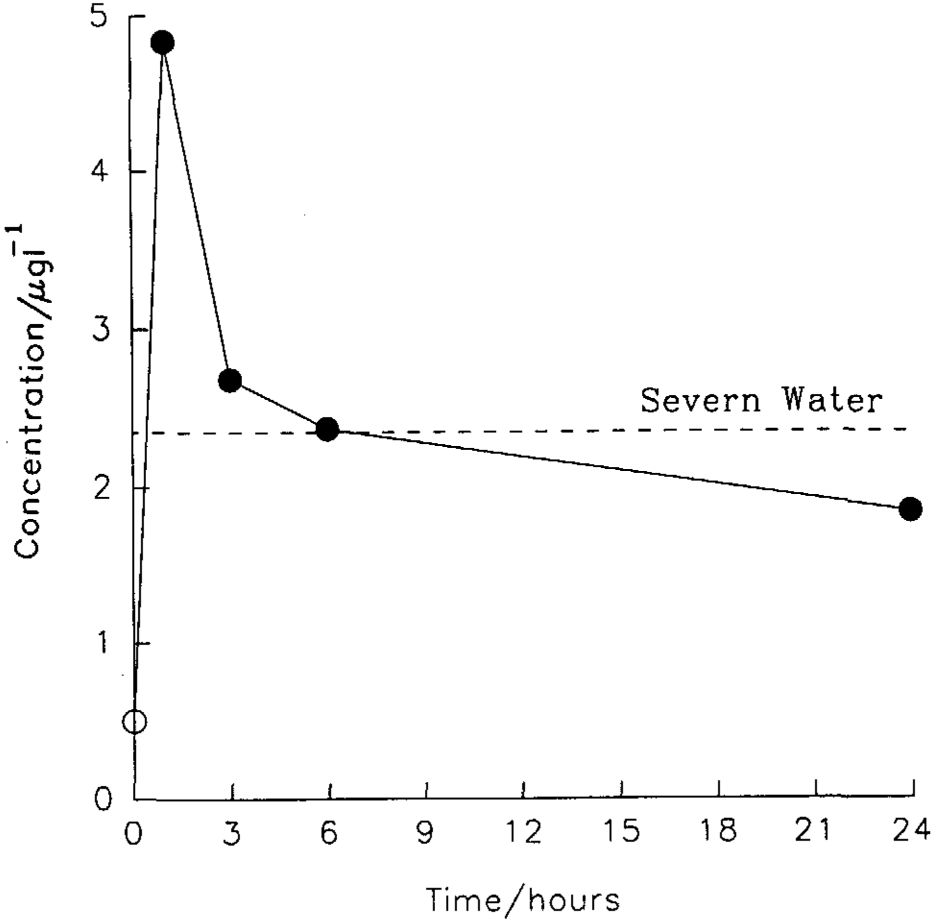
Barium


Severn Water
Concentration/$\mu g l^{-1}$
50
40
30
20
10
0
0
3
6
9
12
15
18
21
24
Time/hours

Cadmium

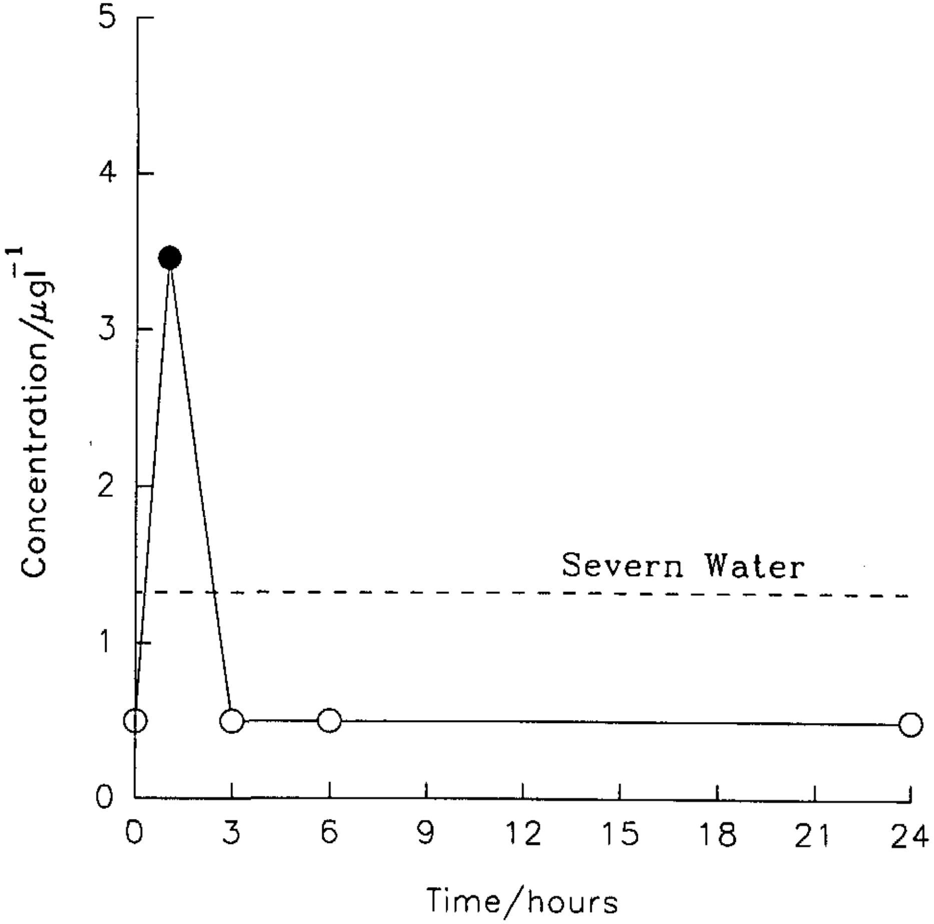

Concentration/μgl^{-1}
10
8
6
4
2
0
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Copper

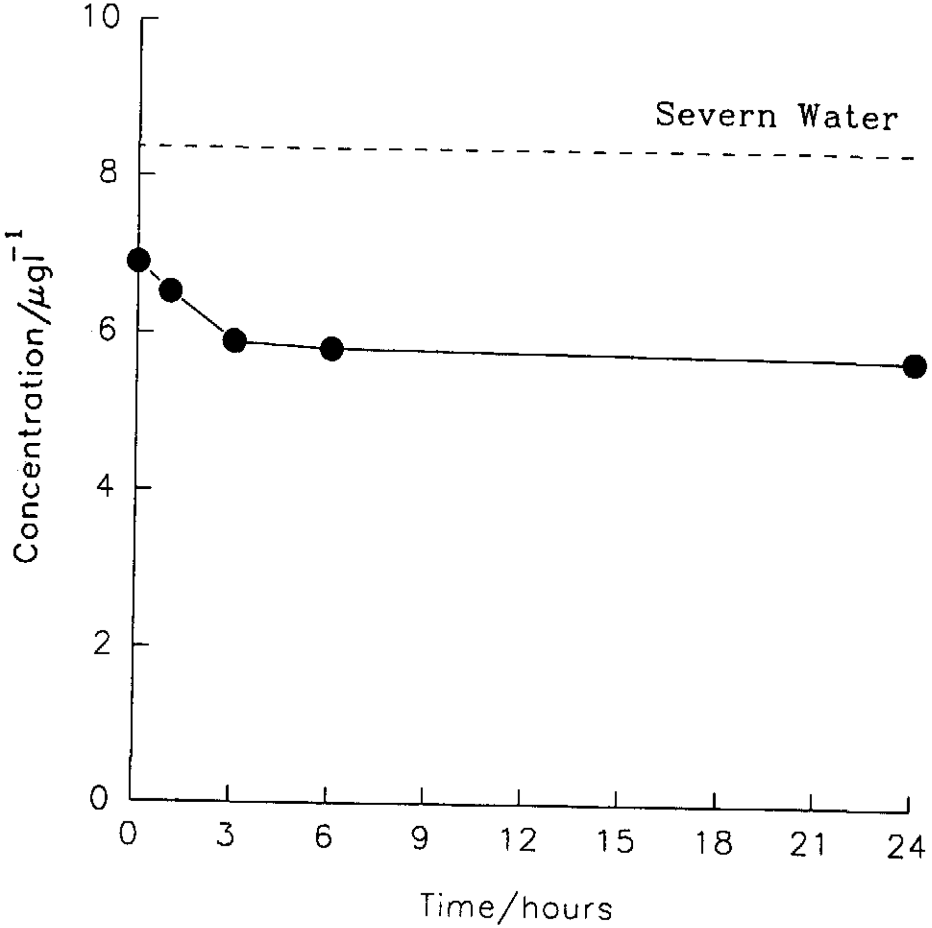


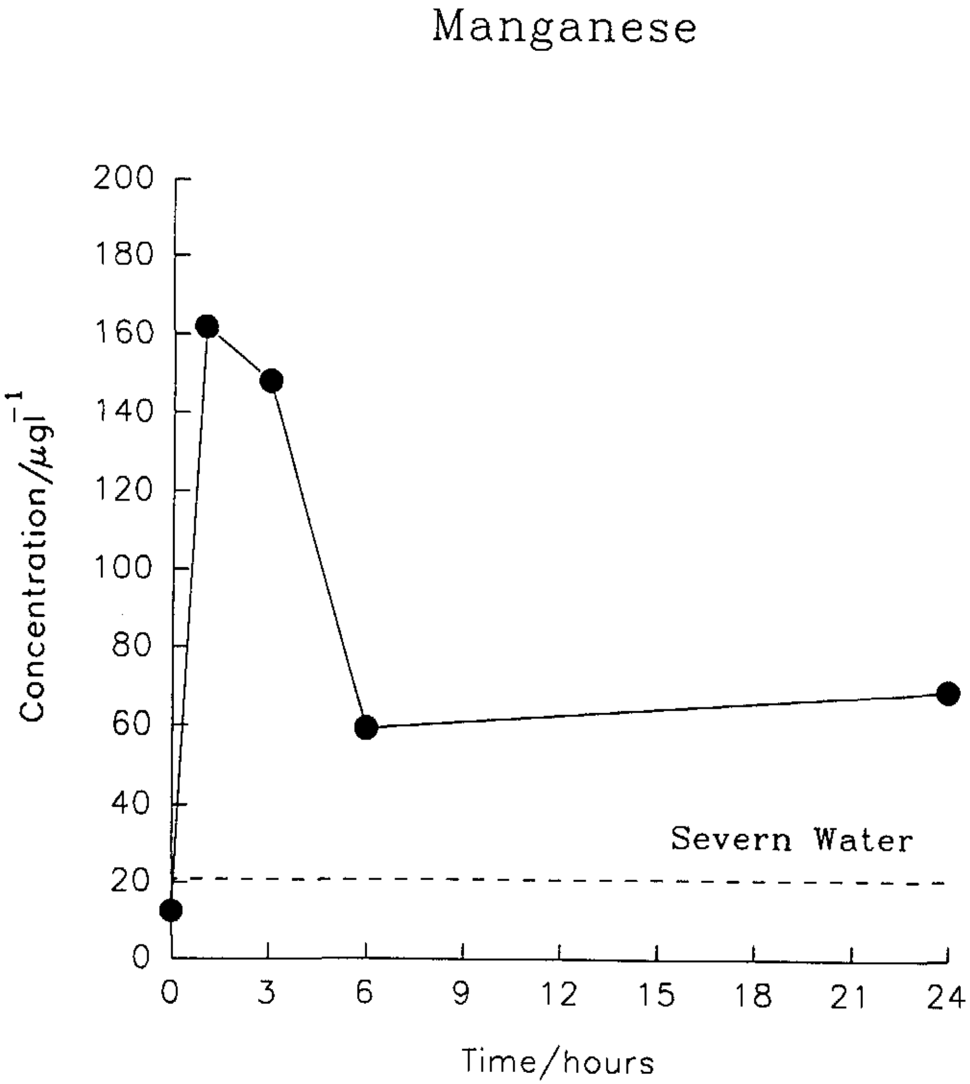
Concentration/$\mu g l^{-1}$
0
1
2
3
4
5
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Lead

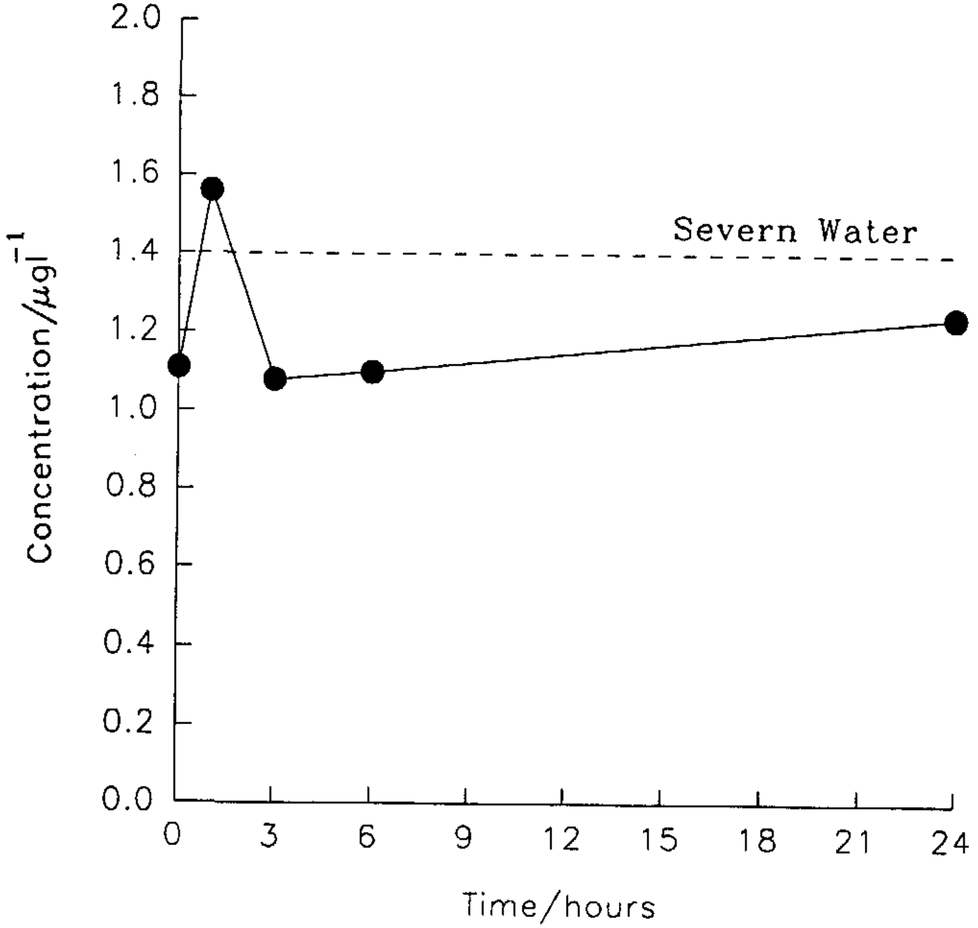

Concentration/μgl^{-1}
5
4
3
2
1
0
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Lithium

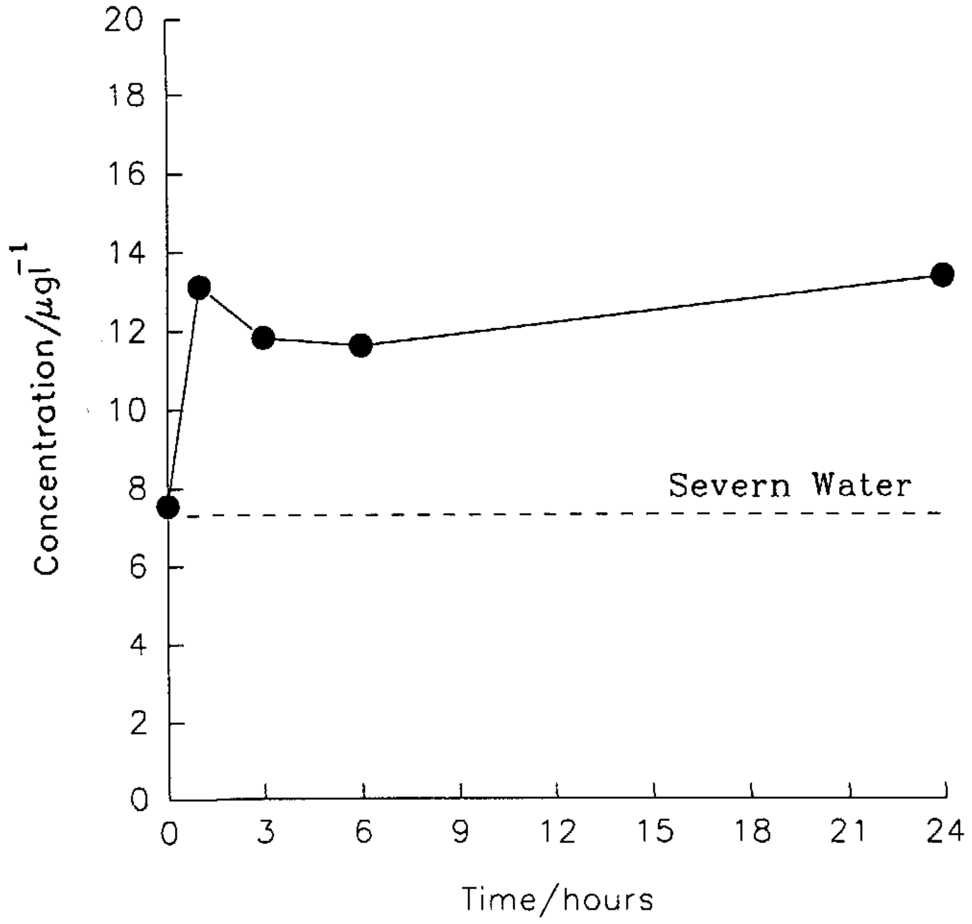

Severn Water
Concentration/$\mu g l^{-1}$
10
8
6
4
2
0
0
3
6
9
12
15
18
21
24
Time/hours


Manganese
Concentration/$\mu g l^{-1}$
0
20
40
60
80
100
120
140
160
180
200
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

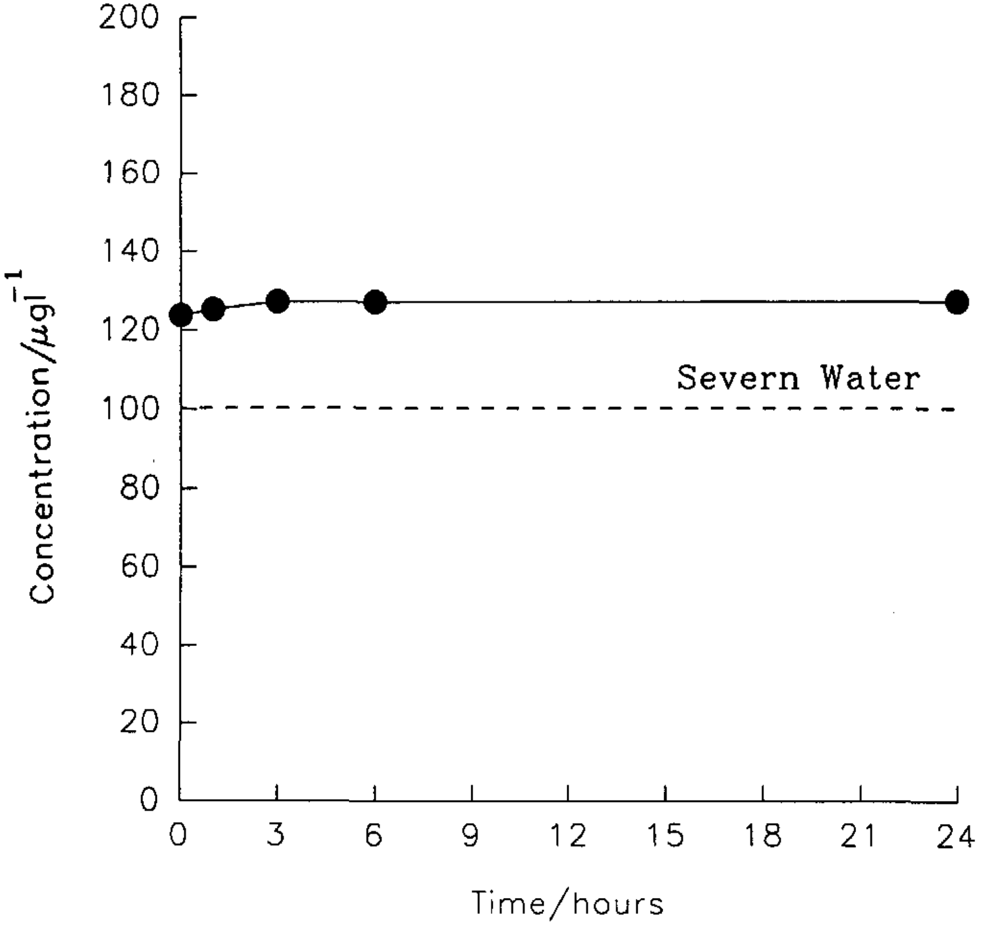
Molybdenum


2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Concentration/$\mu g l^{-1}$
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

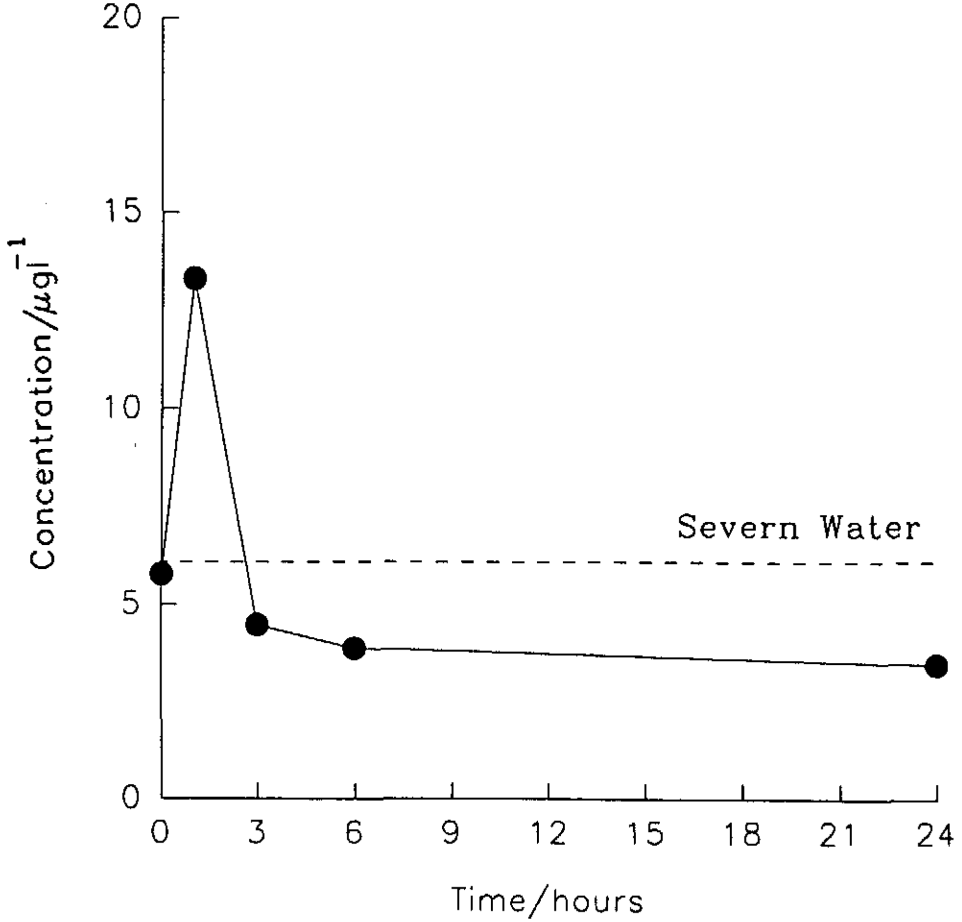
Nickel


Concentration/μgl^{-1}
20
18
16
14
12
10
8
6
4
2
0
0
3
6
9
12
15
18
21
24
Time/hours
Severn Water

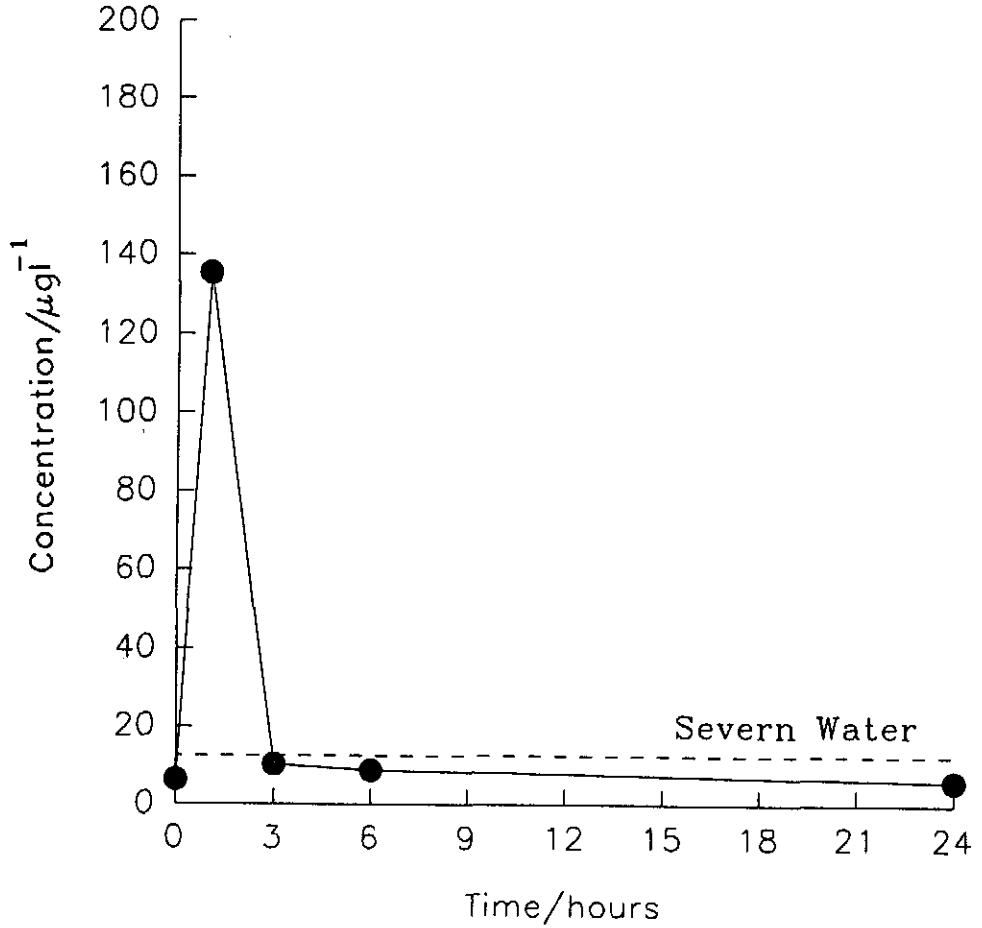
Strontium


Concentration/μgl^{-1}
200
180
160
140
120
100
80
60
40
20
0
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Titanium


Concentration/μgl^{-1}
20
15
10
5
0
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

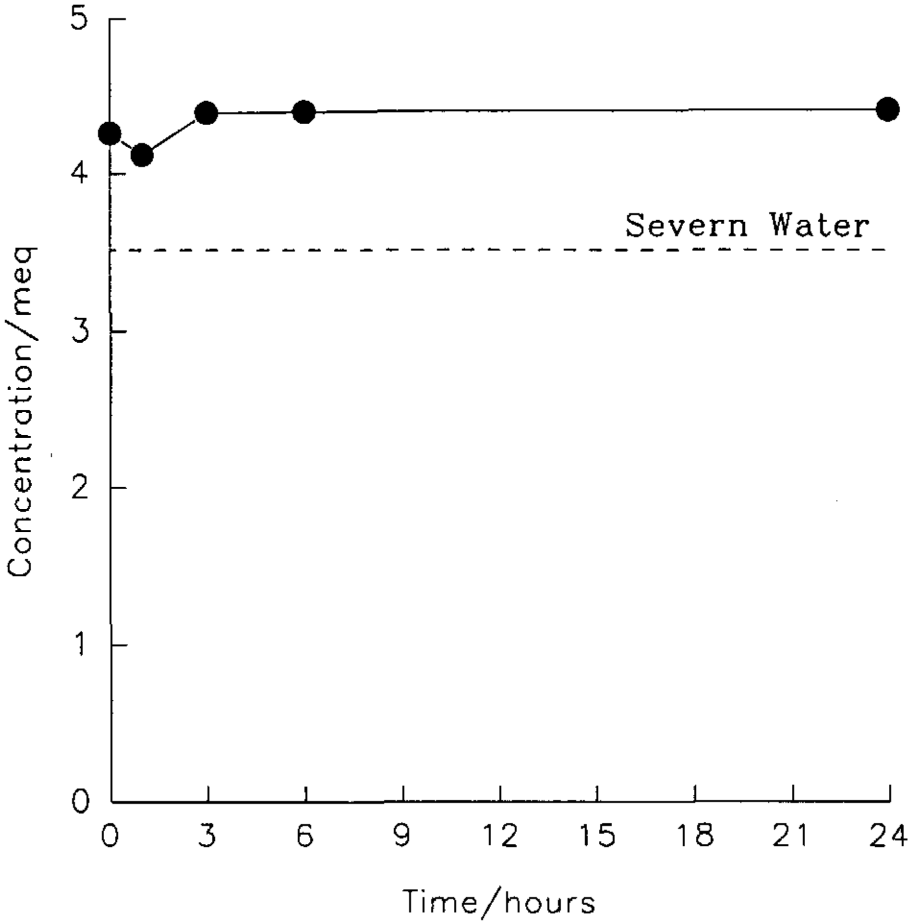
Zinc


200
180
160
140
120
100
80
60
40
20
0
Concentration/μgl^{-1}
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

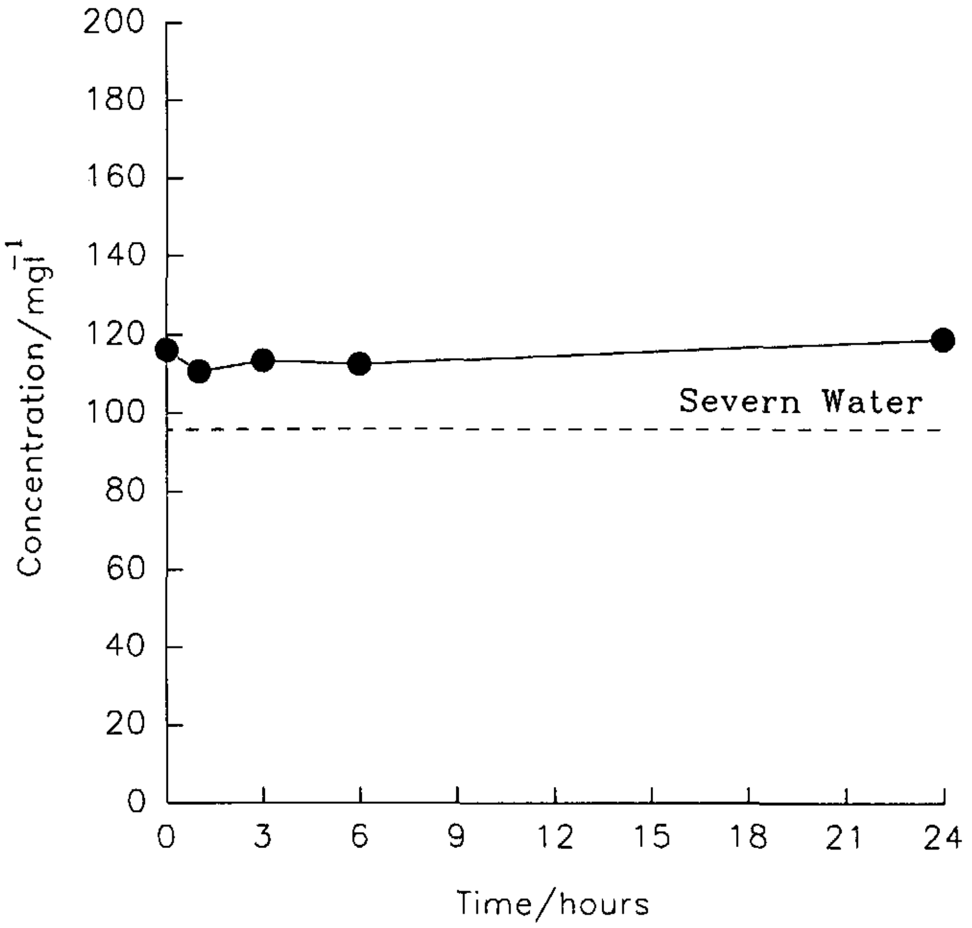
Appendix C

Chemical Changes in Sediment Water Mixing Experiments - Summer

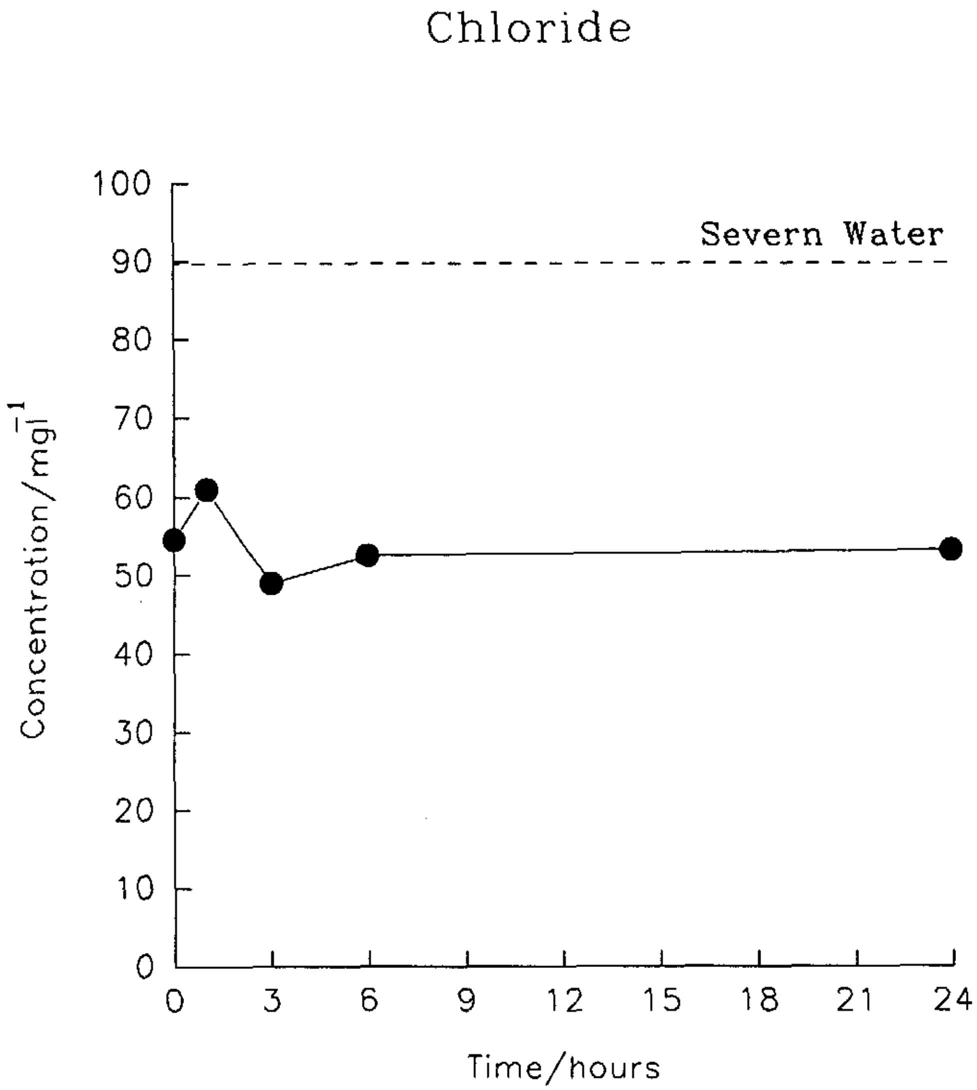
Alkalinity

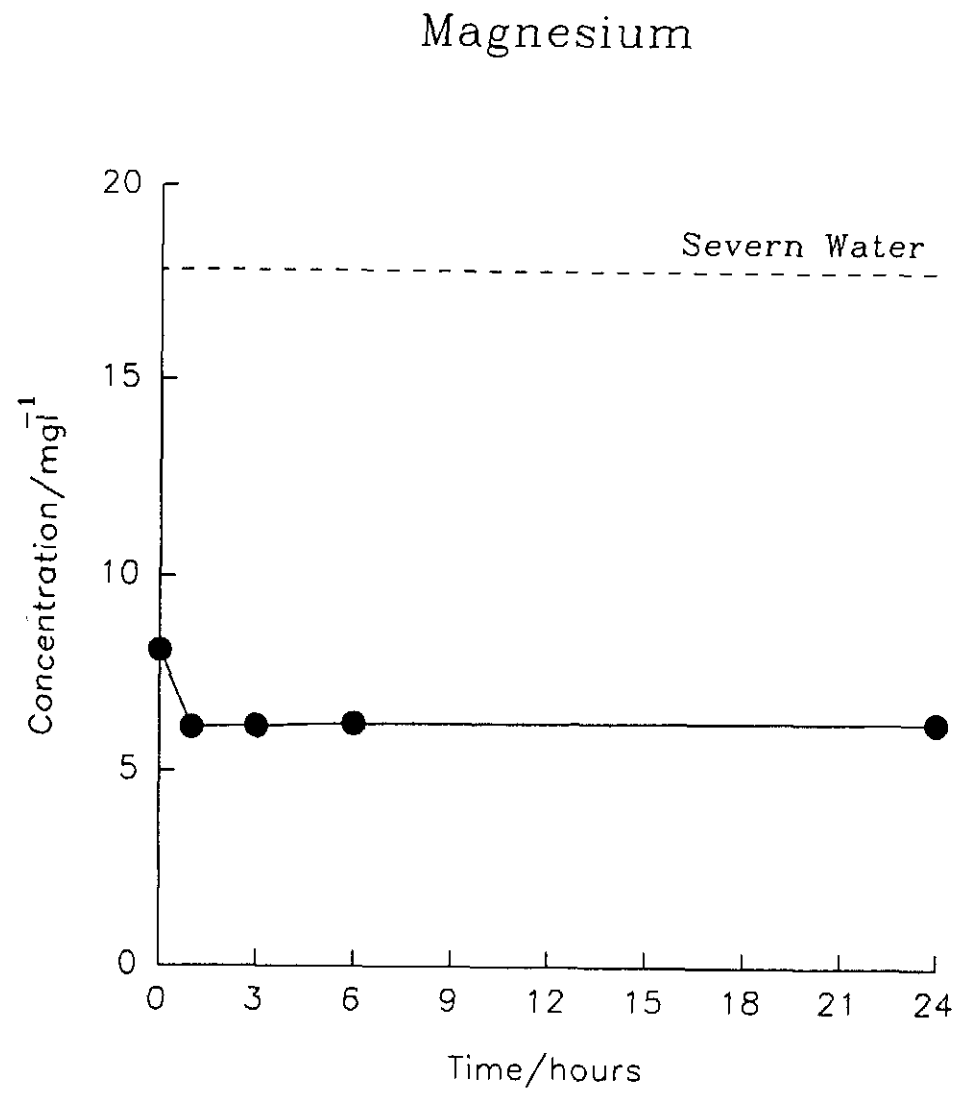

Severn Water
Concentration/meq
0
1
2
3
4
5
0
3
6
9
12
15
18
21
24
Time/hours

Calcium

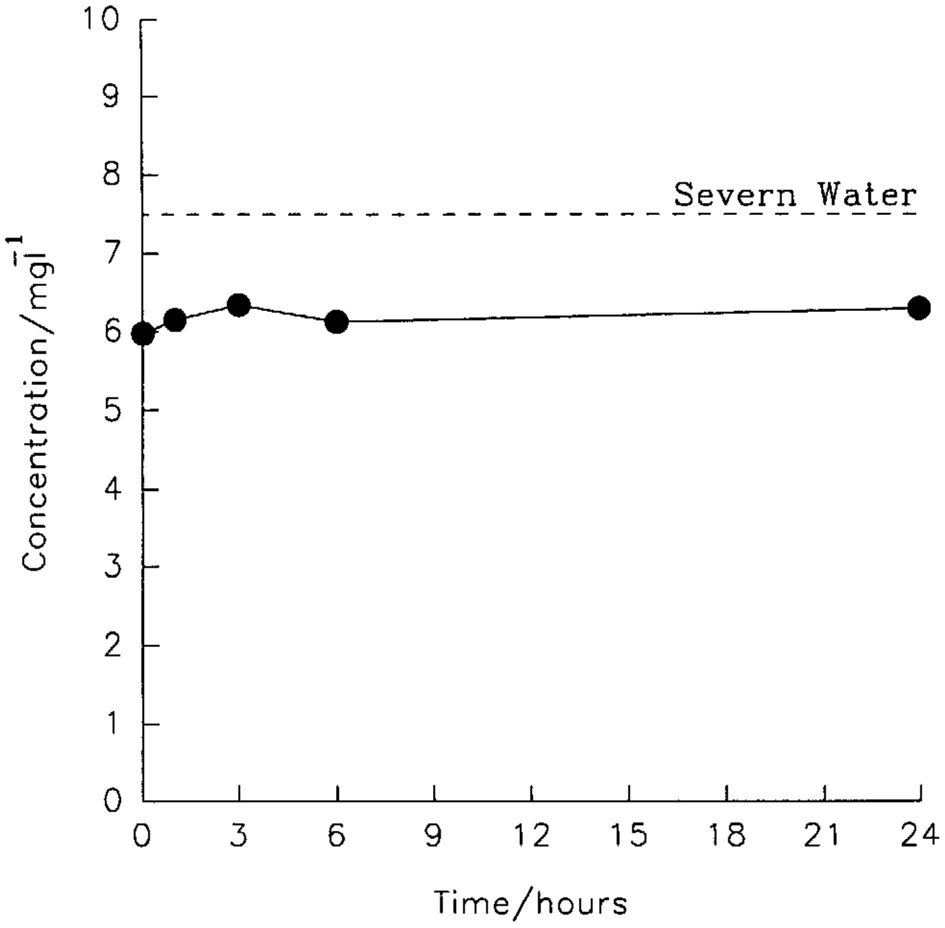


200
180
160
140
120
100
80
60
40
20
0
Concentration/mgl^{-1}
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

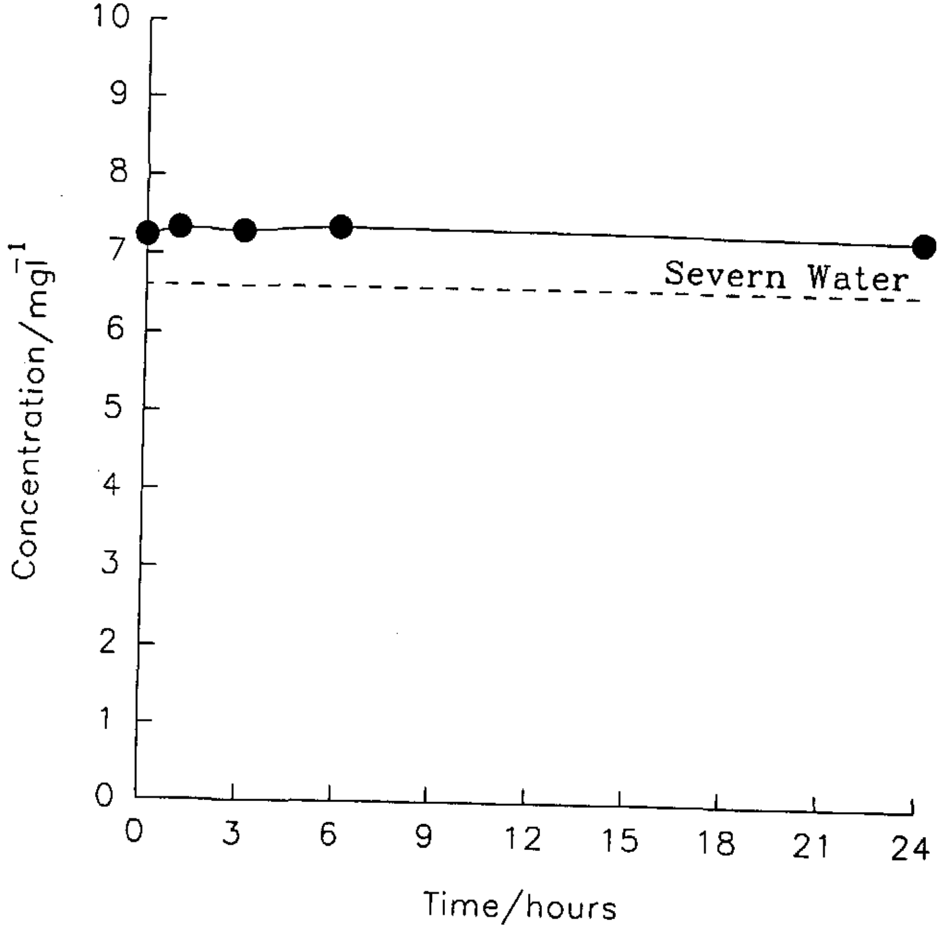

Chloride
Severn Water
Concentration/mgl^{-1}
100
90
80
70
60
50
40
30
20
10
0
0
3
6
9
12
15
18
21
24
Time/hours


Magnesium
Severn Water
Concentration/mgl^{-1}
20
15
10
5
0
0
3
6
9
12
15
18
21
24
Time/hours

Potassium

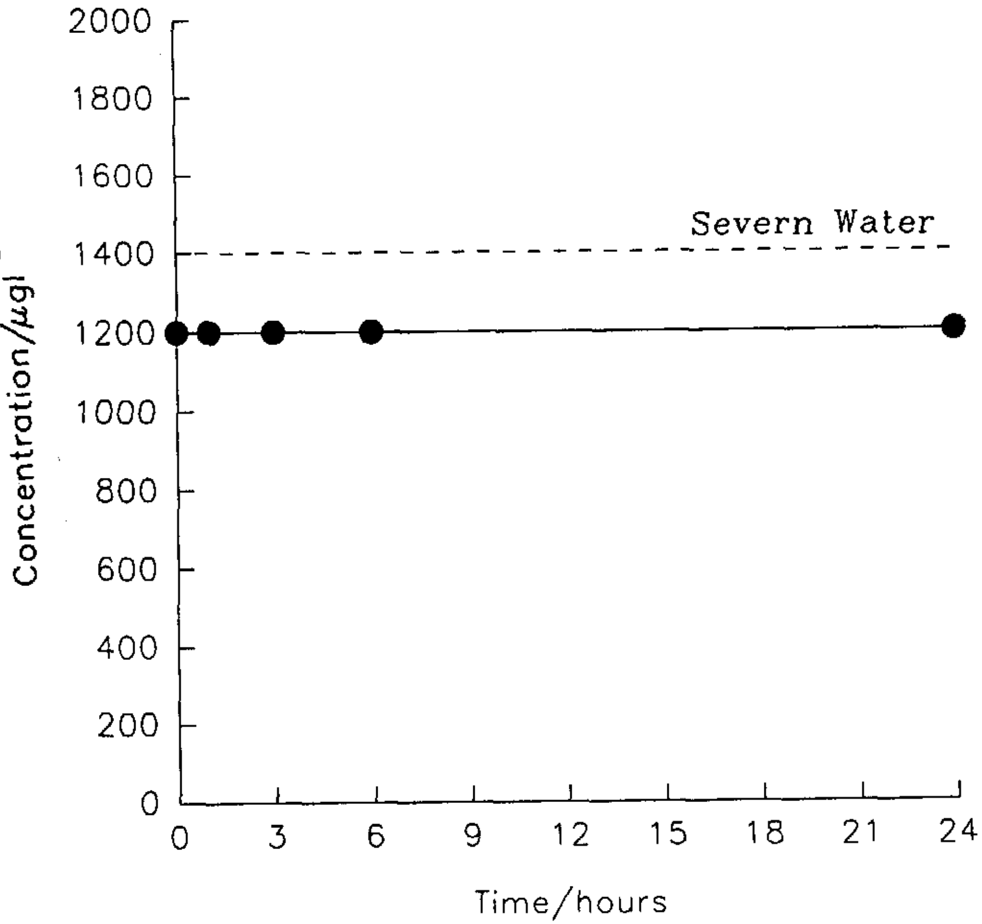

Severn Water
Concentration/mgl^{-1}
0
1
2
3
4
5
6
7
8
9
10
0
3
6
9
12
15
18
21
24
Time/hours

Nitrate N

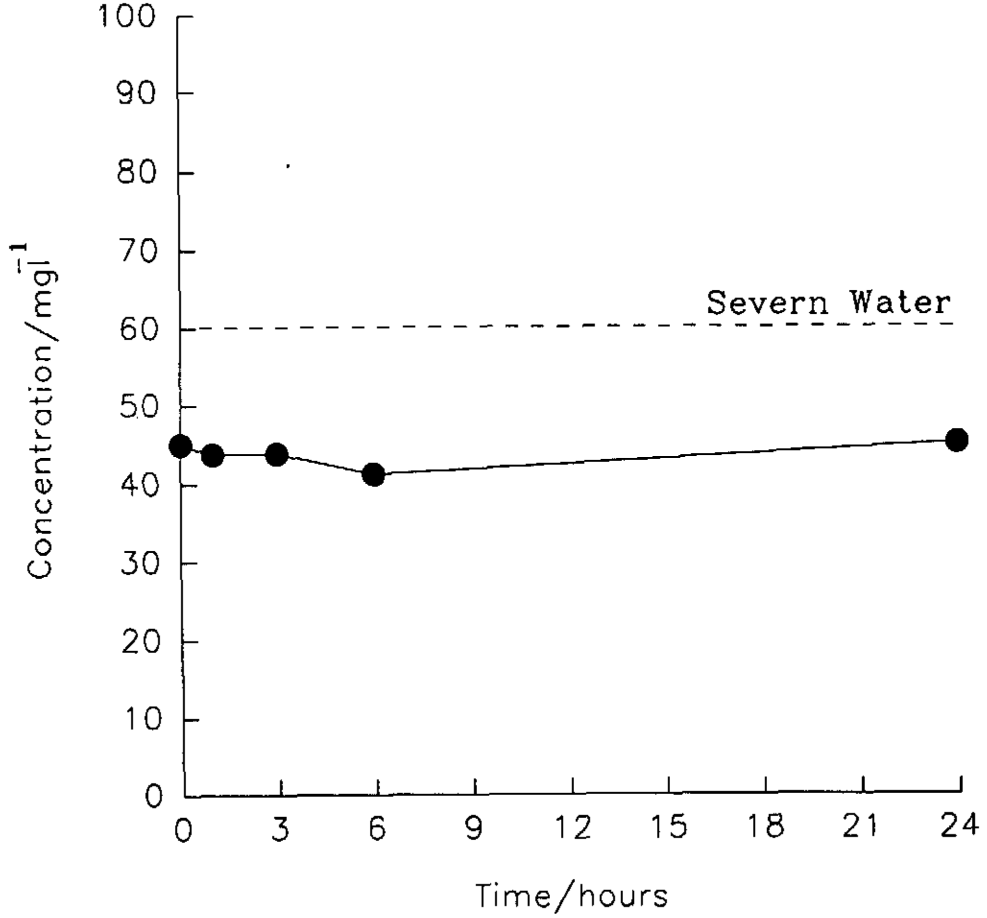


Concentration/mgl^{-1}
10
9
8
7
6
5
4
3
2
1
0
0
3
6
9
12
15
18
21
24
Time/hours
Severn Water

Phosphate P

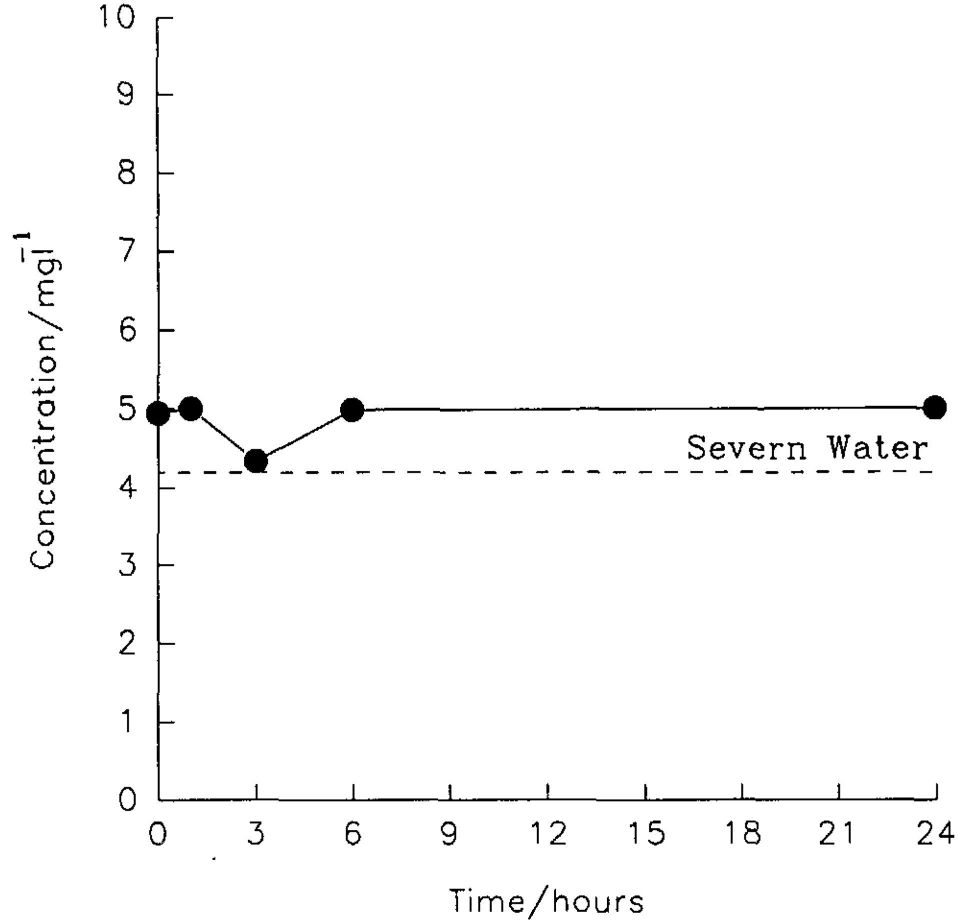

Severn Water
Concentration/μgl^{-1}
2000
1800
1600
1400
1200
1000
800
600
400
200
0
0
3
6
9
12
15
18
21
24
Time/hours

Sodium

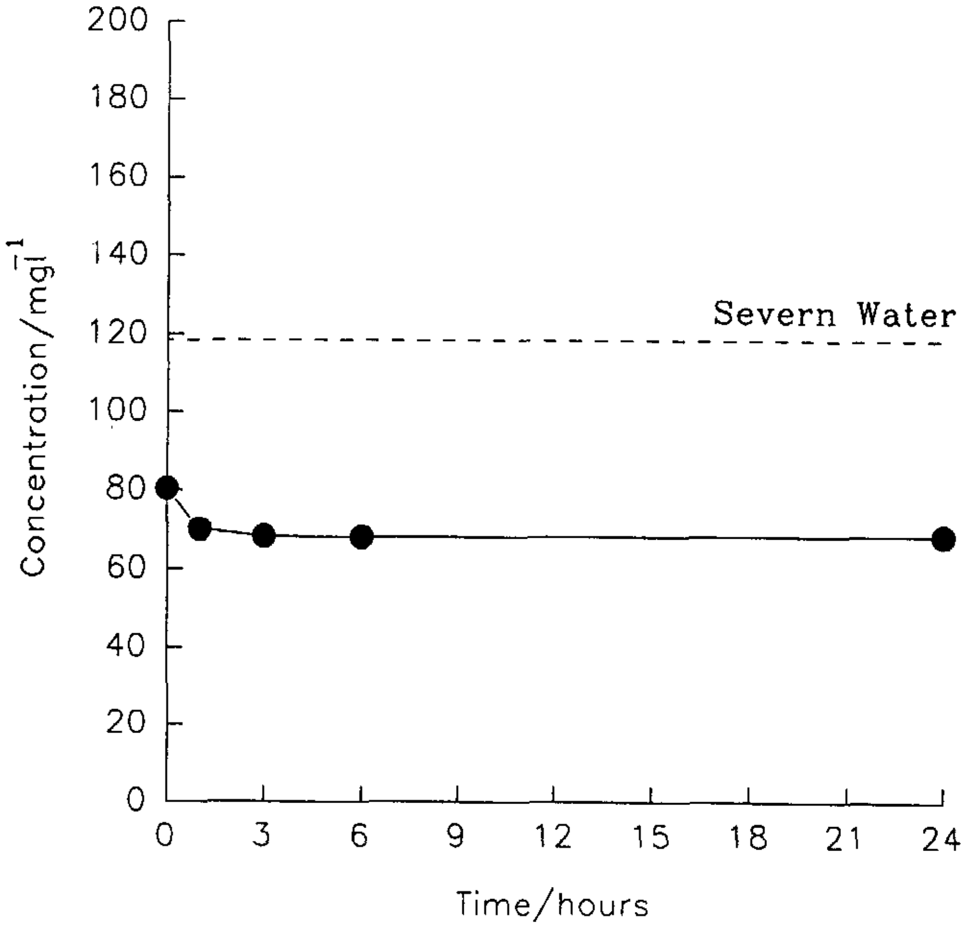


100
90
80
70
60
50
40
30
20
10
0
Concentration/mgl^{-1}
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

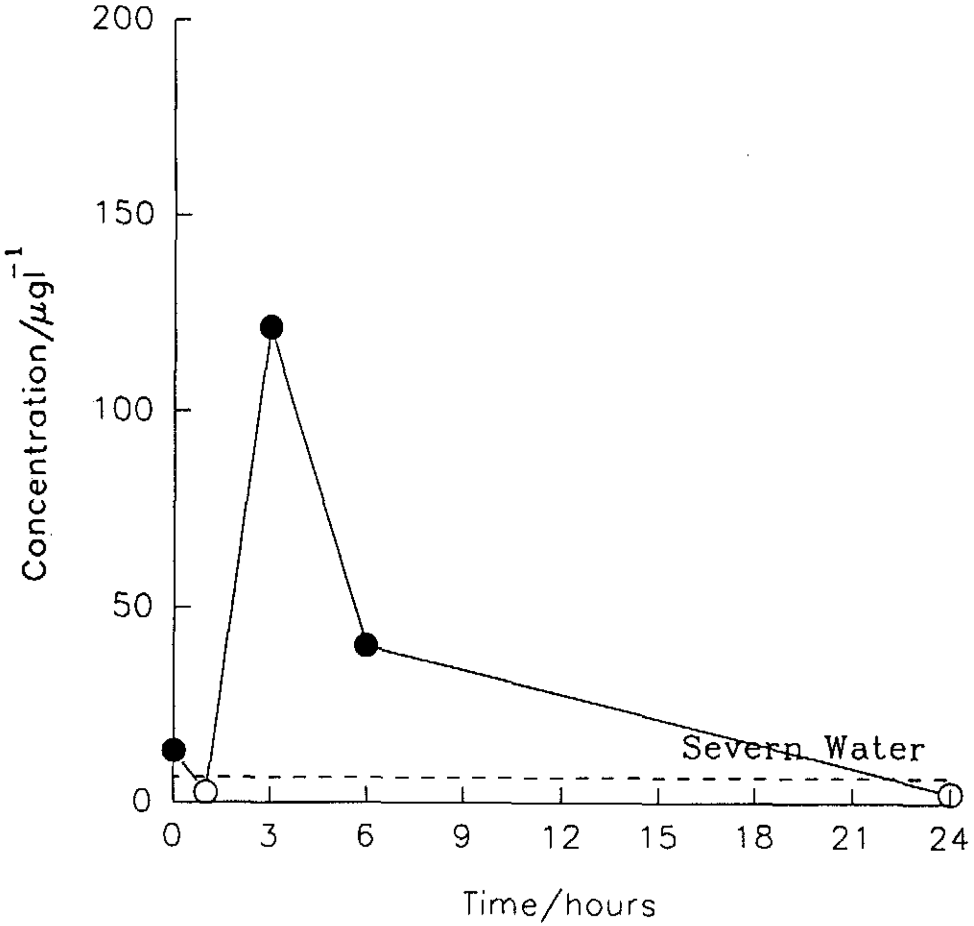
Silica Si


Concentration/mgl^{-1}
10
9
8
7
6
5
4
3
2
1
0
0
3
6
9
12
15
18
21
24
Time/hours
Severn Water

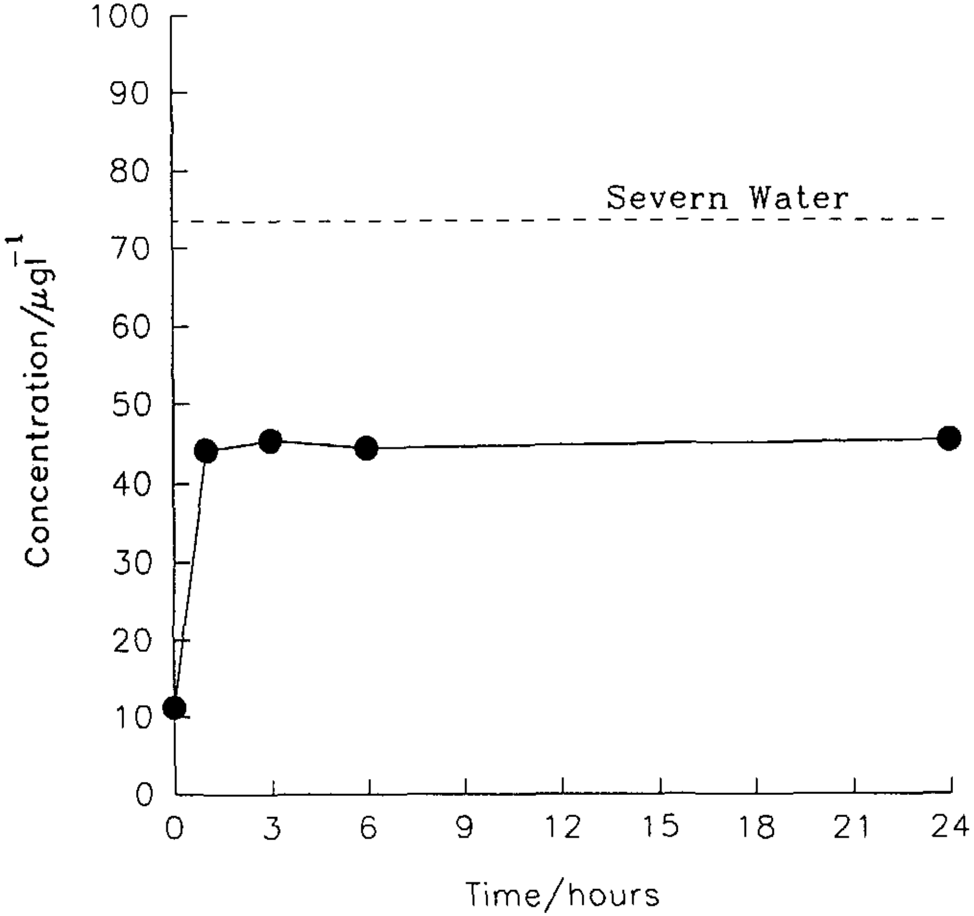
Sulphate


200
180
160
140
120
100
80
60
40
20
0
Concentration/mgl^{-1}
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

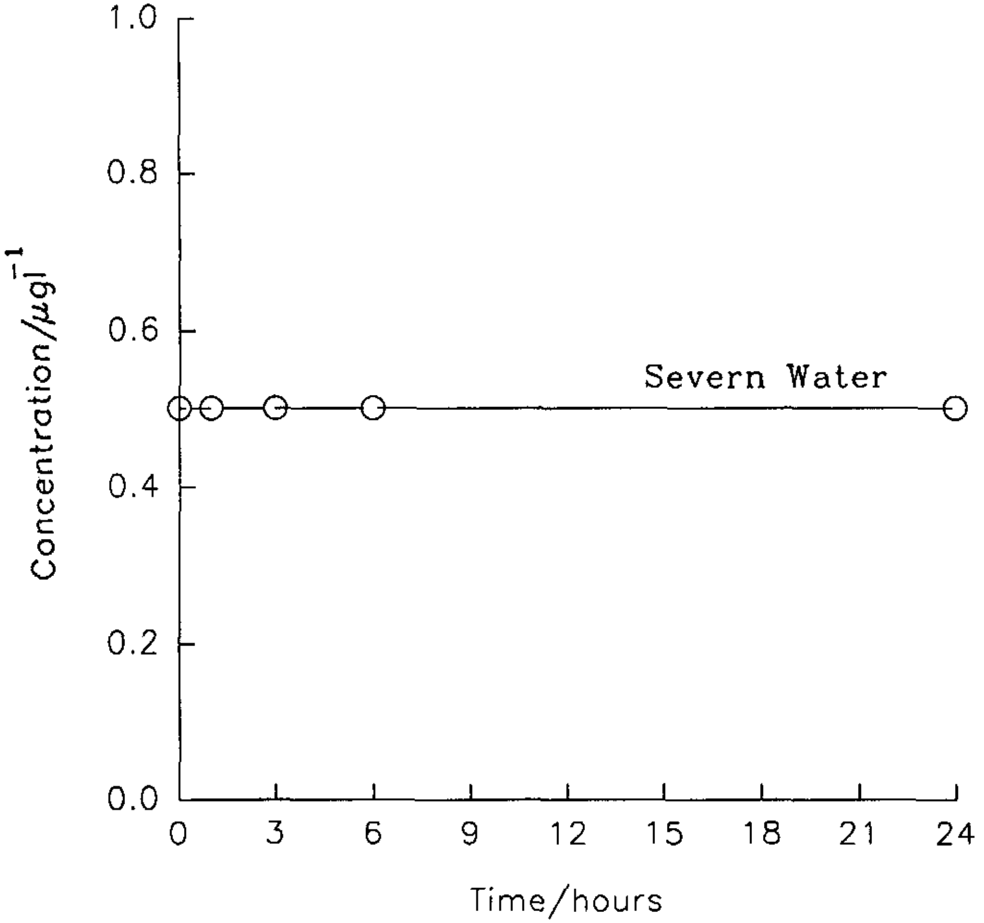
Aluminium


200
150
100
50
0
Concentration/μgl^{-1}
0
3
6
9
12
15
18
21
24
Time/hours
Severn Water

Barium

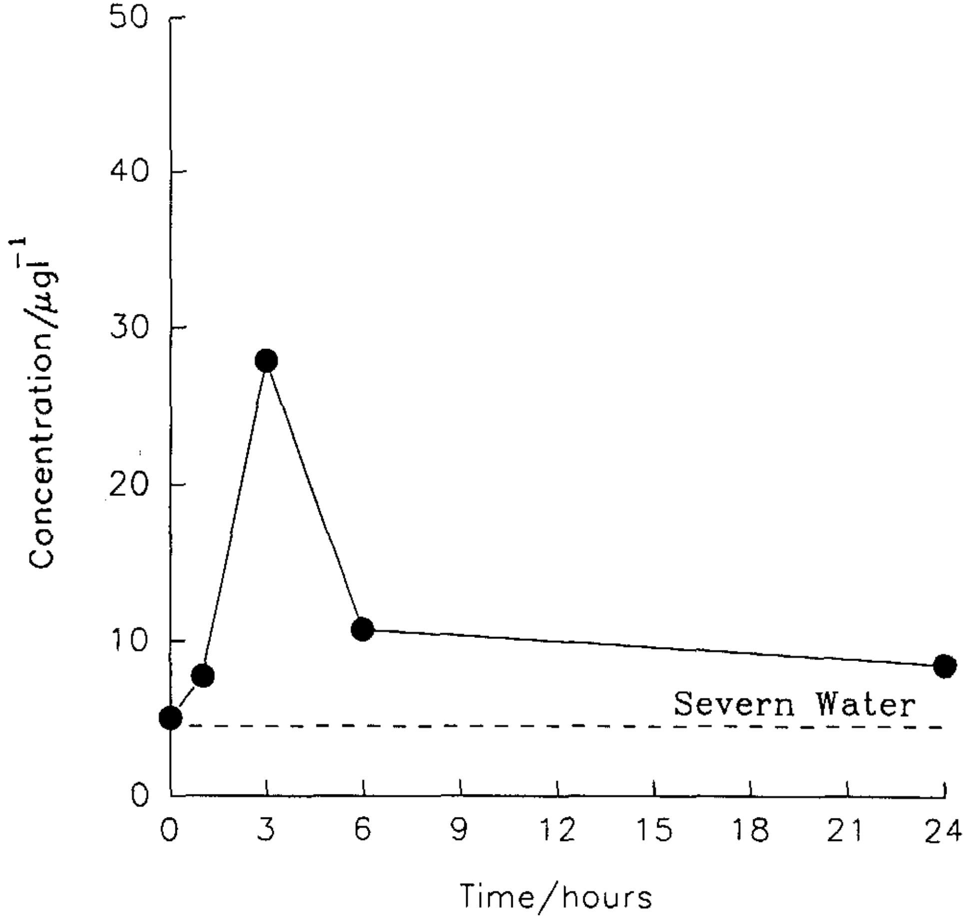

Severn Water
Concentration/$\mu g l^{-1}$
100
90
80
70
60
50
40
30
20
10
0
0
3
6
9
12
15
18
21
24
Time/hours

Cadmium



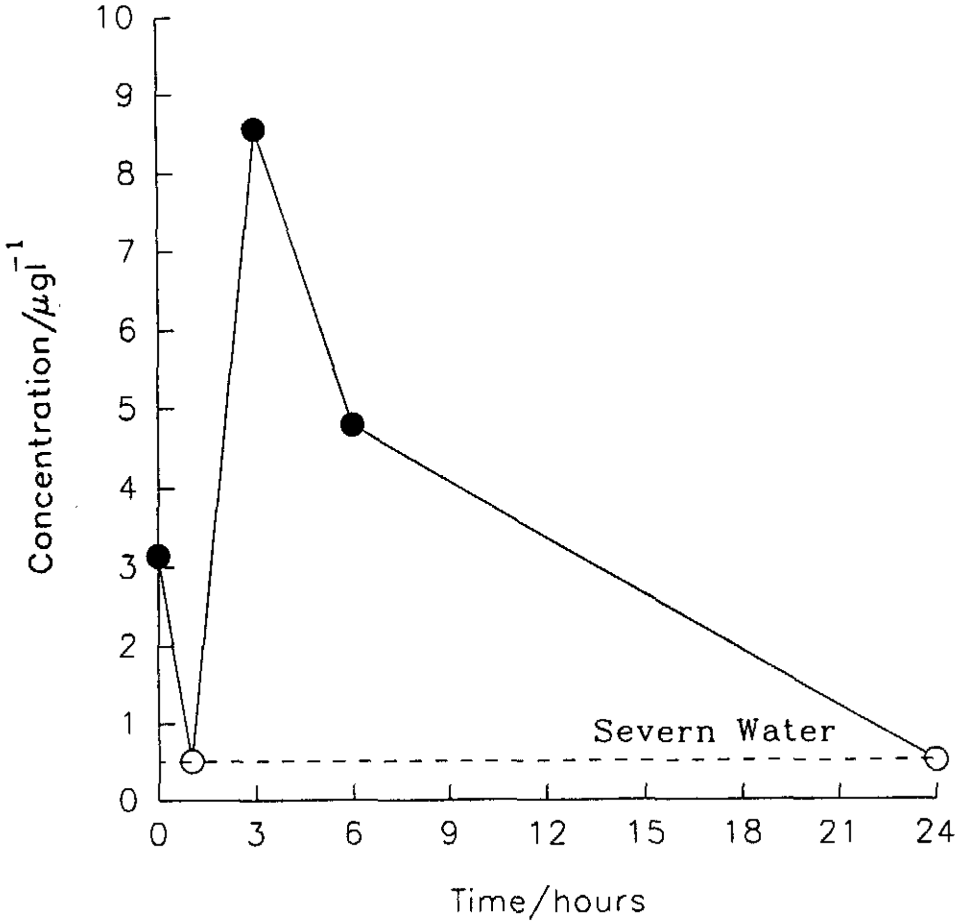
1.0
0.8
0.6
0.4
0.2
0.0
Concentration/$\mu g l^{-1}$
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Copper



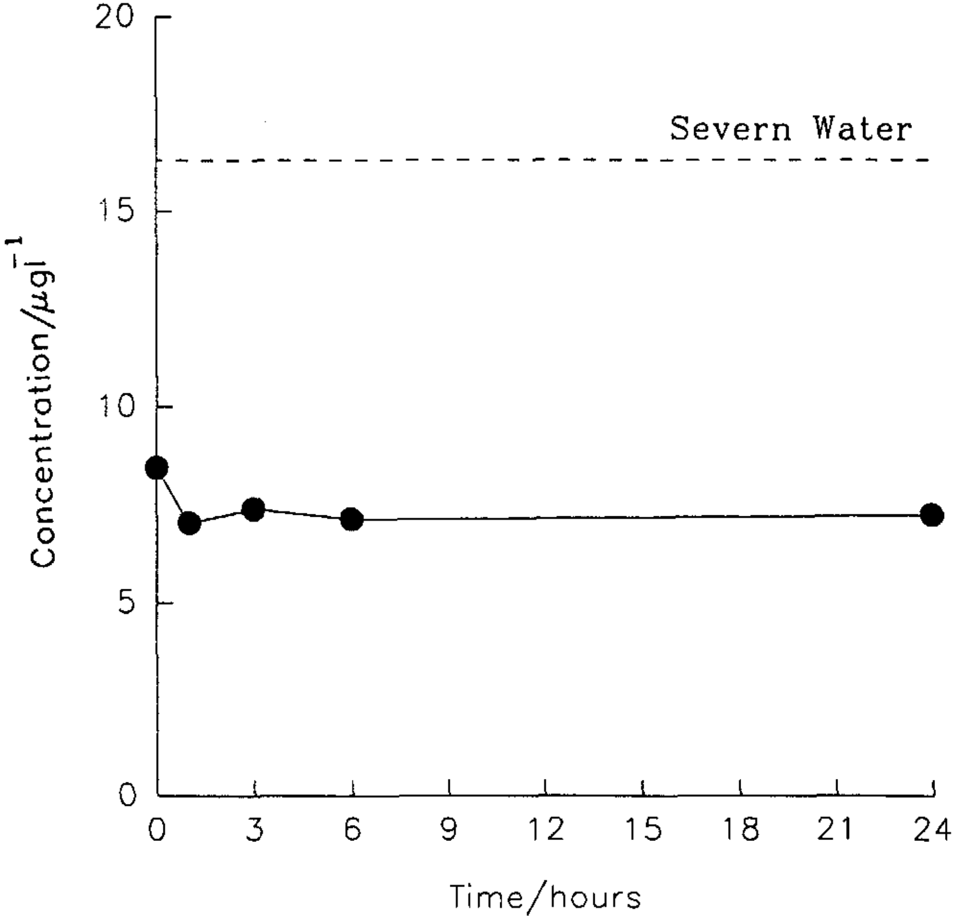
Concentration/$\mu g l^{-1}$
50
40
30
20
10
0
0
3
6
9
12
15
18
21
24
Time/hours
Severn Water

Lead

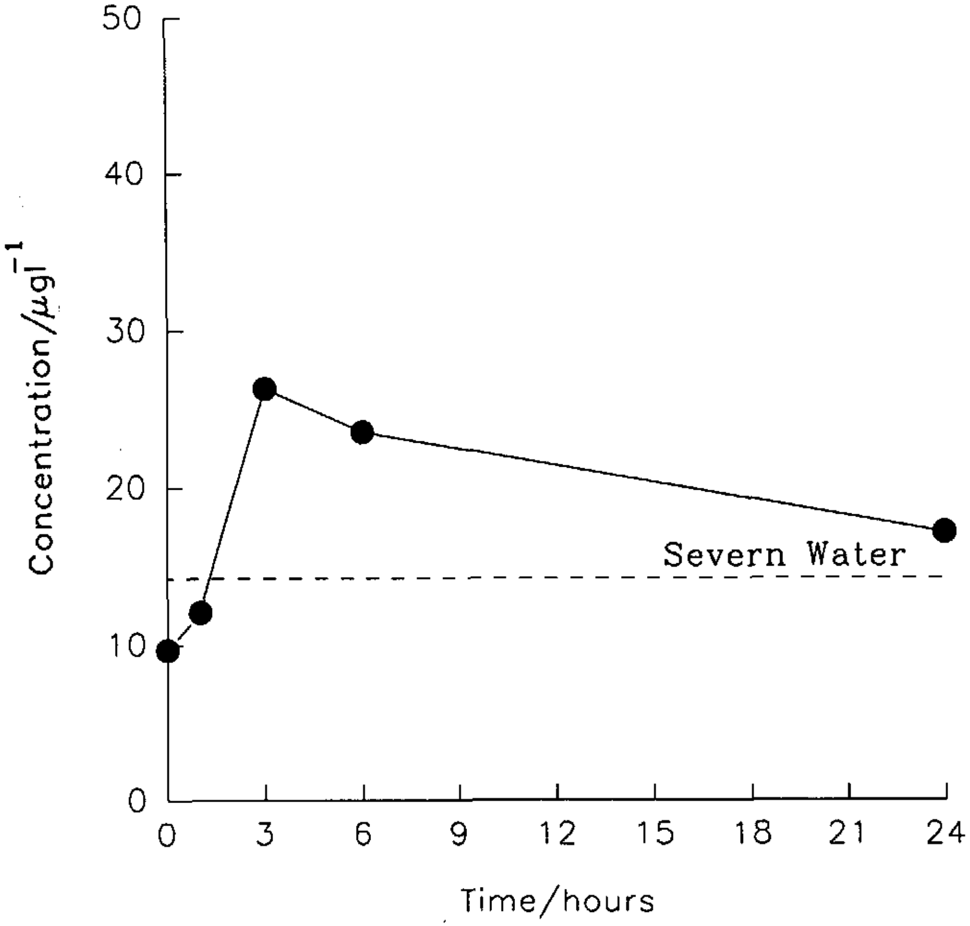


Concentration/μgl^{-1}
10
9
8
7
6
5
4
3
2
1
0
0
3
6
9
12
15
18
21
24
Time/hours
Severn Water

Lithium

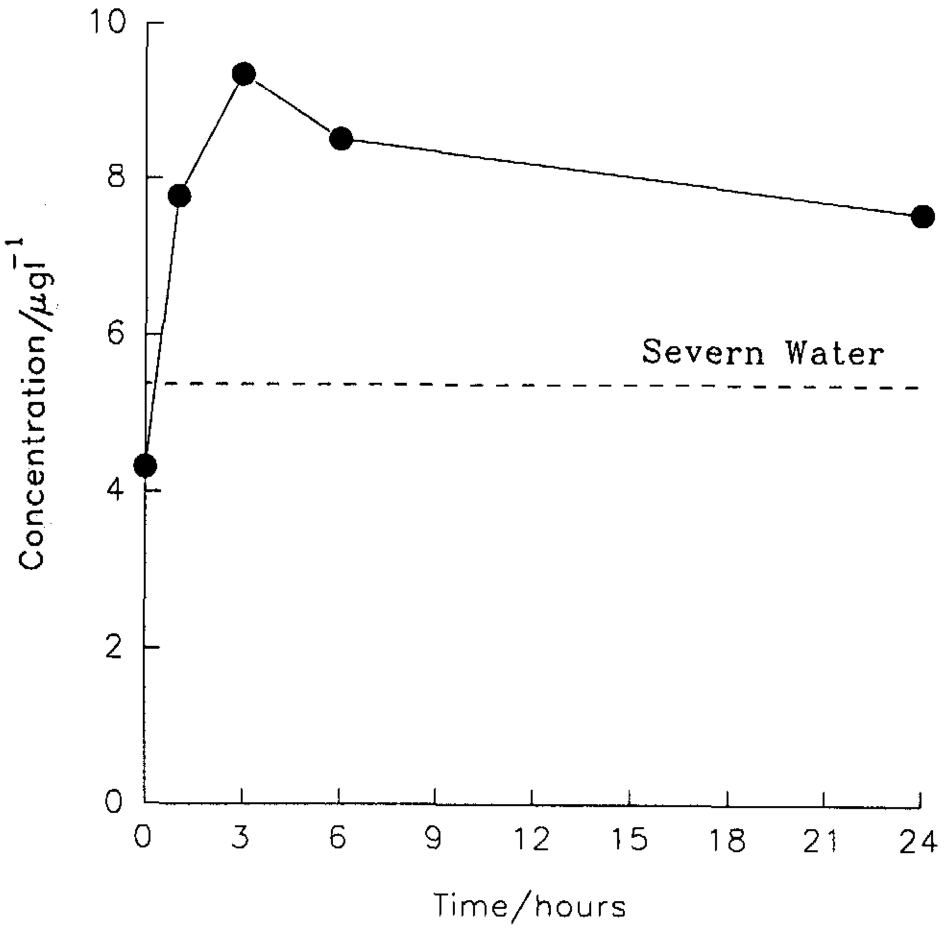

Severn Water
Concentration/μgl^{-1}
20
15
10
5
0
0
3
6
9
12
15
18
21
24
Time/hours

Manganese



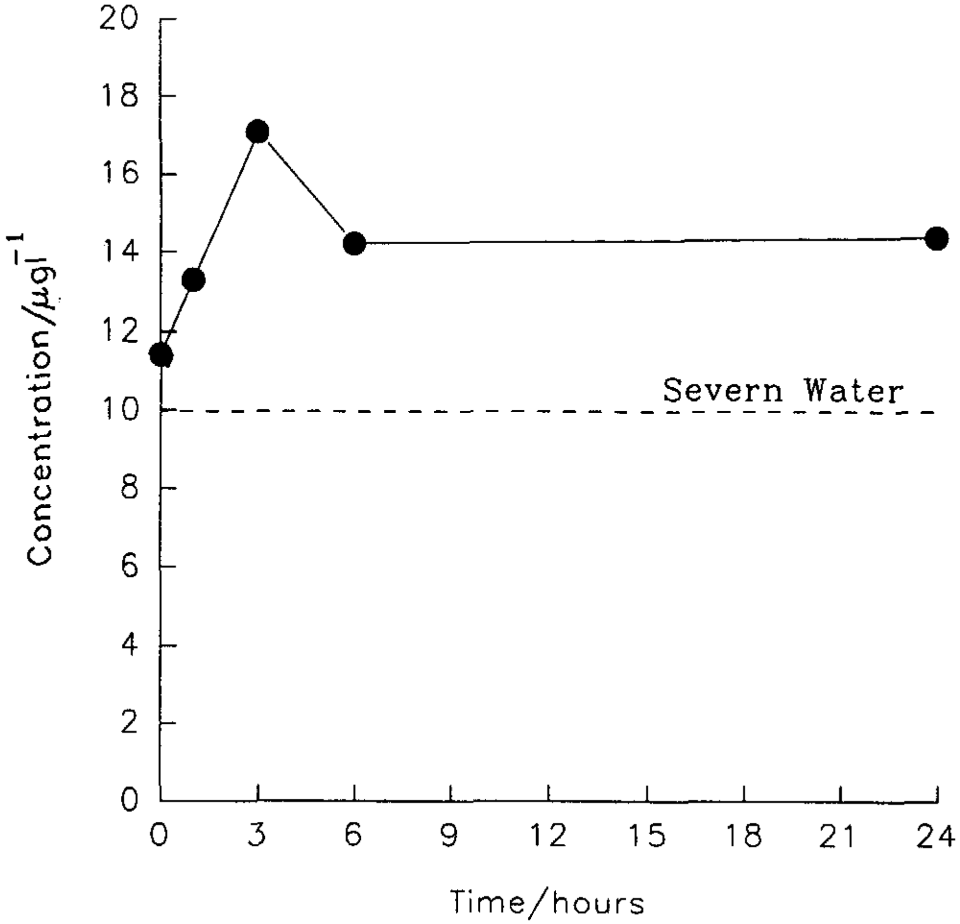
Concentration/$\mu g l^{-1}$
50
40
30
20
10
0
0
3
6
9
12
15
18
21
24
Time/hours
Severn Water

Molybdenum



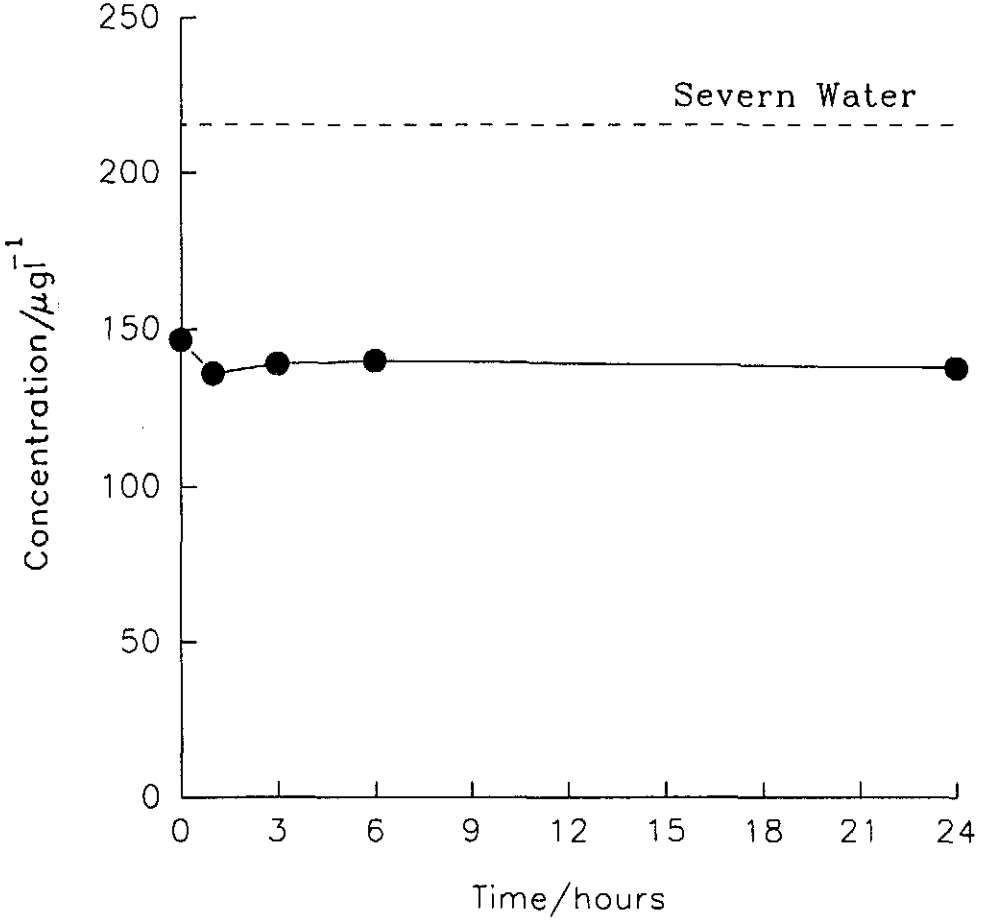
10
8
6
4
2
0
Concentration/$\mu g l^{-1}$
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Nickel

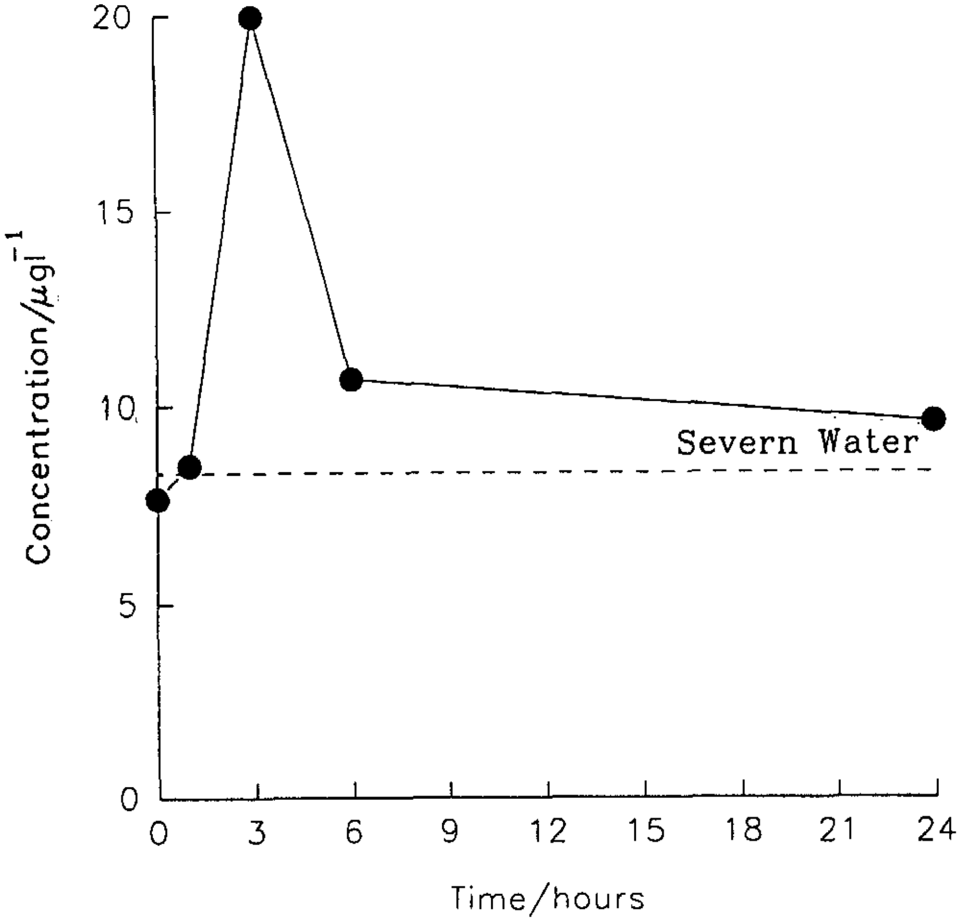


20
18
16
14
12
10
8
6
4
2
0
Concentration/$\mu g l^{-1}$
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

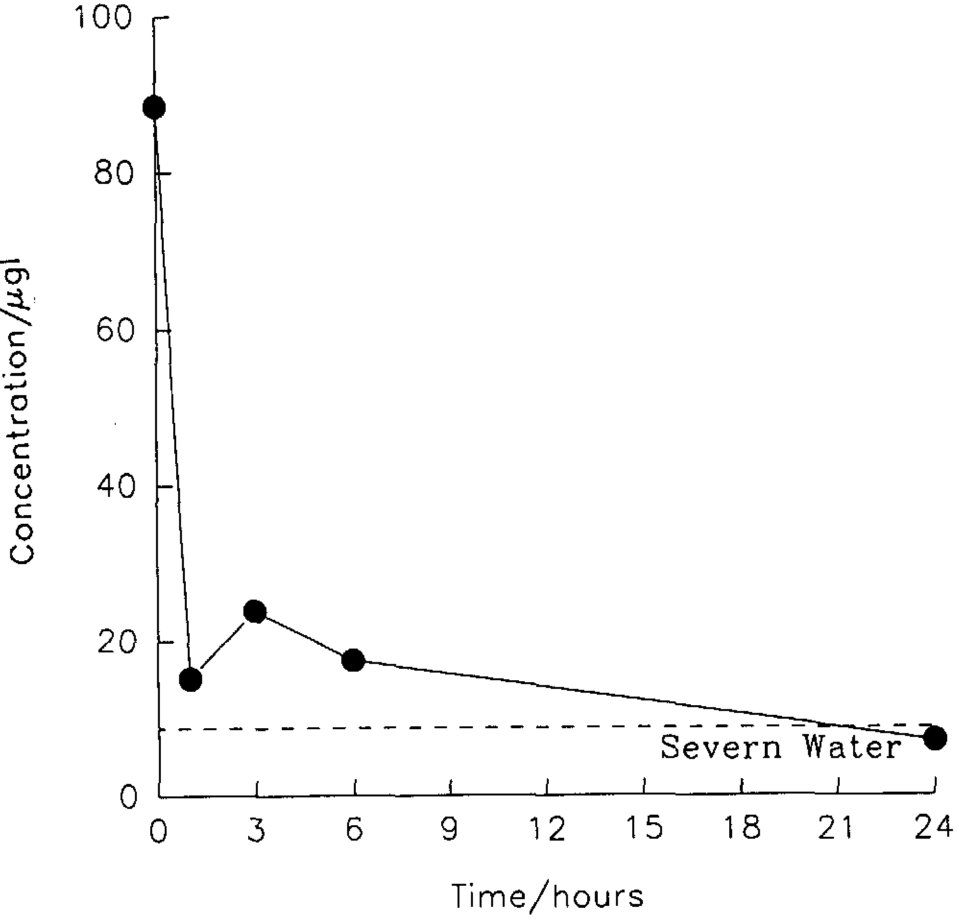
Strontium


Severn Water
250
200
150
100
50
0
Concentration/μgl^{-1}
0
3
6
9
12
15
18
21
24
Time/hours

Titanium


Concentration/$\mu g l^{-1}$
20
15
10
5
0
0
3
6
9
12
15
18
21
24
Time/hours
Severn Water

Zinc

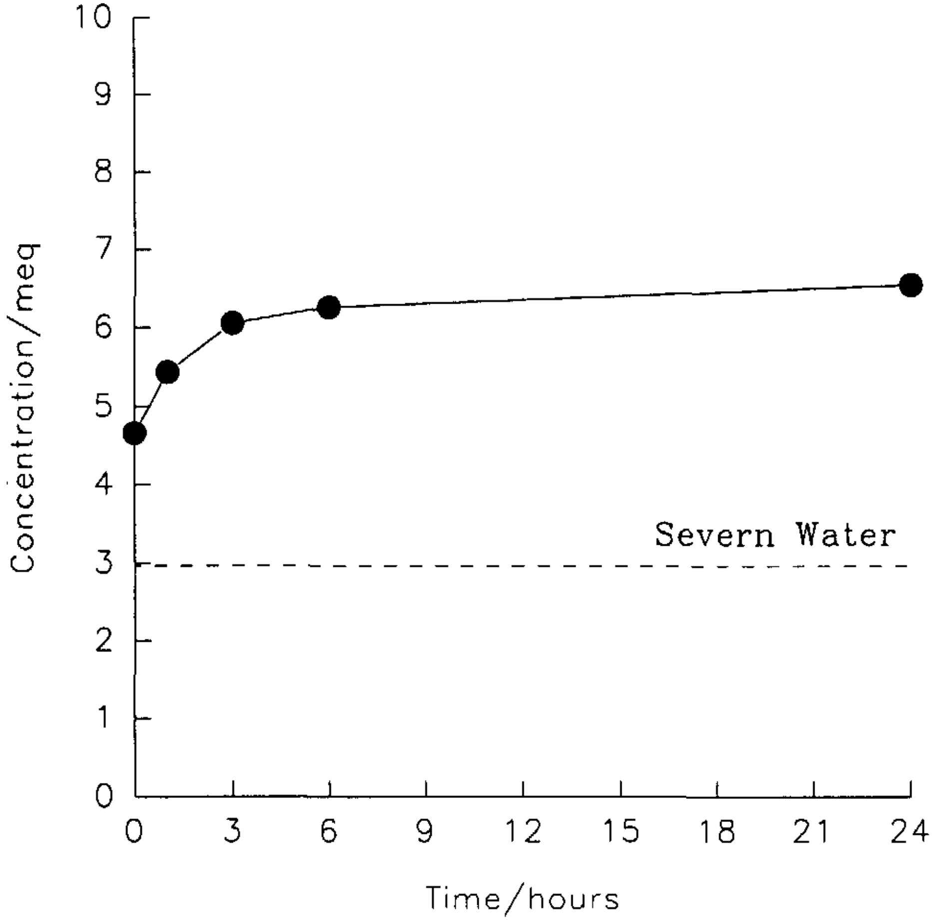


Concentration/$\mu g l^{-1}$
100
80
60
40
20
0
0
3
6
9
12
15
18
21
24
Time/hours
Severn Water

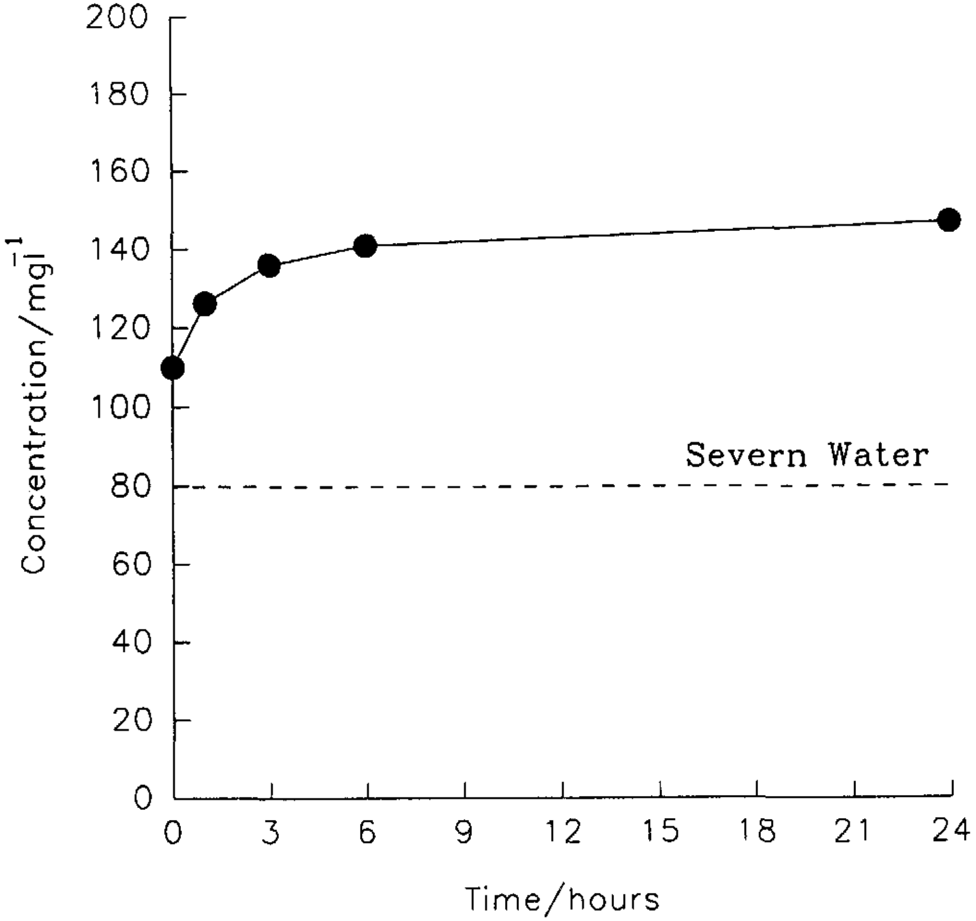
Appendix D

Chemical Changes in Sediment Water Mixing Experiments - Autumn

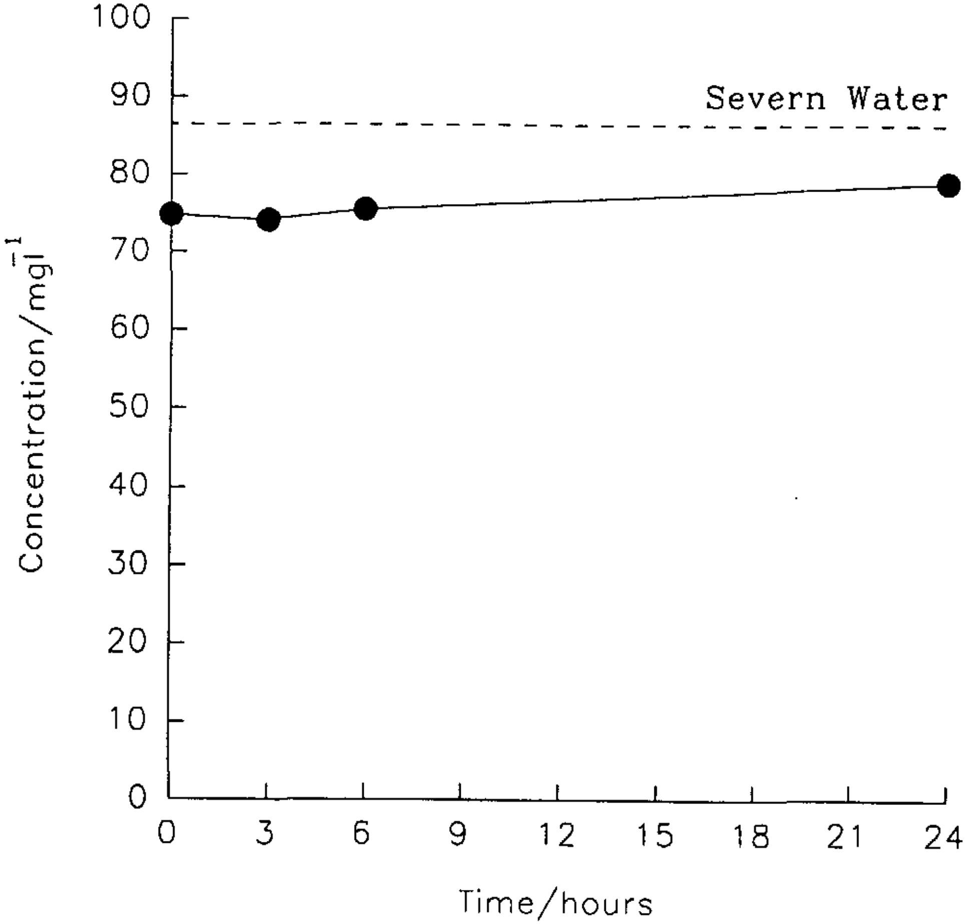
AlKalinity


10
9
8
7
6
5
4
3
2
1
0
Concentration/meq
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

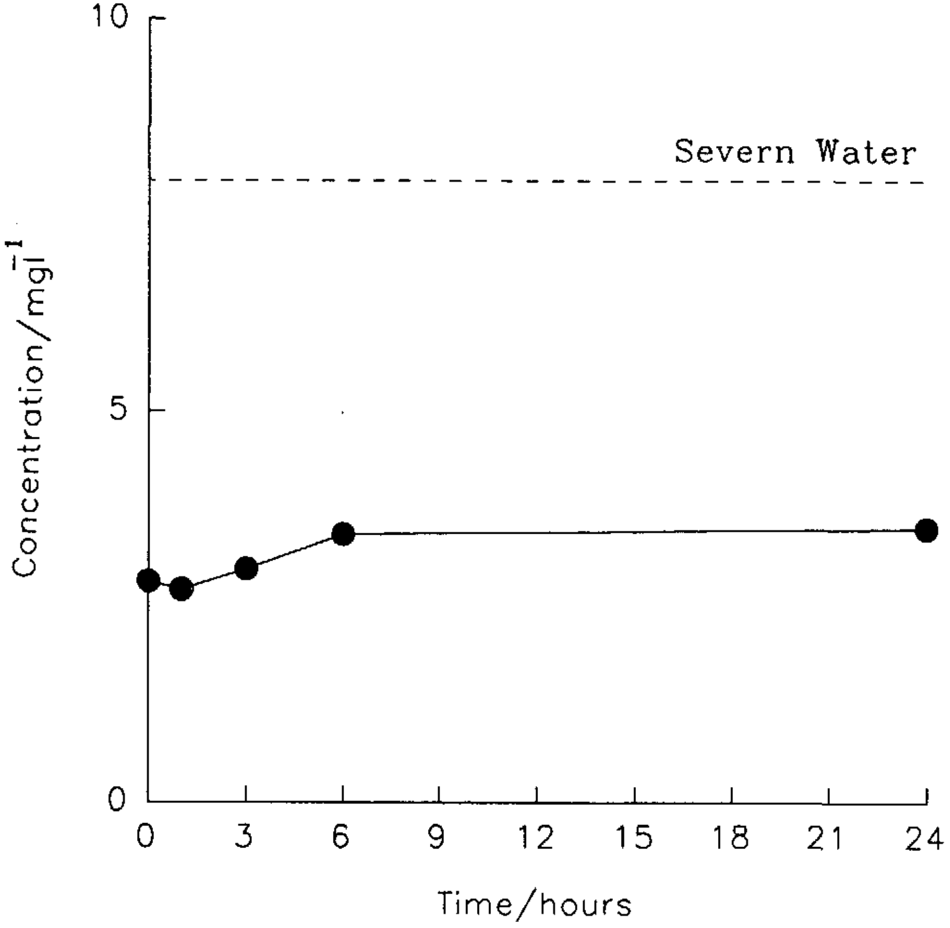
Calcium


200
180
160
140
120
100
80
60
40
20
0
Concentration/mgl^{-1}
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Chloride

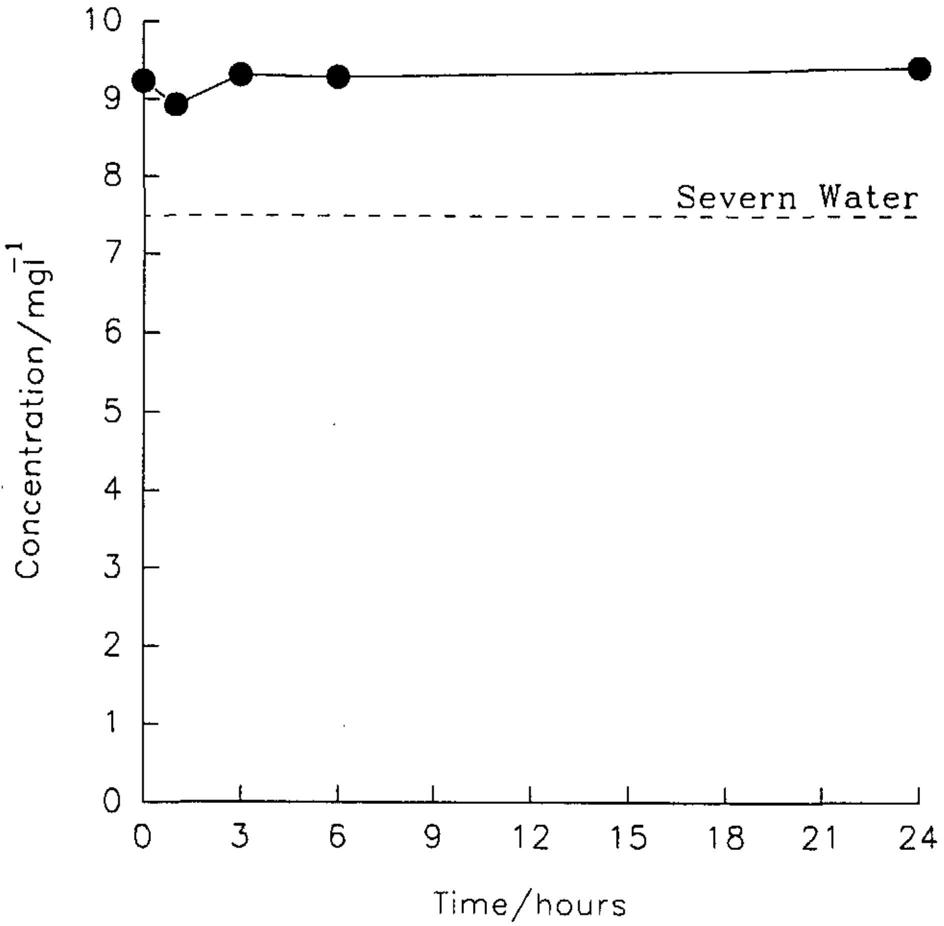

Severn Water
Concentration/mgl^{-1}
100
90
80
70
60
50
40
30
20
10
0
0
3
6
9
12
15
18
21
24
Time/hours

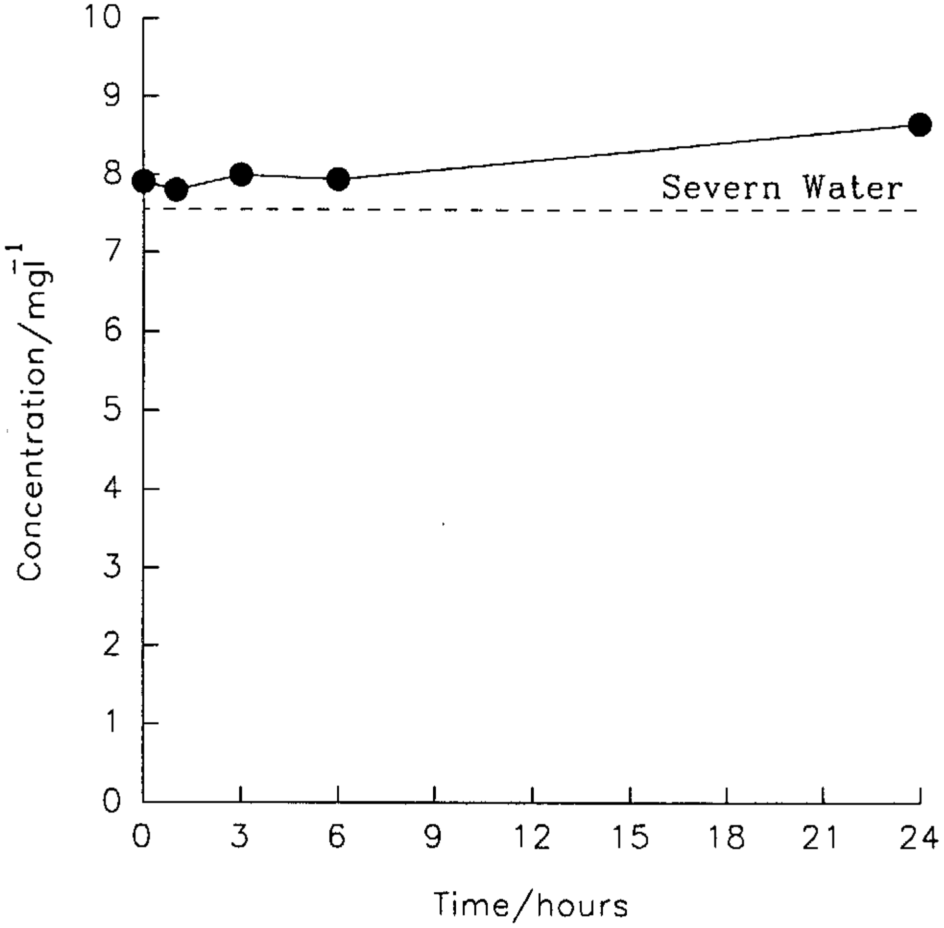
Magnesium



10
5
0
Concentration/mgl^{-1}
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

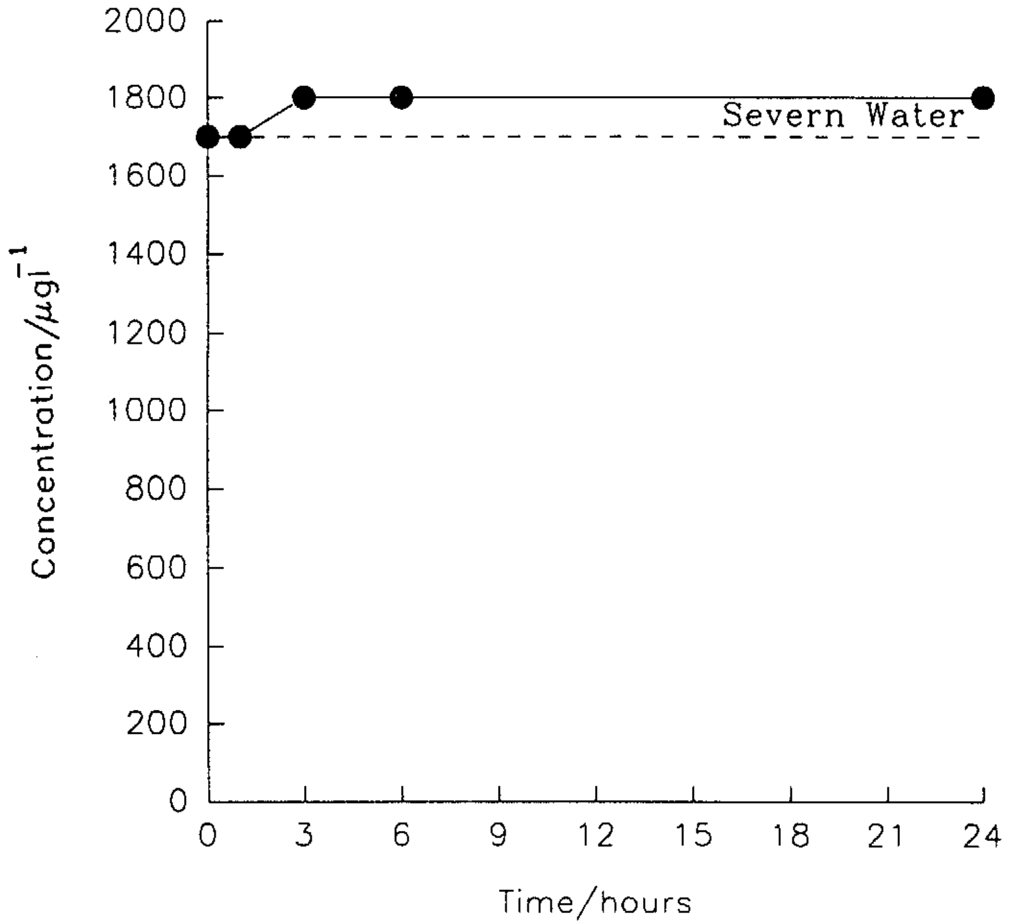
Potassium


Concentration/mgl^{-1}
10
9
8
7
6
5
4
3
2
1
0
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours



Nitrate N

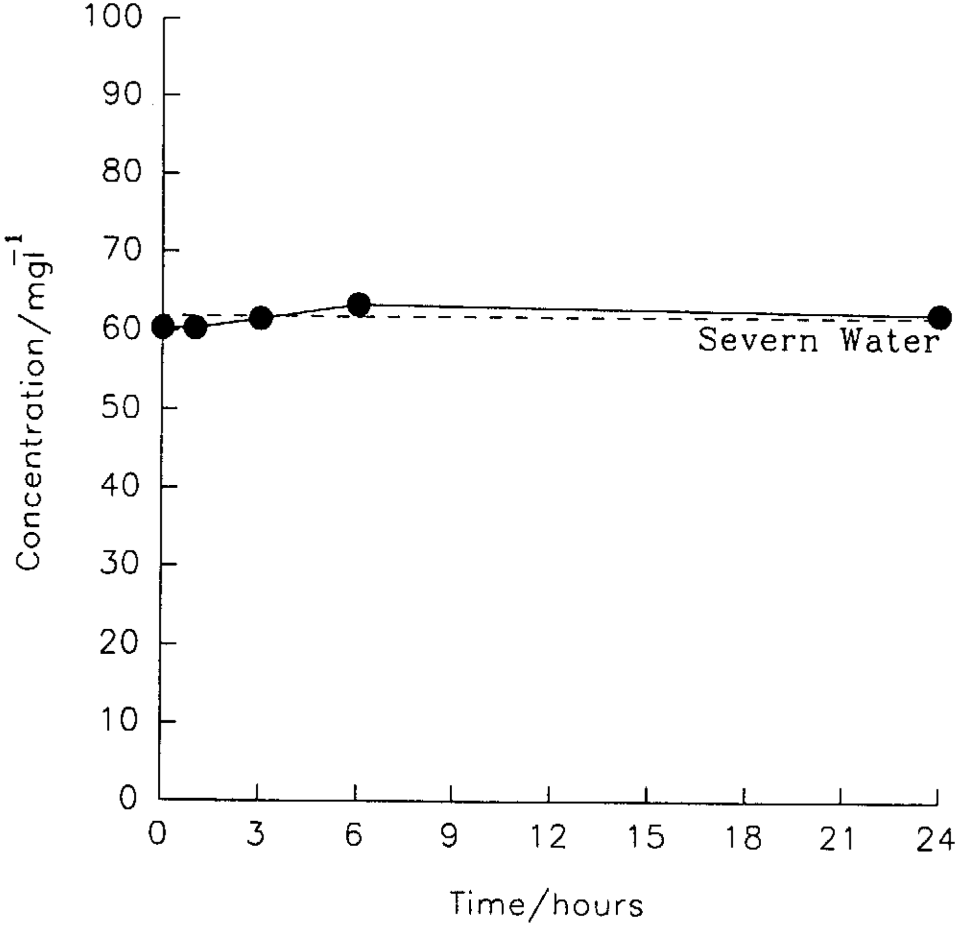
10
9
8
7
6
5
4
3
2
1
0
Concentration/mgl^{-1}
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours



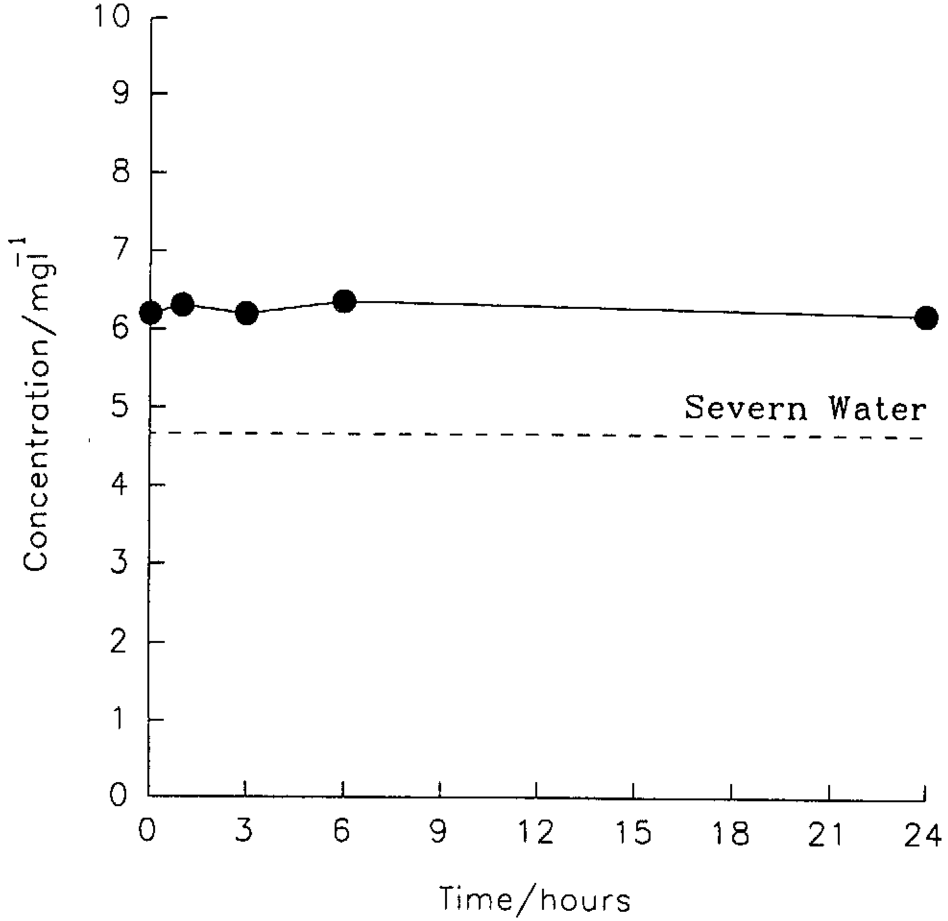
Phosphate P

2000
1800
1600
1400
1200
1000
800
600
400
200
0
Concentration/$\mu g l^{-1}$
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Sodium

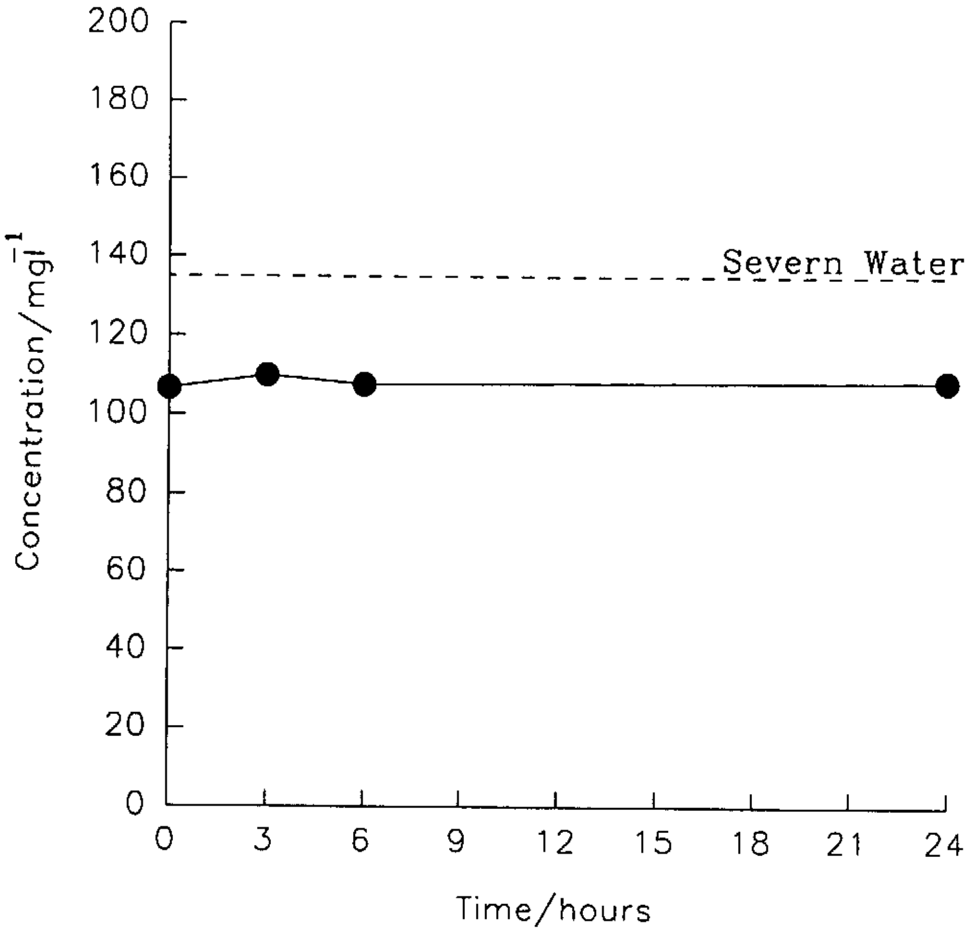

Concentration/mgl^{-1}
100
90
80
70
60
50
40
30
20
10
0
0
3
6
9
12
15
18
21
24
Time/hours
Severn Water

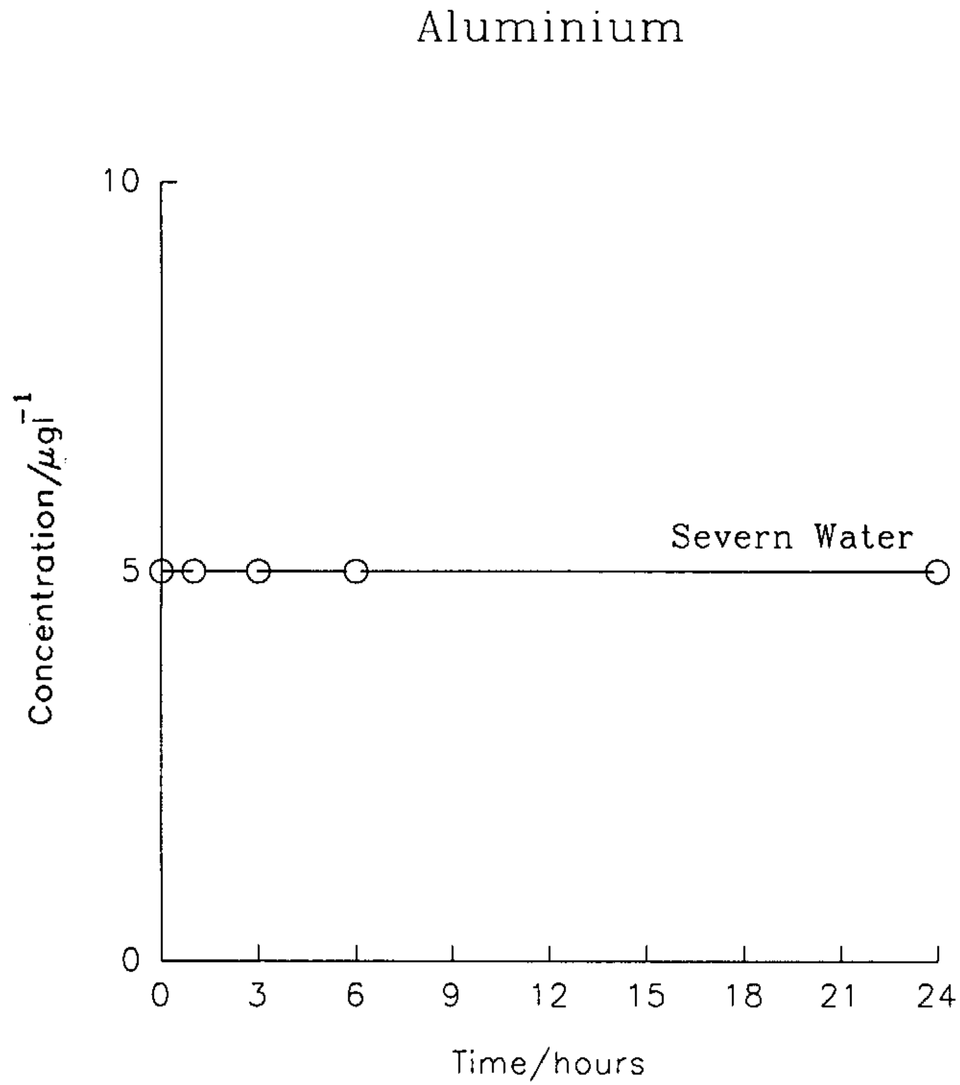
Silica Si



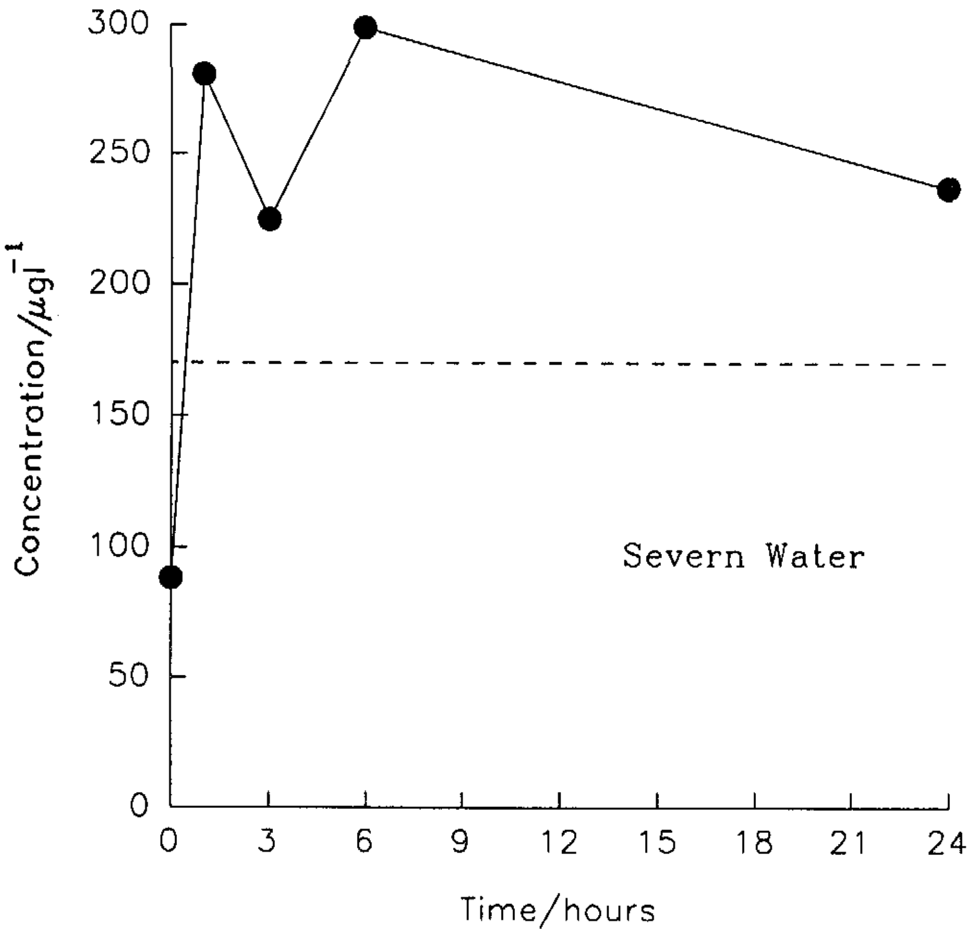
Concentration/mgl^{-1}
10
9
8
7
6
5
4
3
2
1
0
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Sulphate


200
180
160
140
120
100
80
60
40
20
0
Concentration/mgl^{-1}
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

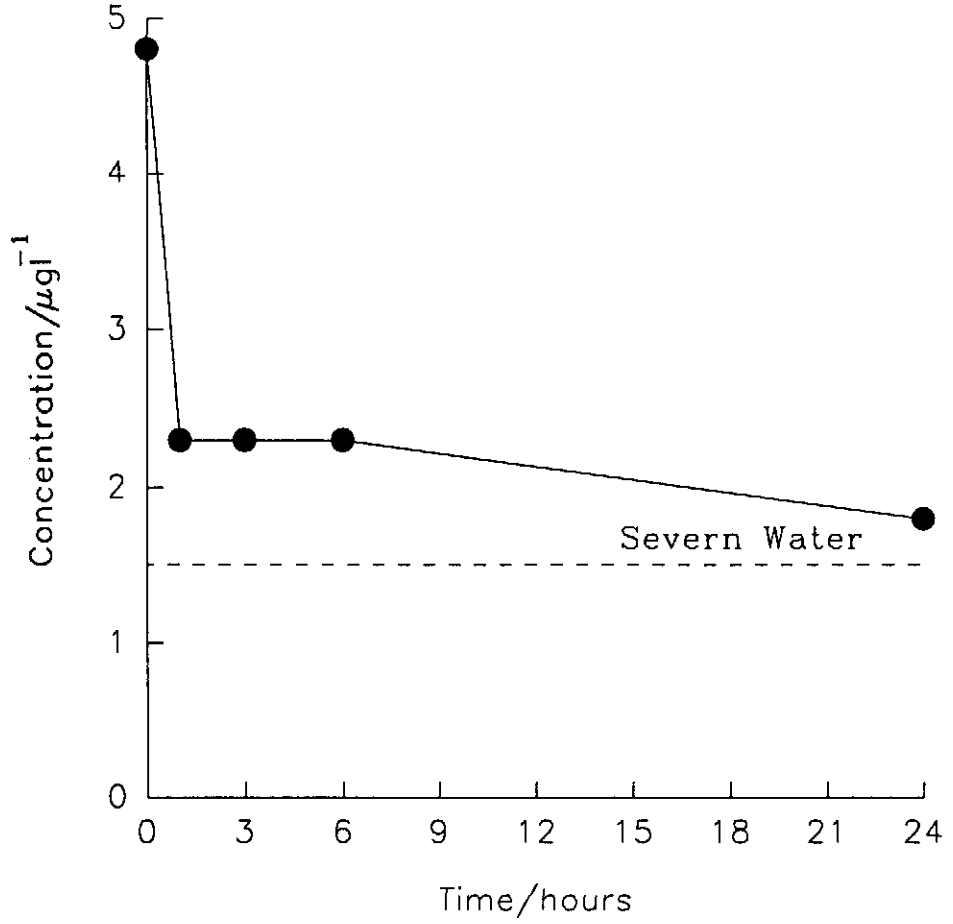

Aluminium
Concentration/μgl^{-1}
10
5
0
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Barium

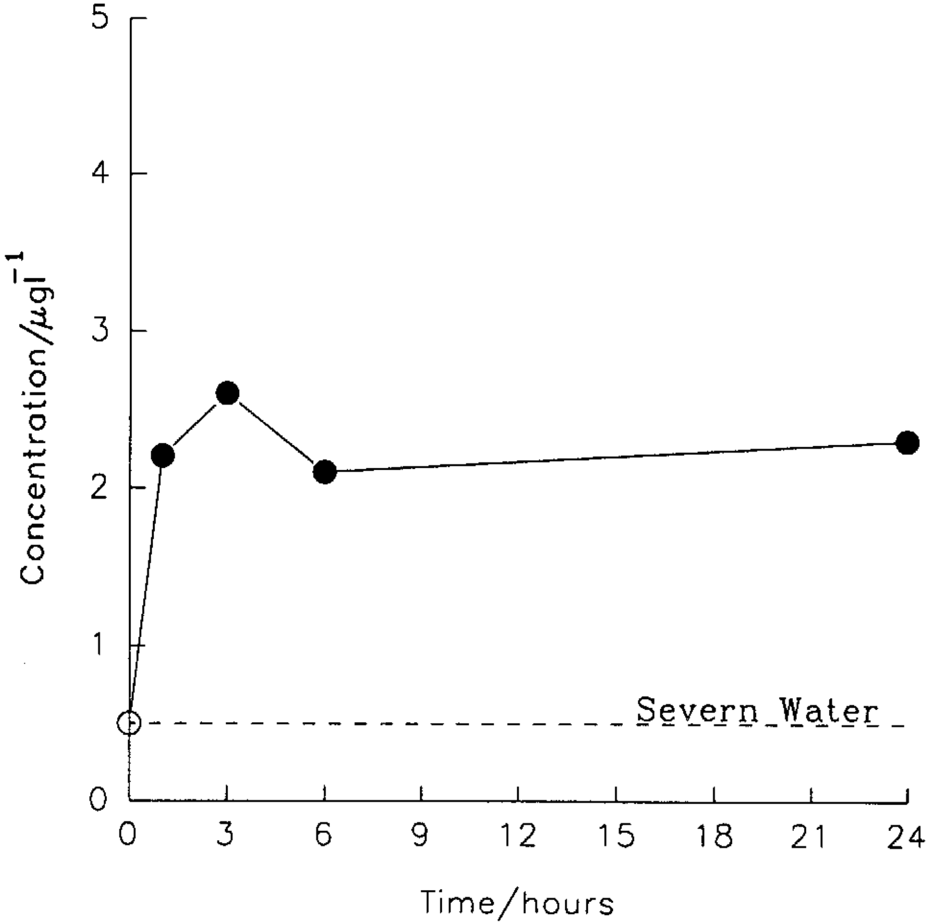


300
250
200
150
100
50
0
Concentration/μgl^{-1}
0
3
6
9
12
15
18
21
24
Time/hours
Severn Water

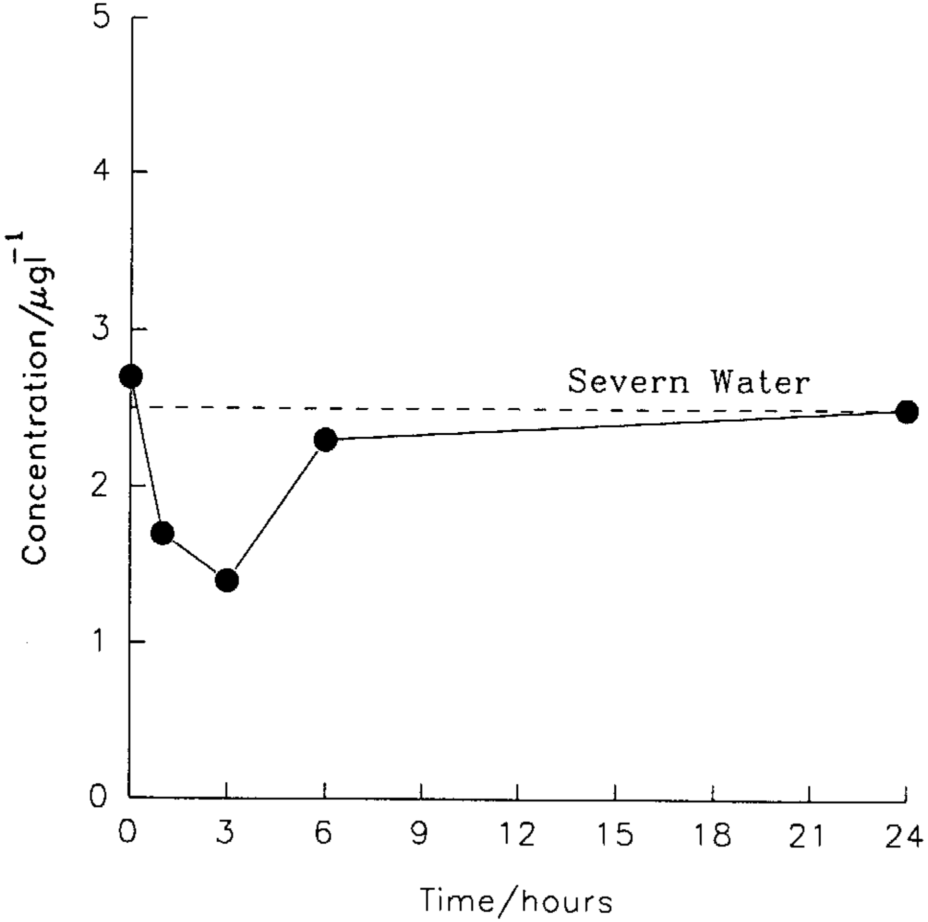
Cadmium


Concentration/$\mu g l^{-1}$
0
1
2
3
4
5
Time/hours
0
3
6
9
12
15
18
21
24
Severn Water

Copper

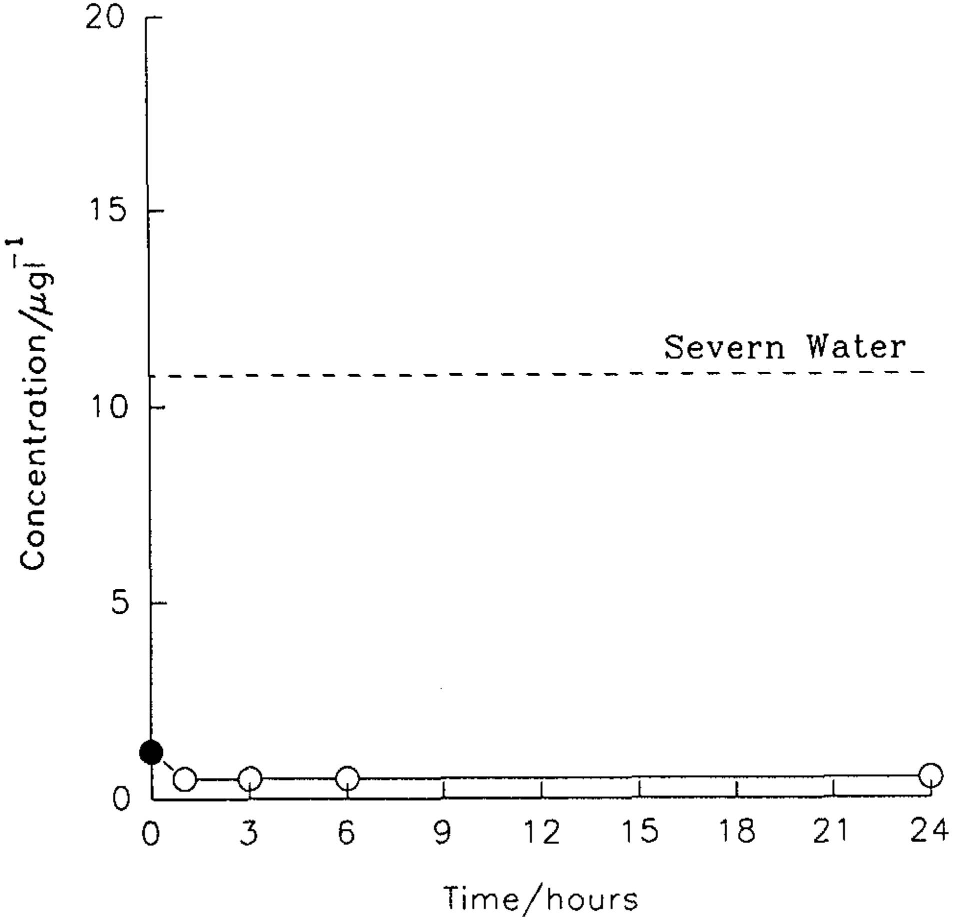

Concentration/μgl^{-1}
5
4
3
2
1
0
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Lead



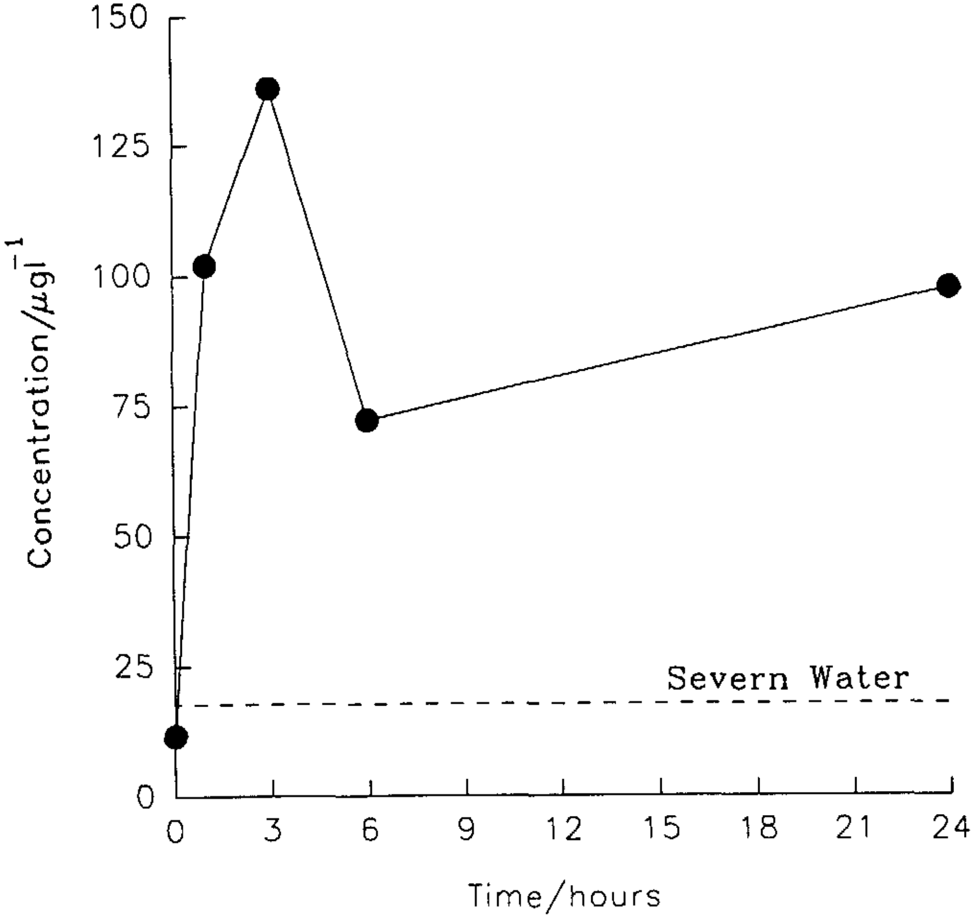
Concentration/$\mu g l^{-1}$
0
1
2
3
4
5
Time/hours
0
3
6
9
12
15
18
21
24
Severn Water

Lithium

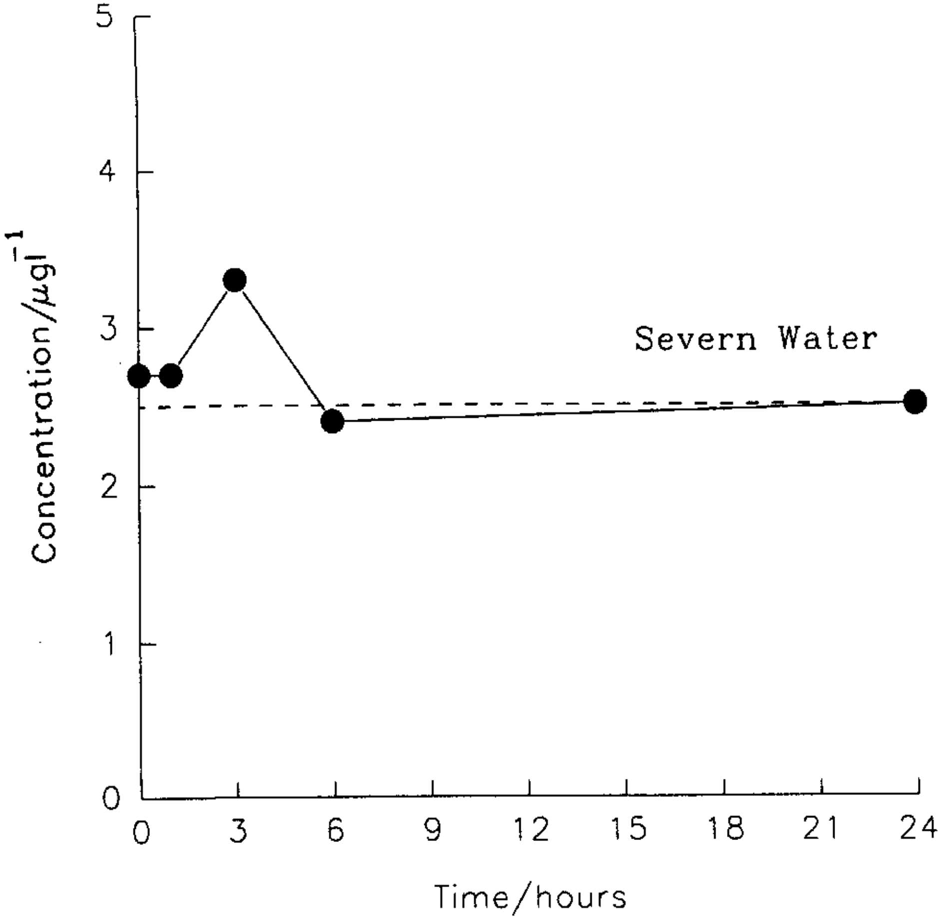


Concentration/μgl^{-1}
20
15
10
5
0
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

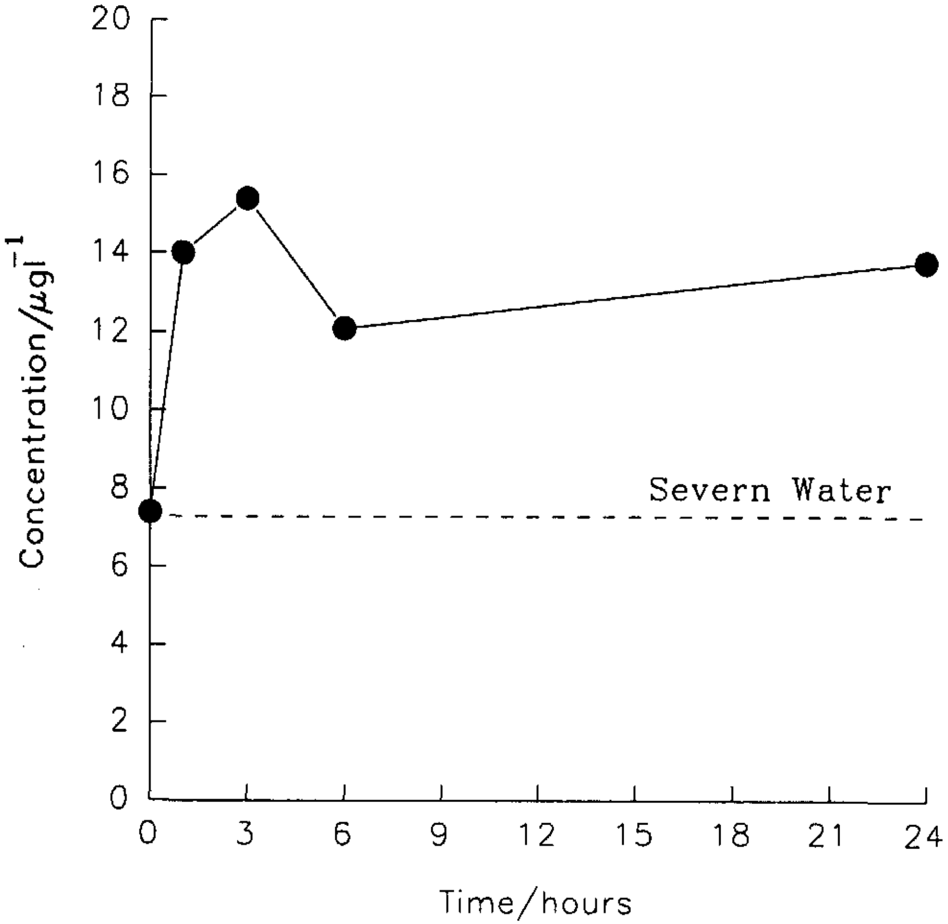
Manganese


150
125
100
75
50
25
0
Concentration/μgl^{-1}
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

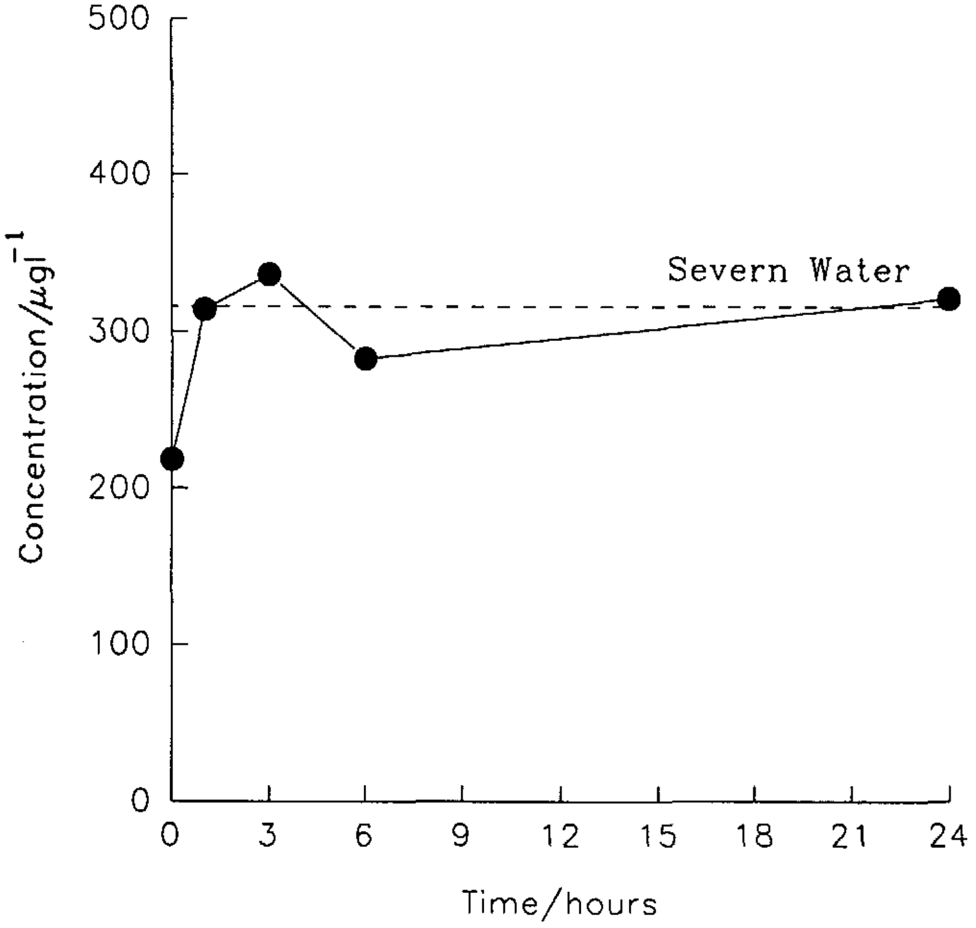
Molybdenum


Severn Water
Concentration/$\mu g l^{-1}$
0
1
2
3
4
5
Time/hours
0
3
6
9
12
15
18
21
24

Nickel

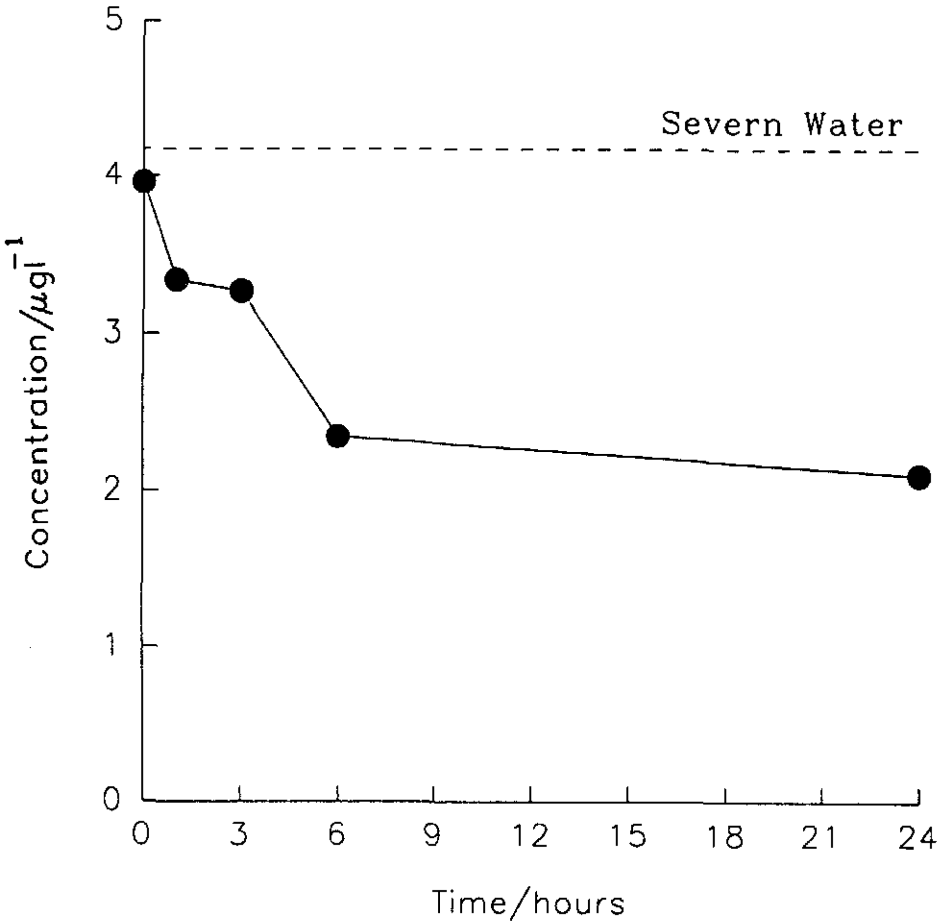

20
18
16
14
12
10
8
6
4
2
0
Concentration/μgl^{-1}
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Strontium

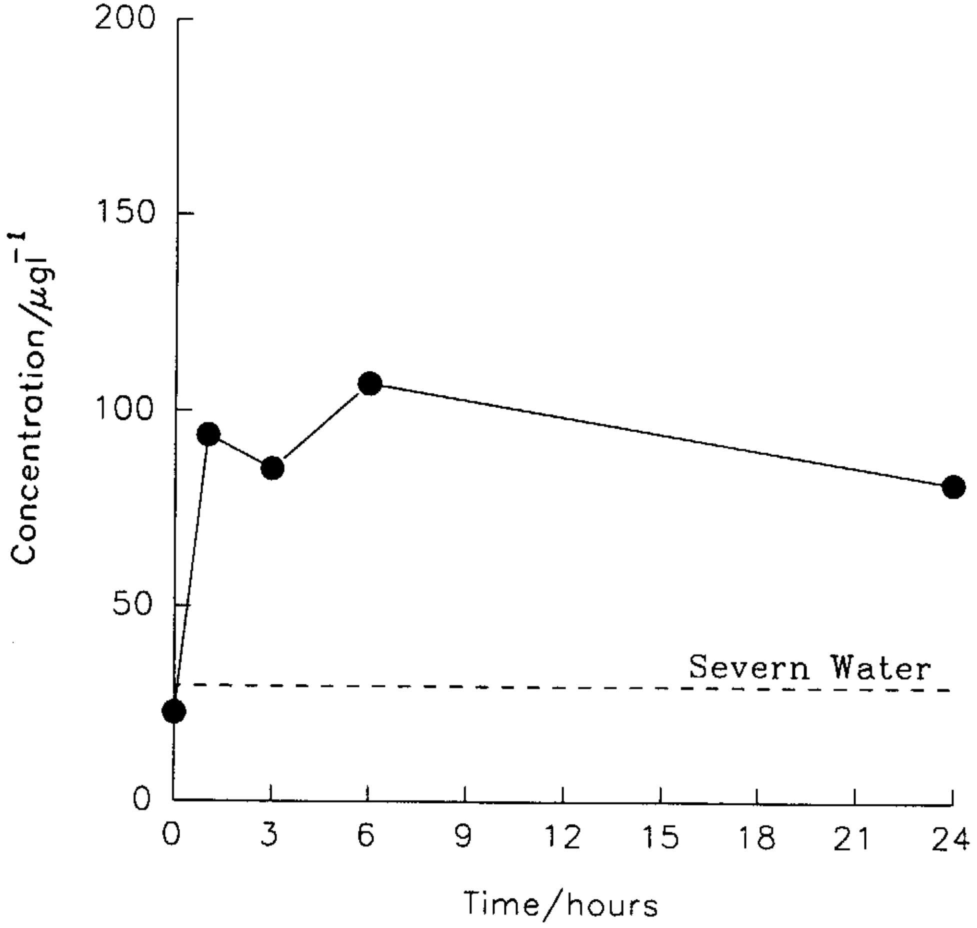


Concentration/μgl^{-1}
500
400
300
200
100
0
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Titanium


Severn Water
Concentration/$\mu g l^{-1}$
5
4
3
2
1
0
0
3
6
9
12
15
18
21
24
Time/hours

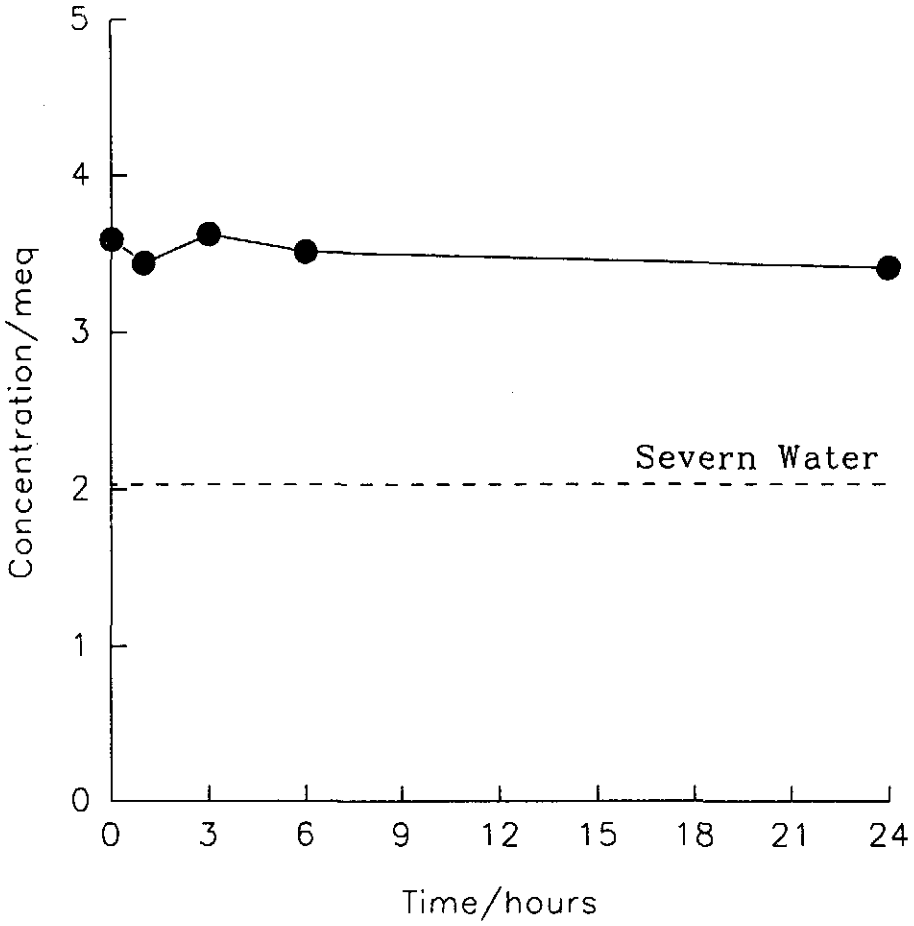
Zinc


200
150
100
50
0
Concentration/μgl^{-1}
0
3
6
9
12
15
18
21
24
Time/hours
Severn Water

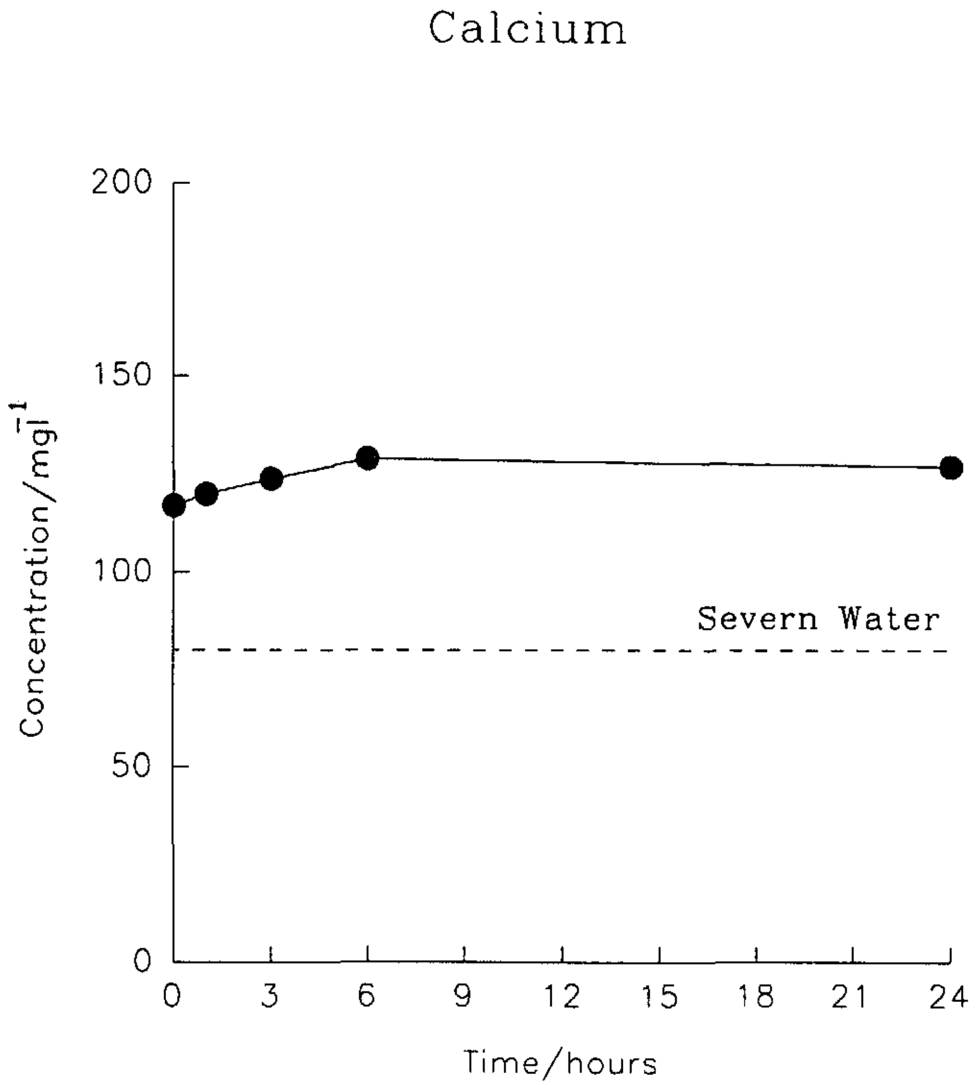
Appendix E

Chemical Changes in Sediment Water Mixing Experiments - Winter

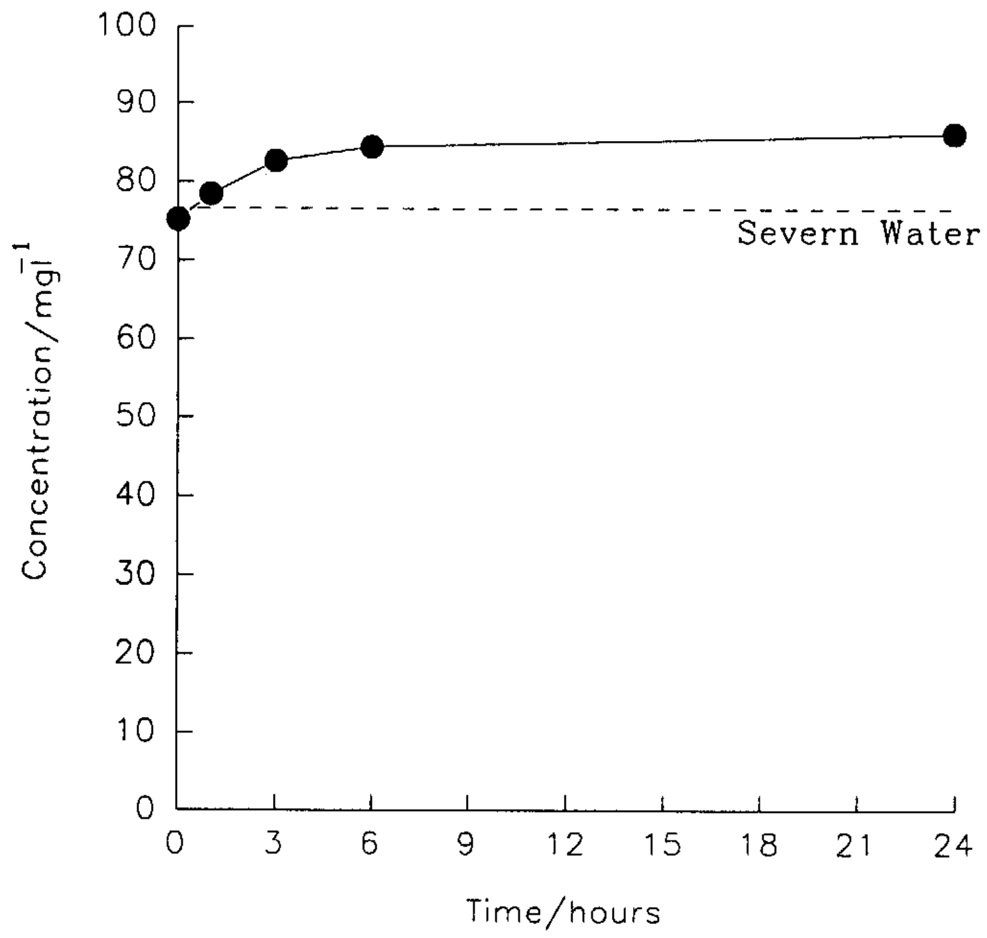
AlKalinity



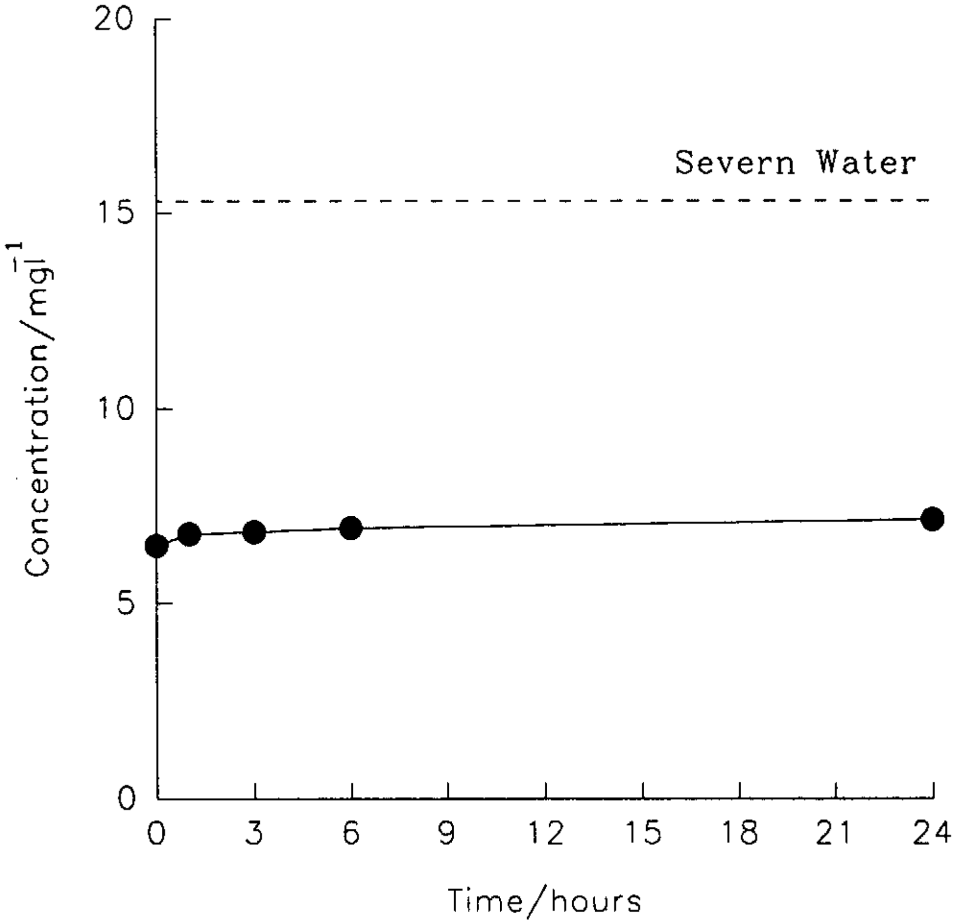
Concentration/meq
5
4
3
2
1
0
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours


Calcium
200
150
100
50
0
Concentration/mgl^{-1}
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

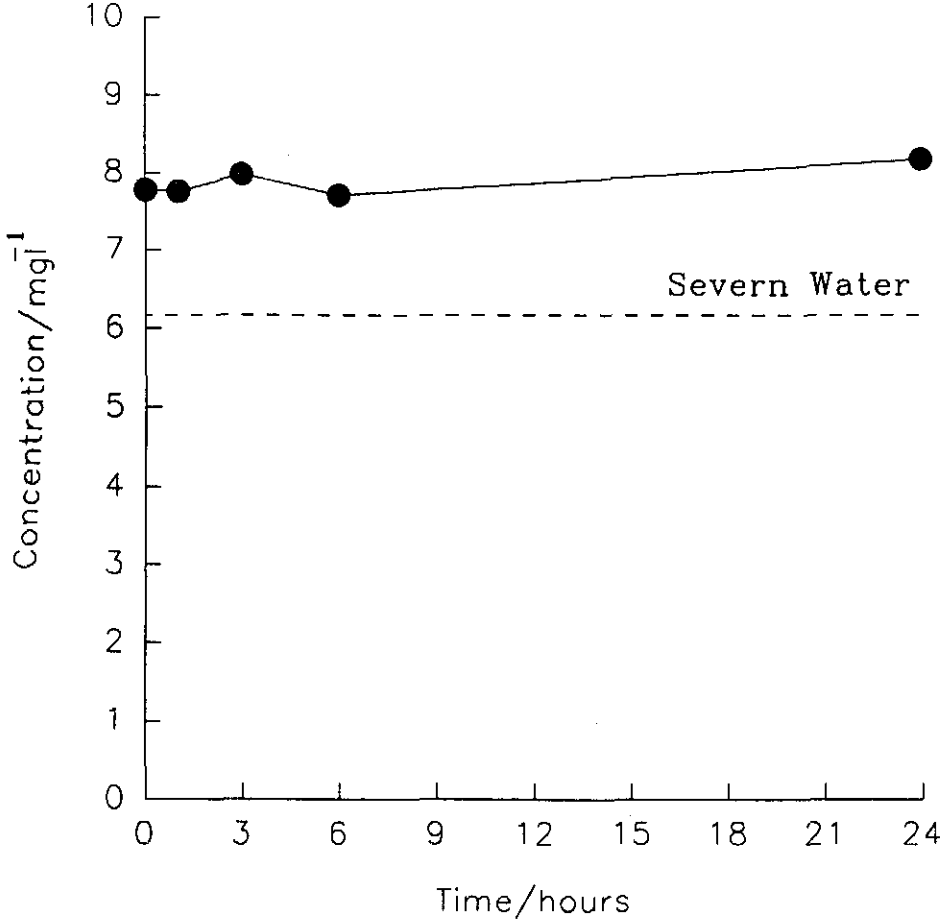
Chloride


Concentration/mgl^{-1}
100
90
80
70
60
50
40
30
20
10
0
0
3
6
9
12
15
18
21
24
Time/hours
Severn Water

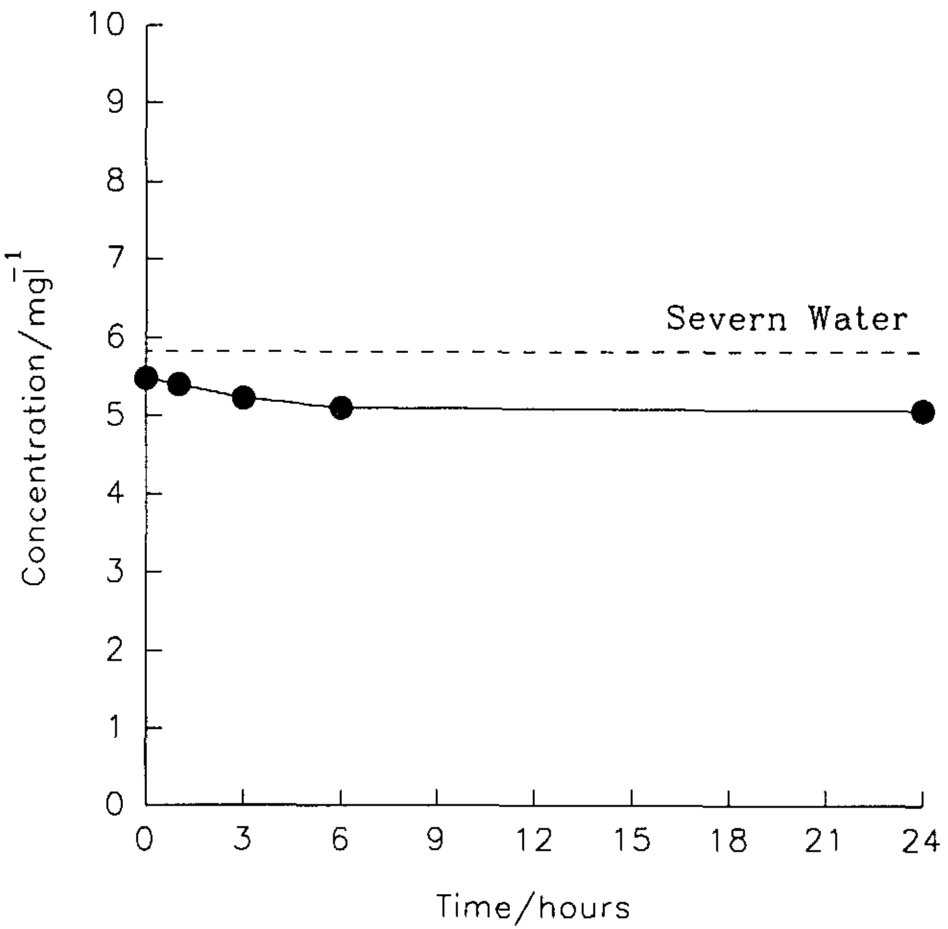
Magnesium


Severn Water
Concentration/mgl^{-1}
20
15
10
5
0
0
3
6
9
12
15
18
21
24
Time/hours

Potassium

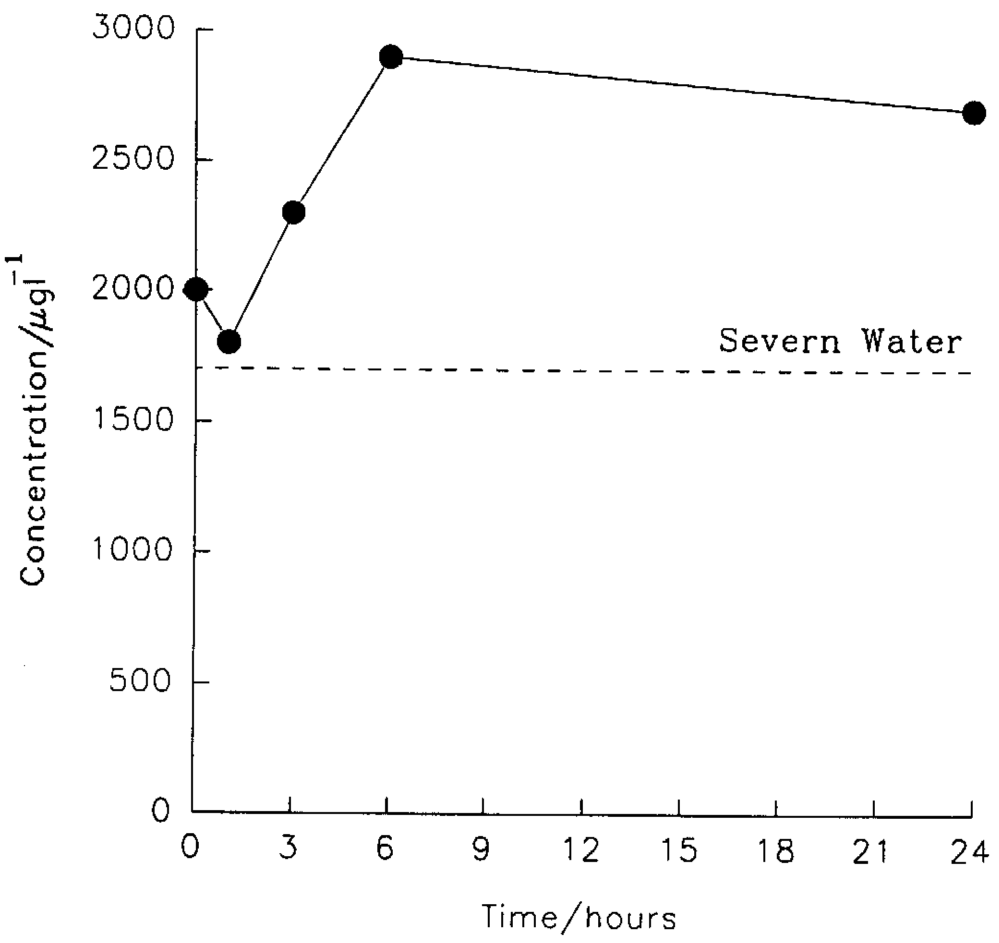

Concentration/mgl^{-1}
10
9
8
7
6
5
4
3
2
1
0
0
3
6
9
12
15
18
21
24
Time/hours
Severn Water

Nitrate N



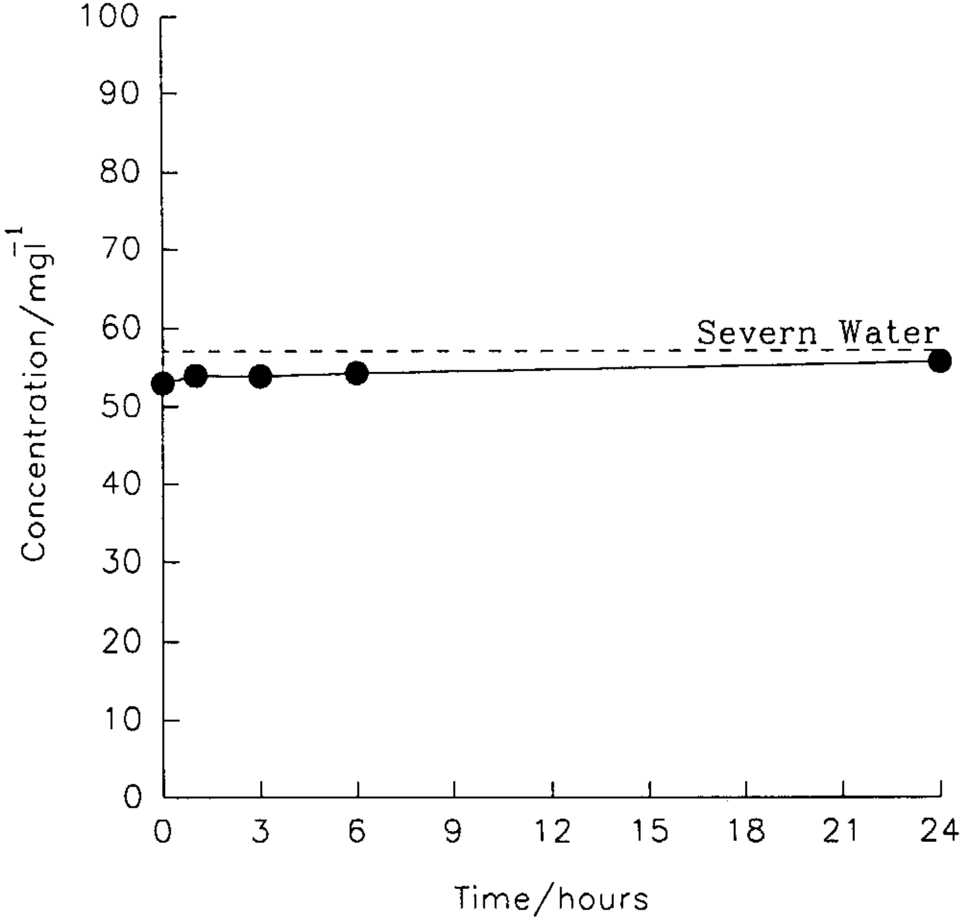
10
9
8
7
6
5
4
3
2
1
0
Concentration/mgl^{-1}
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Phosphate P



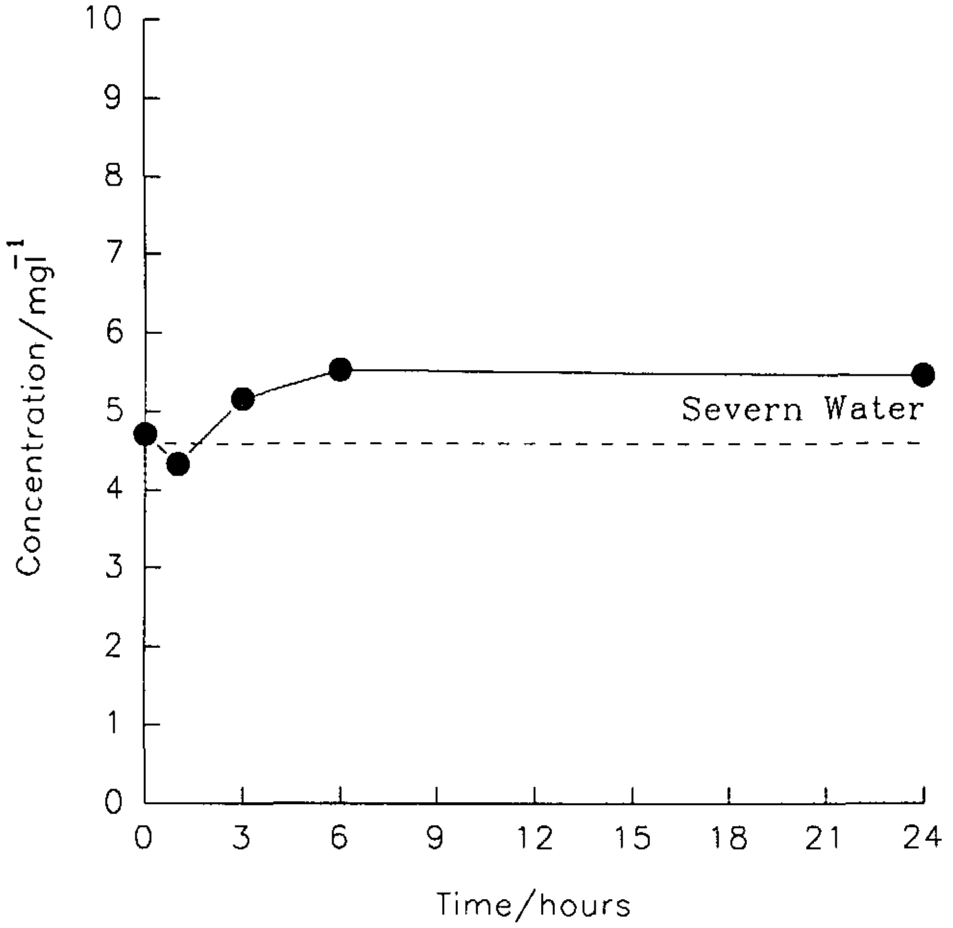
3000
2500
2000
1500
1000
500
0
Concentration/μgl^{-1}
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Sodium

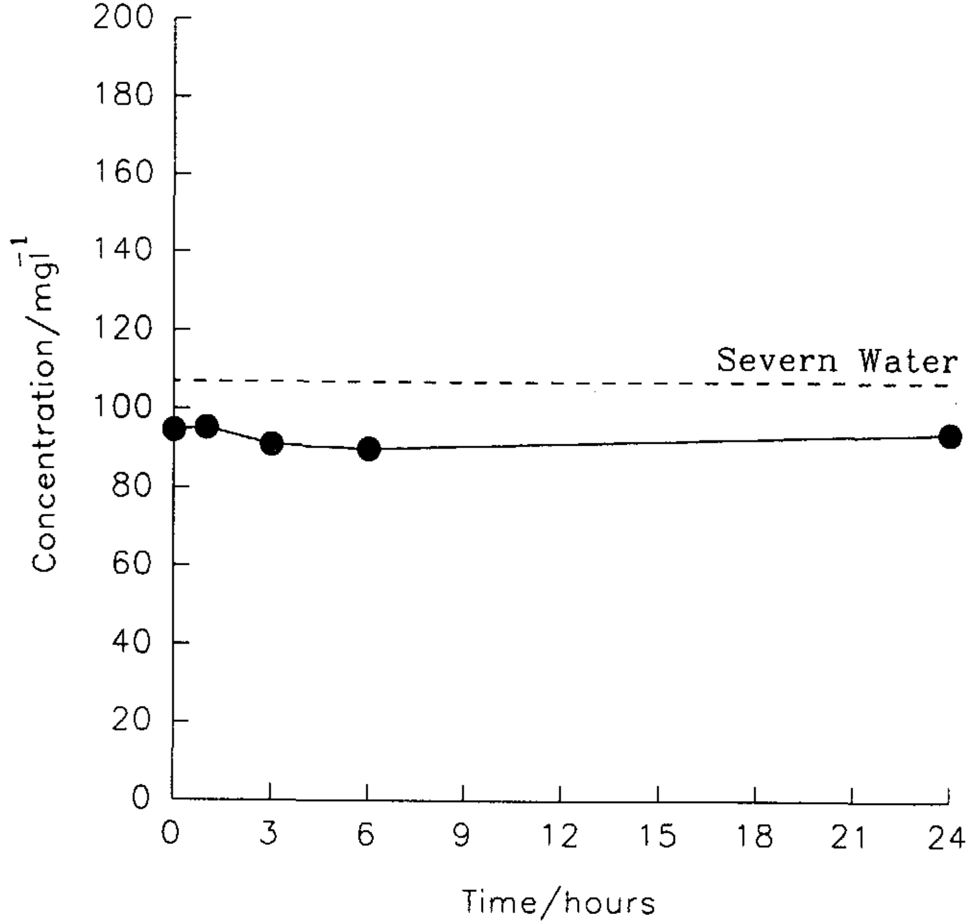


Severn Water
Concentration/mgl^{-1}
0
10
20
30
40
50
60
70
80
90
100
0
3
6
9
12
15
18
21
24
Time/hours

Silica Si



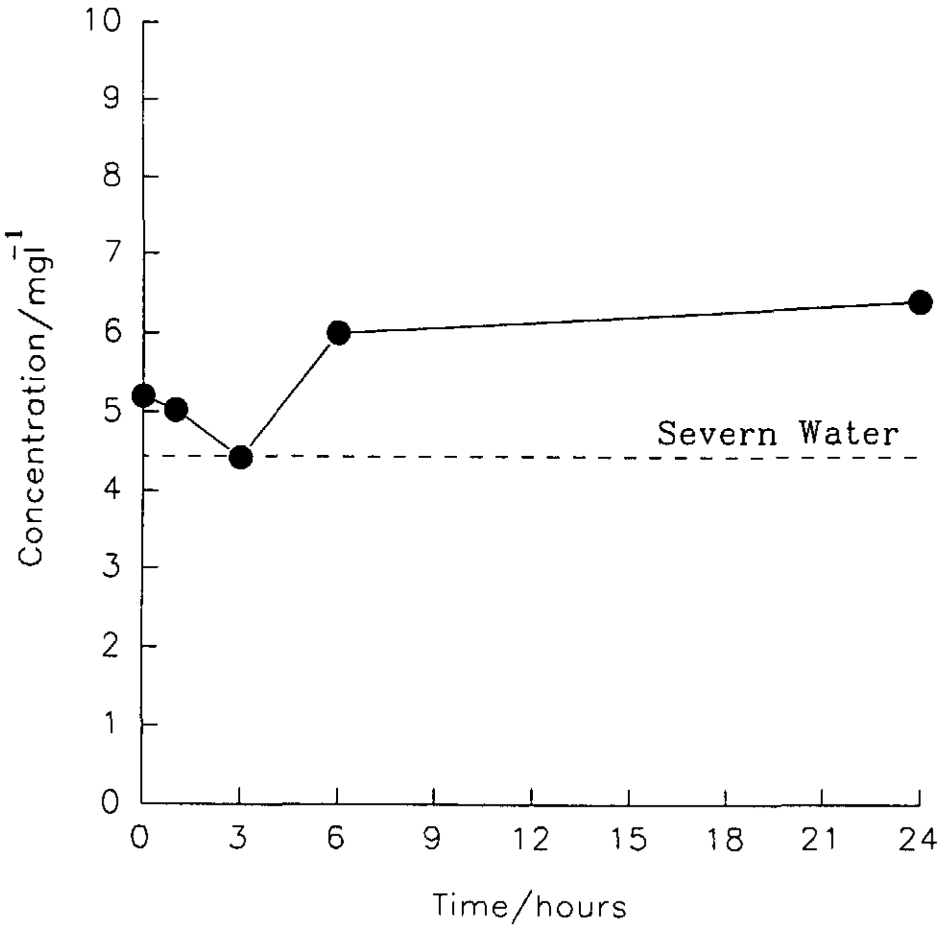
Concentration/mgl^{-1}
10
9
8
7
6
5
4
3
2
1
0
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours



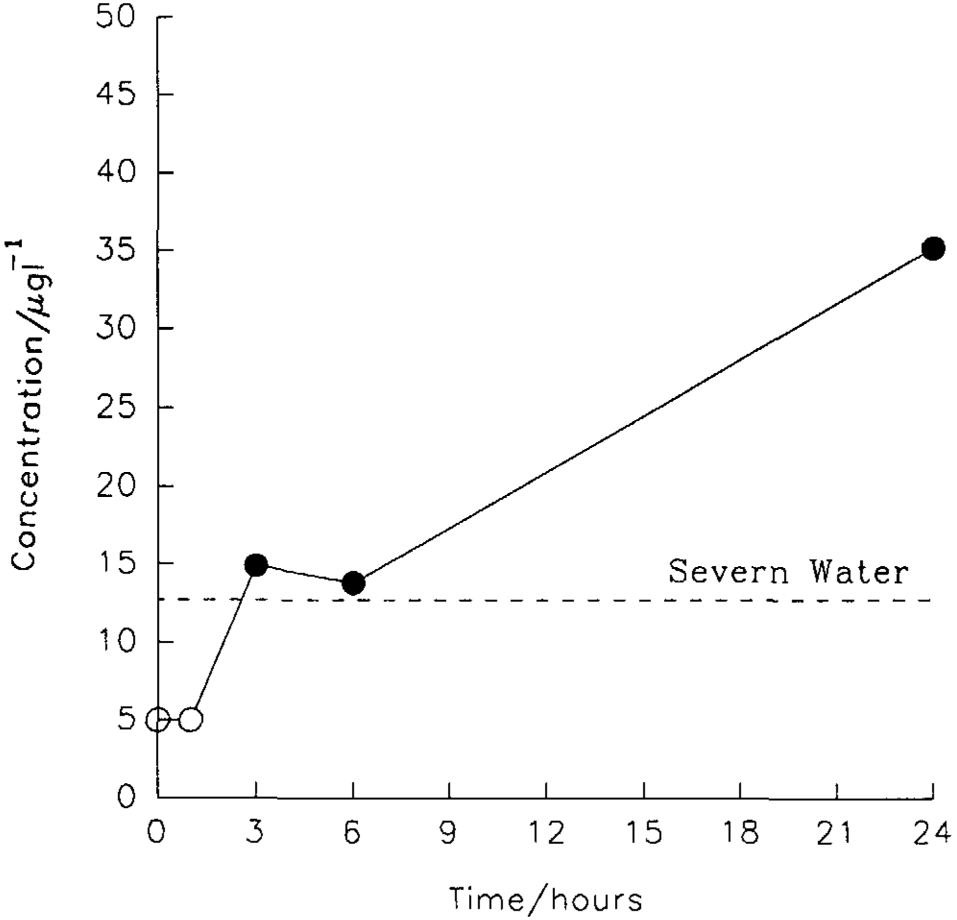
Sulphate

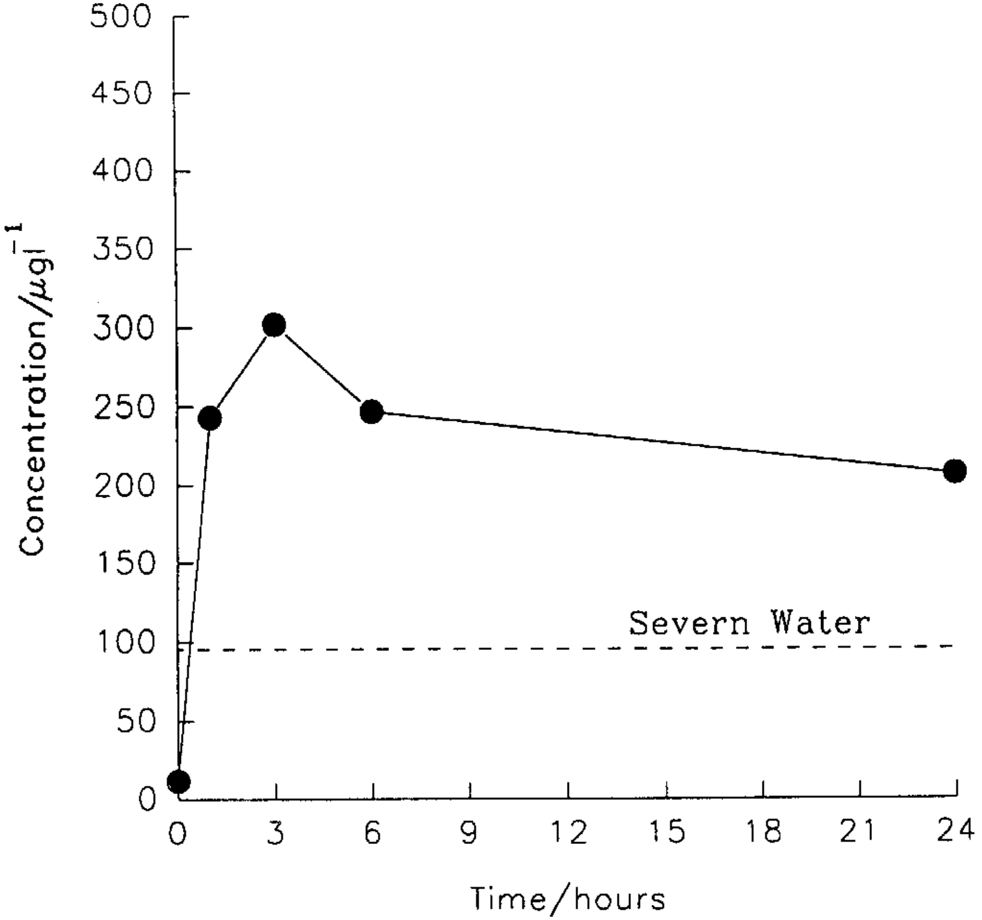
E10

Dissolved Organic Carbon



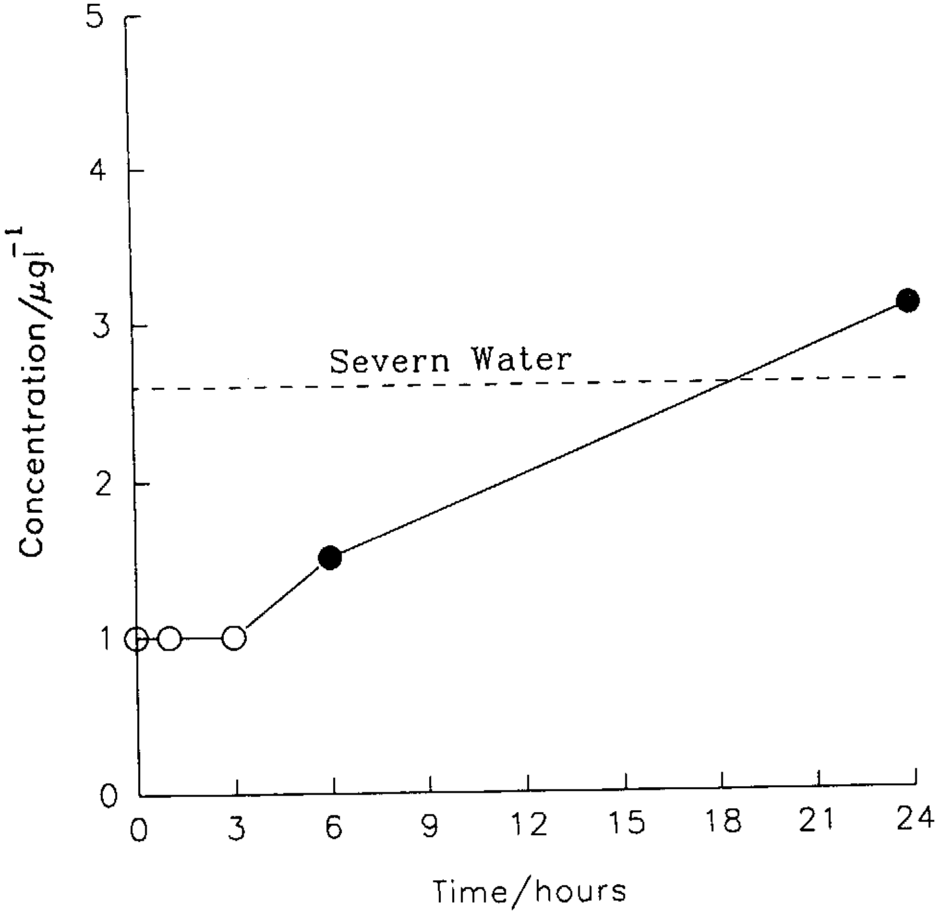
Aluminium


Concentration/$\mu g l^{-1}$
50
45
40
35
30
25
20
15
10
5
0
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

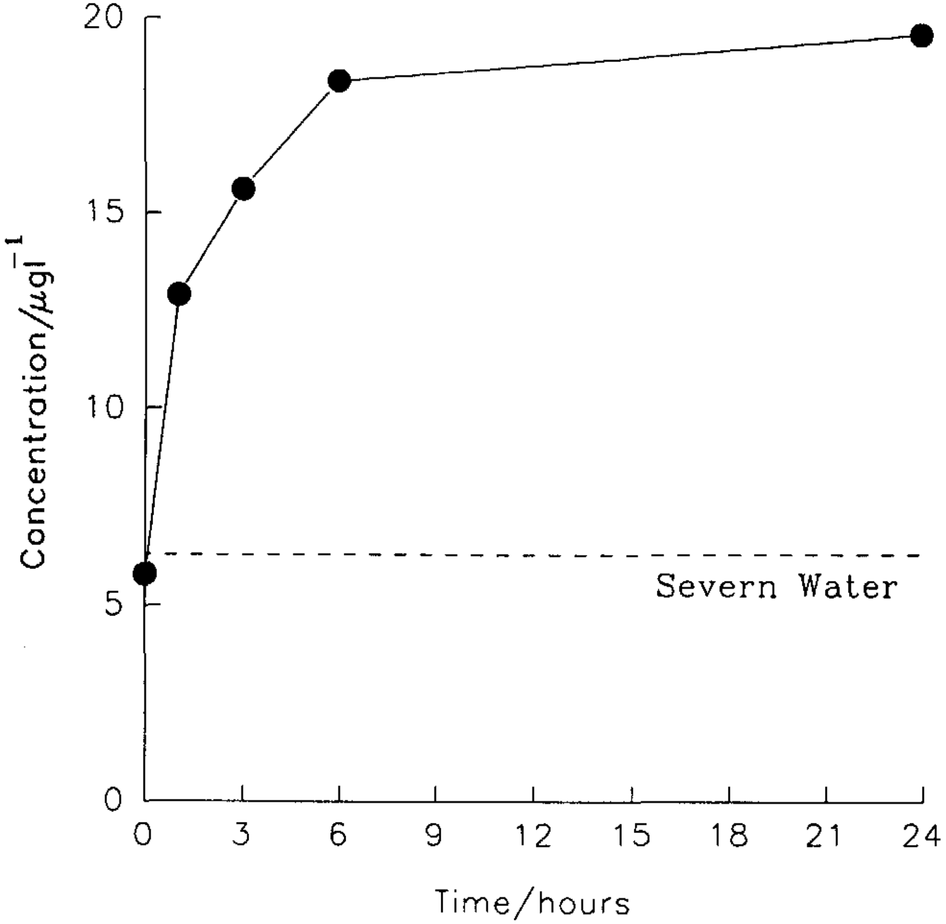

Concentration/μgl^{-1}
500
450
400
350
300
250
200
150
100
50
0
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Barium

Cadmium

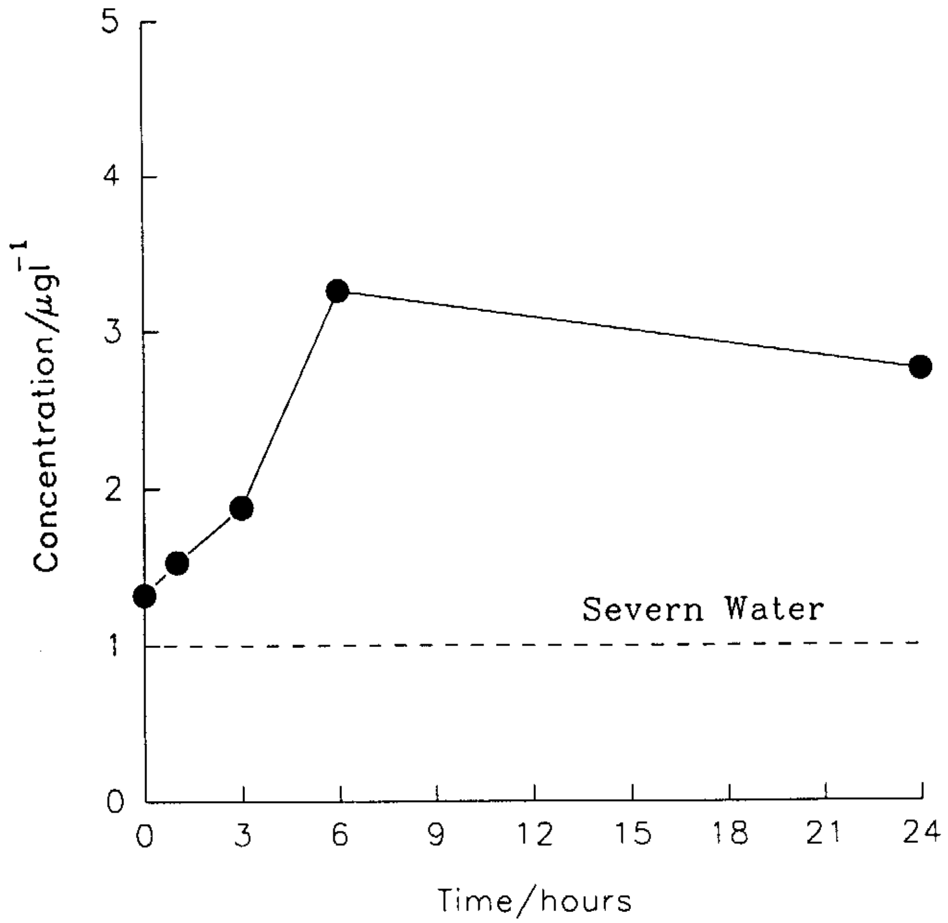

Concentration/$\mu g l^{-1}$
5
4
3
2
1
0
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Copper

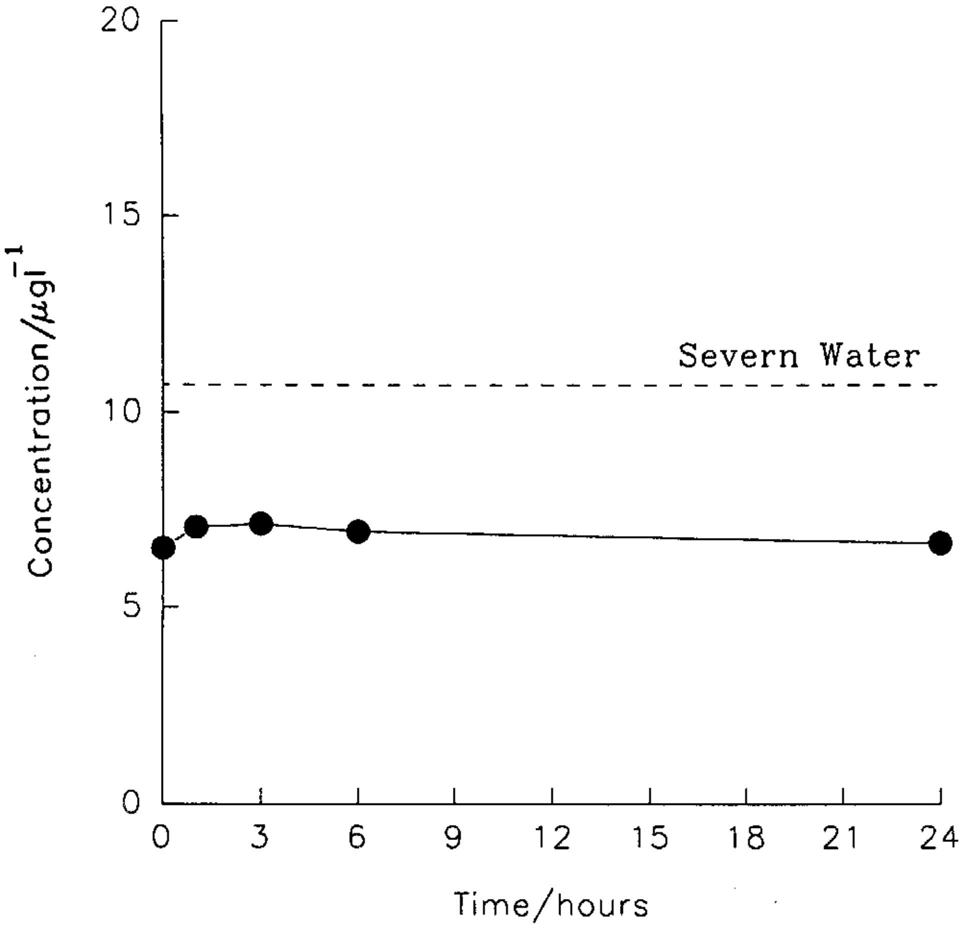


20
15
10
5
0
Concentration/μgl^{-1}
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Lead

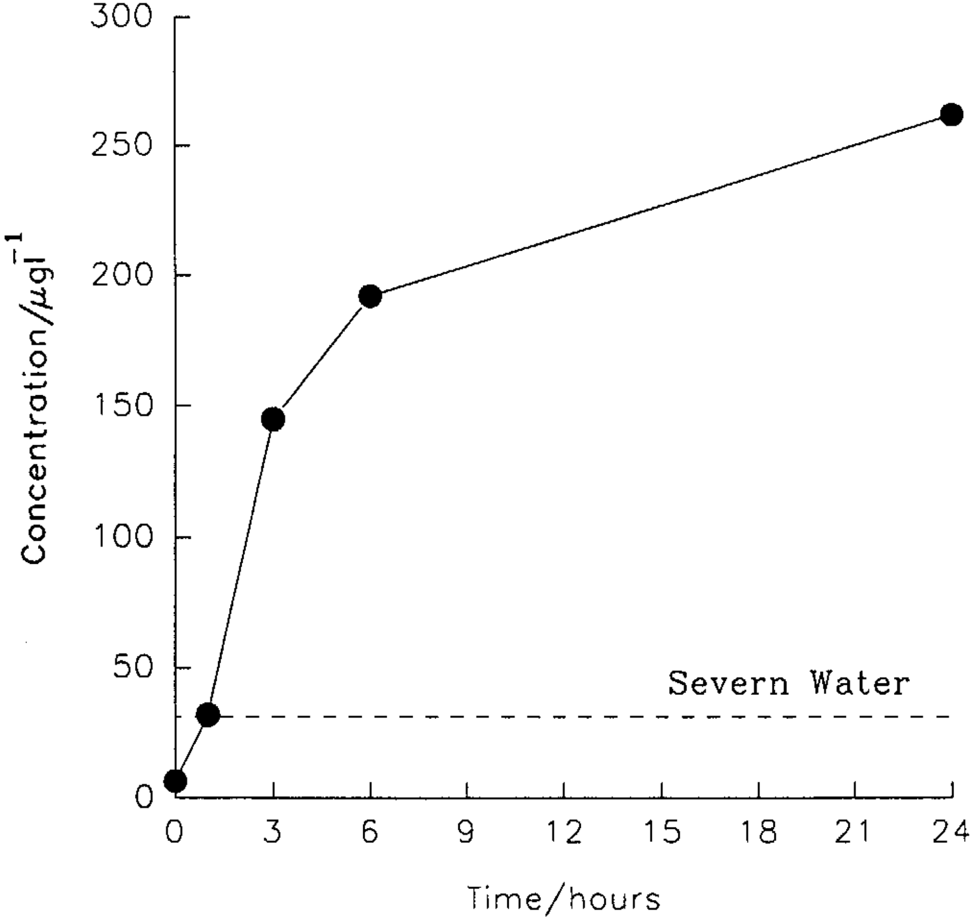

Concentration/μgl^{-1}
5
4
3
2
1
0
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Lithium

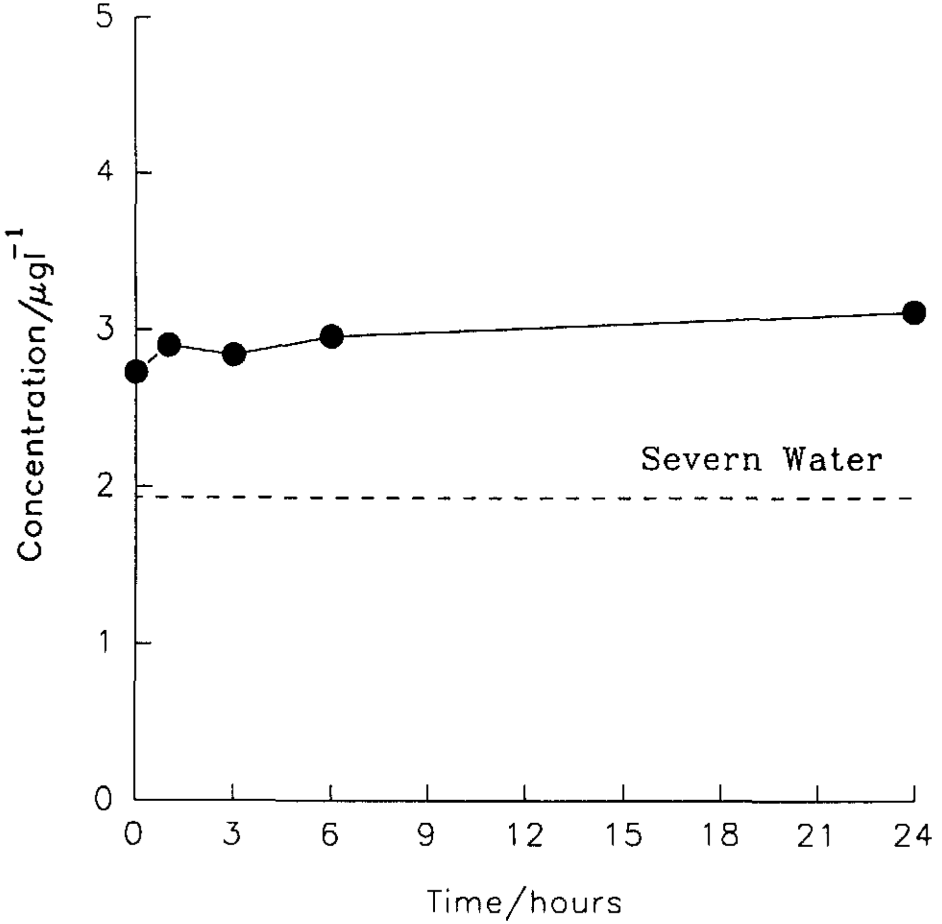


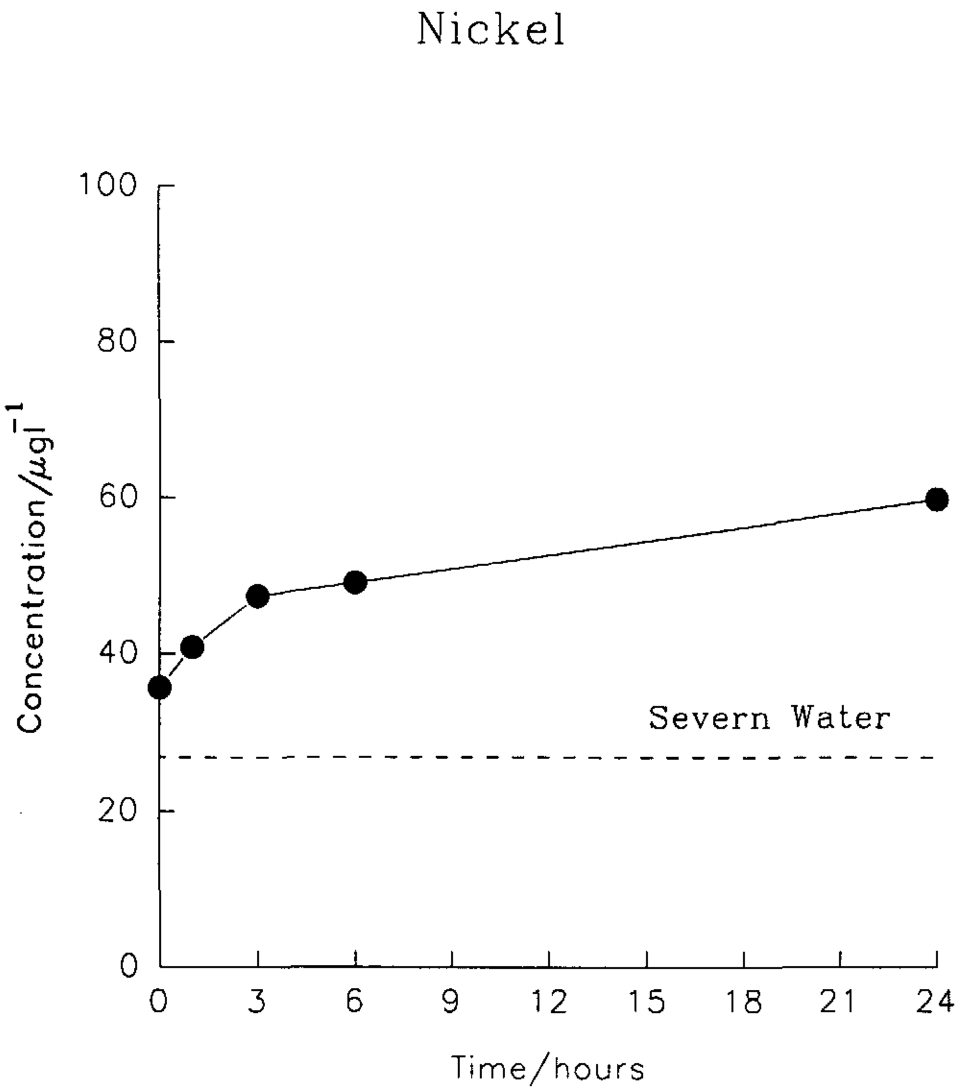
20
15
10
5
0
Concentration/μgl^{-1}
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Manganese

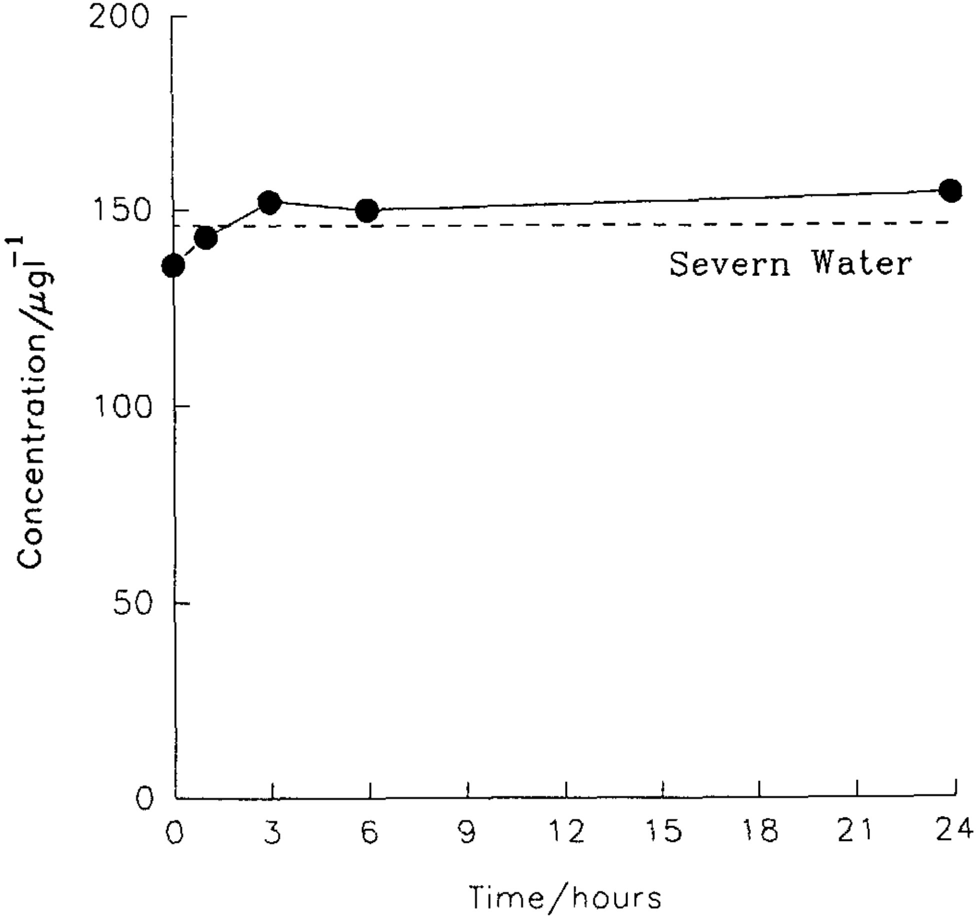

300
250
200
150
100
50
0
Concentration/μgl^{-1}
0
3
6
9
12
15
18
21
24
Time/hours
Severn Water

Molybdenum


5
4
3
2
1
0
Concentration/$\mu g l^{-1}$
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

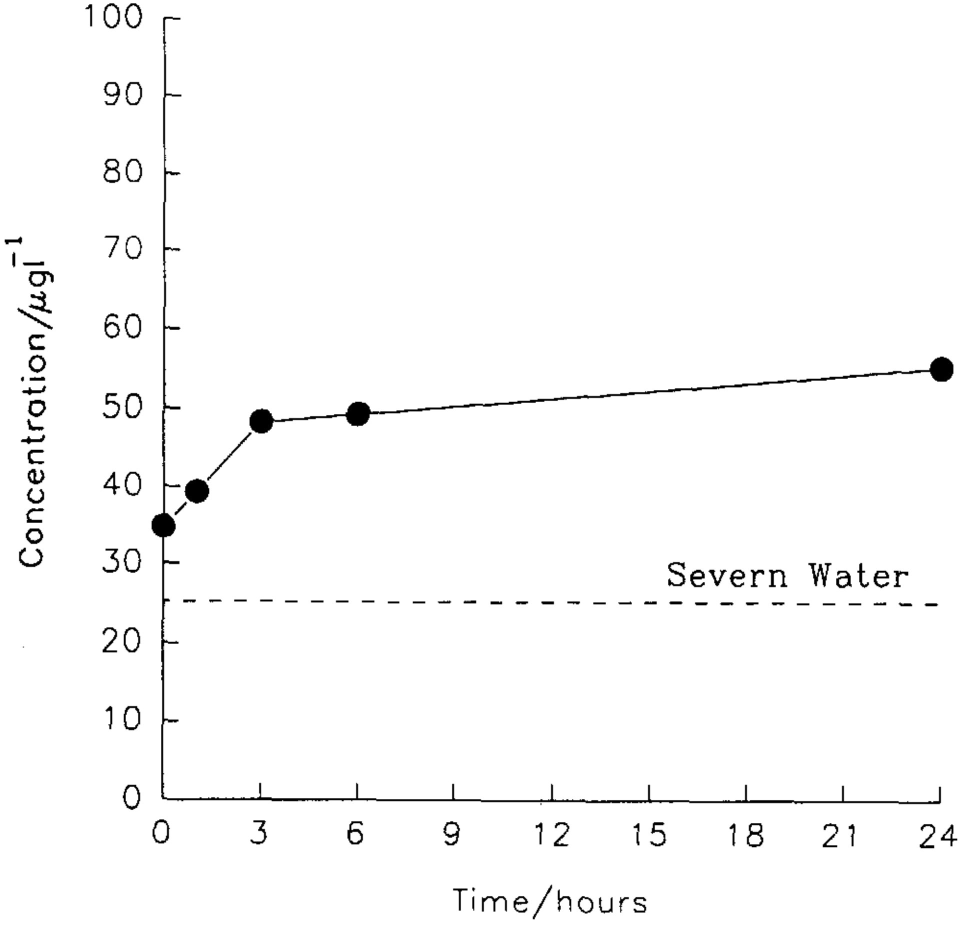

Nickel
100
80
60
40
20
0
Concentration/$\mu g l^{-1}$
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Strontium

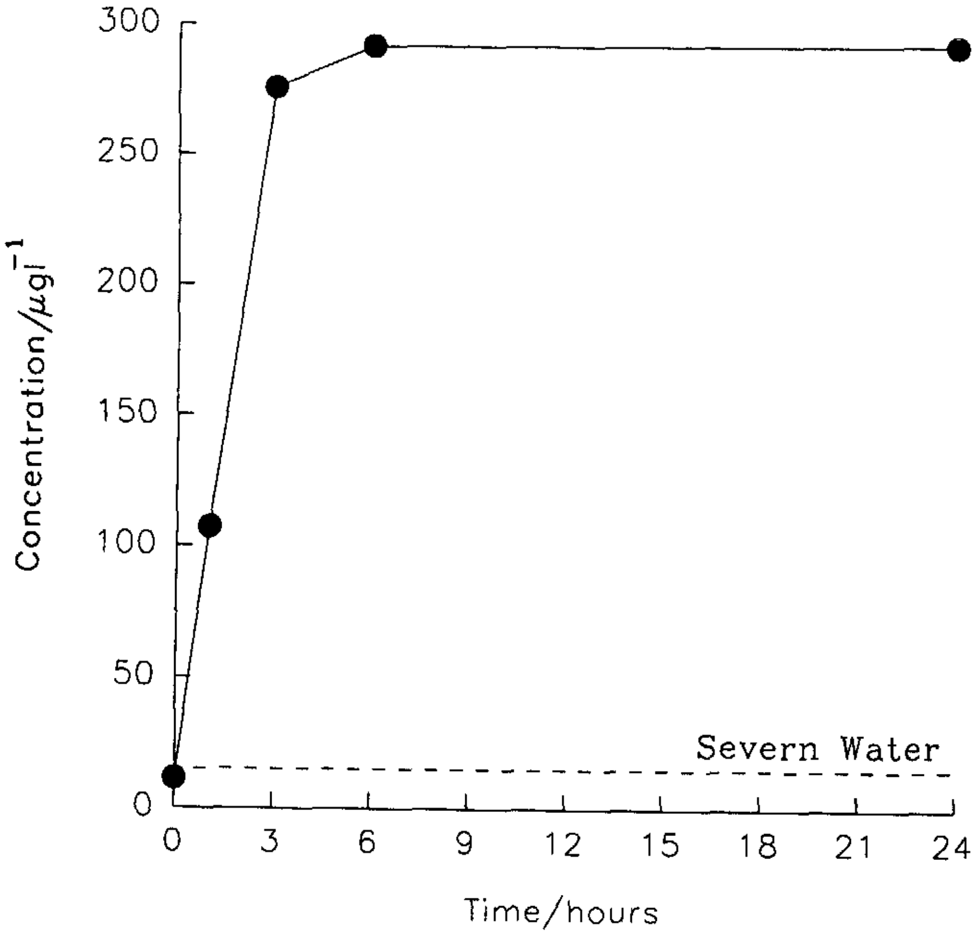


200
150
100
50
0
Concentration/$\mu g l^{-1}$
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Titanium


100
90
80
70
60
50
40
30
20
10
0
Concentration/μgl^{-1}
Severn Water
0
3
6
9
12
15
18
21
24
Time/hours

Zinc


Concentration/$\mu g l^{-1}$
300
250
200
150
100
50
0
0
3
6
9
12
15
18
21
24
Time/hours
Severn Water

Appendix F

Assessment of the Chemistry of Micro-organic Species During Transfer

The data received from Thames Region and Severn-Trent Region, Environmental Agency for the year 1995-6 has been evaluated. Sites were; Thames, Farmoor and Severn, Haw-Bridge.

The salient points to projected transfer of water from the Severn to the Thames are:-

(i) As can be seen from Table A, most micro-organics which are measured by either region are below the limits of detection given in Table A. Detected species are given in Table B. Micro-organic materials which are detected tend to be sporadic rather than continually present. Not surprisingly spring, summer and autumn tend to exhibit higher pesticide levels than in winter.

(ii) The source water for transfer (Haw Bridge) has detected pesticide concentrations for the following species:-

> Atrazine, γ-HCH (Lindane), Simazine, Isoproturon, Mecoprop, Chloroform, Trichlorethylene, Tributyltin & Triphenyltin. Diazinon also recorded a solitary value at 0.011 $\mu g l^{-1}$ which was only just the minimum detection limit. In all cases maximum concentrations for any species in any sample were <0.2 $\mu g l^{-1}$

Of these compounds, organotins and trichloroethylene are not measured by Thames Region and only showed positive values for 2 in 13, 1 in 10 and 2 in 10 determinations respectively. All other species detected except one - namely chloroform, for which there is a solitary positive value ($0.25 \mu g l^{-1}$) similar magnitude to that found in Thames samples (0.21 & $0.46 \mu g l^{-1}$) - all are pesticides. These are as follows:-

(a) **Simazine & Atrazine**. These two herbicides are chemically very similar. The concentrations of these compounds in each river seems generally similar with most samples (approximately 75%) below detection and all samples less than $0.1 \mu g l^{-1}$.

(b) **γ-HCH (Lindane)**. This is the only pesticide in which concentrations may be consistently higher in the Severn although the sensitivity of measurement ($0.005 \mu g\ l^{-1}$) is partly responsible for the large number of positive detections of Lindane (8 out of 19); the highest recorded concentration at Haw Bridge was $0.022 \mu g l^{-1}$.

(c) **Isoproturon**. The maximum values recorded for isoproturon were similar in size to those for the Thames. Significantly whilst the Severn had no detectable levels of the similar compounds, diuron, linuron and chlorotoluron, the Thames had detectable traces of all of these.

(d) **Mecoprop**. Only one positive detection was recorded for this micro-organic species in the Severn out of a mere three analyses so it is important not to draw too much from it. However it is comparable in size to the range of concentrations found in the Thames data.

(e) The micro-organics, dichlorbenzil, MCPA, PAH (as total) and bromoform were all found in the Thames but were either not detected or not measured in the Severn.

In conclusion the micro-organic content of the water at Haw Bridge seems to be of comparable quality than that of the Thames at Farmoor on the basis of this information. Therefore, assuming that both water systems are in relative equilibrium with regard to their micro-organic content, this data may lead to the conclusion that little change may be expected in mixing the two waters. However there are two considerations which may be significant in considering any chemical changes in micro-organic content resulting from transfer.

(i) The determinations of the Severn for surfactants were given in mgl^{-1} and were all therefore below detection when expressed in this way. Therefore it is impossible to compare directly information on surfactant concentrations.

(ii) The relative role of sediment and the solvent, water, on the behaviour of micro-organics may be important and has been considered. Predictions of the fate during transfer of such species by pipeline, and the effect of settling ponds etc., is severely hampered by lack of reliable information on distribution coefficients for individual micro-organic species on sediment minerals, biological material, organic phases etc.

This effect is also compounded the large differences in volume between solution (water) and suspended material, typically comprising >99.99% & <0.01% of the system respectively. Apparent distribution coefficients between these phases could therefore be potentially affected by small changes in solution concentration producing large changes in the micro-organic content of solid phases, especially if as with many organic phases in water, solvation is relatively poor - the interaction being often largely hydrophobic. The net result is that accurate prediction of relative importance of solution, sediment and biological material is difficult if not impossible.

This assessment assumes that the data received from Thames region EA, from the site at Farmoor is applicable to that at Buscot. The site at Farmoor is a considerable distance downstream of Buscot, below the confluence of the R. Thames with the R. Windrush. However it seems unlikely that the site upstream (Buscot) would have significantly high micro-organic contamination without affecting the downstream site at Farmoor.

Table A. Microorganic Species Below Limit of Detection; Species Monitored in Both Rivers are in Capitals, species monitored only in the R. Severn (Haw Bridge) are in lower case; species monitored only in R. Thames (Farmoor) are in italics; all units $\mu g\ l^{-1}$

Organic Species	Limit	Organic Species	Limit	Organic Species	Limit
HEXACHLOROBUTADIENE	0.005	TETRACHLOROETHYNE	0.100	ALDRIN	0.005
HEPTACHLOR	0.005	HEPTACHLOR EPOXIDE	0.005	ENDOSULFAN-A	0.006
DIELDRIN	0.005	ENDRIN	0.005	TDE - P,P	0.005
DDE - P,P	0.005	DDT - 0,P	0.005	DDT - P,P	0.005
PARATHION	0.020	CHLORFENVINPHOS	0.020	PCSD/PAD	0.050
β-HCH	0.005	FENTHION	0.020	FENITROTHION	0.020
α-HCH	0.005	METHYL AZINPHOS	0.020	ETHYL AZINPHOS	0.020
2,4,D	0.050	MCPB	0.025	2,4,5-TCPA	0.040
MALATHION	0.020	PENTACHLOROPHENOL	0.100	HEXACHLOROBENZENE	0.005
TETRACHLOROMETHANE	0.100	1,2,3-TRICHLOROBENZENE	0.010	1,3,5-TRICHLOROBENZENE	0.010
1,2,4-TRICHLOROBENZENE	0.010	TRIFLURALIN	0.010	PCB IUPAC NO 28	0.005
PCB IUPAC NO 52	0.005	PCB IUPAC NO 101	0.005	PCB IUPAC NO 118	0.005
PCB IUPAC NO 138	0.005	PCB IUPAC NO 153	0.005	PCB IUPAC NO 180	0.005
ISODRIN	0.005	1,2 DICHLOROETHANE	1.000	CARBOPHENOTHION	0.020
TRICHLOROETHENE	0.100	PERMETHRINS	0.010	2-Methylphenol	0.500
Phenol	0.500	4-Methyphenol	0.500	3-Methylphenol	0.500
2,4 Dichlorophenol	0.500	2,4,6 Trichlorophenol	0.500	2-Chlorophenol	0.500
4-Chloro,3-Methylphenol	0.500	Carbaryl	0.100	Cyflutrin	0.010
Dichlorvos	0.020	S-Methyl Demeton	0.010	Endosulfan-B	0.005
Fenuron	0.100	Diflurobenzuron	0.100	Propazine	0.030
Methyl Parathion	0.015	Ioxynil	0.040	Bromoxynil	0.040
Propetamphos	0.010	Sn-Dibutyls (as Sn)	0.005	Sn-Tetrabutyls (as Sn)	0.005
Detergents, nonionic (units, $\mu g\ l^{-1}$*?)*	0.020	*δ-HCH*	0.005	*DDT-Total*	0.020
TDE, o,p	0.005	*Methoxychlor*	0.005	*Chlordane*	0.010
PCB's Total	0.035	*Trichlorobenzene Total*	0.030	*Bromodichloromethane*	0.050
Dibromochloromethane	0.050	*Drins, Total*	0.020	*TCB, Total(1/2LOD)*	0.0075
Drins, Total(1/2LOD)	0.010	*DDT, Total (1/2LOD)*	0.010	*Trichloroethane, 1,1,1*	0.100
Tecnazene	0.005	*Phenols, Total*	0.500	*Fluoroxypyr*	0.020
Dimethoate	0.020				

Table B. Detected Microorganic Species: Species Monitored for Both Rivers are in Capitals. Species. Monitored only in the R. Severn (Haw Bridge) are in lower case; species monitored only in R. Thames(Farmoor) are in italics All units in µg l^{-1}

Organic Species	Limit	No. of Samples Below Detection		Detected Concentrations	
		Thames	Severn	Thames	Severn
ATRAZINE	0.030	8	13	0.038, 0.038, 0.070	0.098, 0.070, 0.054
γ-HCH	0.005	11	9	0.011, 0.009	0.022, 0.014, 0.010, 0.007, 0.011, 0.009, 0.010, 0.009
DIAZINON	0.010-0.020	11	16	0.457?	0.011
DICHLORBENZIL	0.005-0.010	9	3	0.025, 0.008, 0.012	---
DIURON	0.010-0.020	1	2	0.030, 0.030, 0.040, 0.060, 0.030, 0.030, 0.350, 0.040, 0.040, 0.120, 0.090	---
MCPA	0.020-0.040	10	3	0.070, 0.071	---
SIMAZINE	0.030	8	11	0.052, 0.138	0.032, 0.087, 0.080, 0.059
LINURON	0.010-0.020	7	3	0.060, 0.190, 0.090, 0.140, 0.150	---
ISOPROTURON	0.010-0.020	4	1	0.570, 0.050, 0.060, 0.130, 0.130, 0.040, 0.060, 0.500	0.130, 0.100
CHLOROTURON	0.010-0.02	7	3	0.080, 0.270, 0.020	
MECOPROP	0.020-0.040	6	2	0.120, 0.070, 0.040, 0.030, 0.030, 0.030, 0.020, 0.033	0.084
CHLOROFORM	0.100-0.200	11	10	0.460, 0.210	0.250
DETERGENT, ANIONIC	***	3	13	0.050, 0.060, 0.060, 0.140, 0.050, 0.070, 0.070, 0.070, 0.050, 0.090, 0.100	***
Trichloroethylene	0.100	---	11	---	0.120, 0.160
Sn-Tributyl (as Sn)	0.005	---	9	---	0.025
Sn-Triphenyl (as Sn)	0.002	---	8	---	0.010, 0.027
PAH's	0.010?	0	---	0.013, 0.160	---
Bromoform	0.050	8	---	0.050, 0.060, 0.060, 0.050	---
HCH's, Total (1/2LOD)	0.0075	8	---	0.016, 0.014	---
T.H.M's, Total	0.250	7	---	0.610, 0.360, 0.250, 0.260, 0.260, 0.250	---
Hydrocarbons (dissolved)	60.0	2	---	160.0	---

*** Anionic Detergents were measured in units of mg l^{-1} at Haw Bridge and were not detected at this level. The detected values for the Thames were not given units but are assumed to be µg l^{-1}.