THE ANALYSIS AND FATE OF ACRYLAMIDE MONOMER IN AQUEOUS ENVIRONMENTS.

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Preface

The use of acrylamide based polymers for various water treatments is increasing. Concern has been expressed at this prospect as these polymers contain the neurotoxin acrylamide as a contaminant. A potential therefore exists for the pollution of water supplies. This research project, which was carried out for and funded by the Department of the Environment, was established to achieve the following objectives:-

1. To produce an analytical procedure for the determination of mono acrylamide in aqueous solutions capable of being used on a variety of effluents and UK waters without interference.

2. To assess the extent of adsorption of acrylamide monomer onto sludge and sediments.

3. To study the rate and extent of degradation or change of monoacrylamide in natural water samples and sediments (laboratory and _in situ_)

The ensuing report details information obtained at Plymouth Polytechnic during the successful completion of this project.

Introduction

Acrylamide may cause neurological disorders in humans and experimental animals as it affects the mitochondrial metabolism of certain neurofilaments in the distal nerve endings [1 - 8]. Cases of neurological disorders owing to acrylamide poisoning through gross contamination of well water have occurred [3]. This pollution was as a result of sewer grouting. Most other cases of acrylamide poisoning have been limited to persons handling solid acrylamide monomer or through the artificially dosing of experimental animals. Dosings likely to cause definable neurological effects are in the order of greater than 1 mg Kg^{-1}. The recommended maximum acrylamide concentration in potable waters is 0.25 $\mu g \ell^{-1}$ [9]. Acrylamide contamination of water courses is likely to occur from both the manufacture and usage of polymers and polyelectrolytes based on acrylamide monomer. Croll *et al* [10] showed that acrylamide could pass through a water treatment works and would therefore occur in tapwater at concentrations equivalent to those of the water source.

Commercial polyelectrolytes used as flocculents during the preparation of potable waters may not contain in excess of 0.05% acrylamide [9].

Unregulated polyelectrolytes, however, may be used for effluent treatment. Such polyacrylamides may contain up to 5% monomer [10]. Recent advances in the polymerisation procedures has meant that many non-potable water grade polymers now have monomer contents of less than 0.3% [11 - 12]. Croll *et al.* [10] have shown that acrylamide might be lost during sewage treatment and that degradation of acrylamide occurred over a period of days in river water incubations. The addition of acrylamide to solutions which had previously degraded acrylamide exhibited more rapid degradation.. Whether this was as a result of increased microbial numbers in the solution or acclimatisation in the sense of metabolic changes to accommodate a new substrate was unclear as was the significance to an *in situ* situation.

Many questions therefore required solution at the onset of this project, i.e.

1) Which analytical methods to apply to the routine monitoring of acrylamide
2) How widespread is acrylamide pollution and what are the major sources to the aquatic environment
3) Is acrylamide adsorbed on to the surface of solids (sewage sludge, natural sediments, etc).
4) How widespread is the ability of bacteria to degrade acrylamide and what factors affect this rate of degradation
5) Would acrylamide present in river water be lost and, if so, would this be owing to sediment adsorption or bacterial degradation
6) How effective are current sewage treatments at removing acrylamide and how might such processes be modified to increase their efficiency.

7) How stable is acrylamide in potable water supplies

8) The degradation pathway of acrylamide

This project has successfully answered all but the last of the above questions through the implementation of both routine and novel experimentation. In addition, an analytical method for acrylic acid (a possible degradation product) and data on the <u>in situ</u> toxicity of acrylamide have been obtained.

Analytical Methodology

Croll and Simkins[13] derivatised acrylamide to α β dibromopropionamide in order to concentrate acrylamide from water and produce a compound which was electron capture sensitive and therefore detectable at concentrations in excess of 0.25 $\mu g \ell^{-1}$. Hashimoto et al[14] further developed the bromination procedure and gas chromatography technique to increase the efficiency and applicability to routine analysis. Polarography[15] and high performance liquid chromatography (HPLC) with ultra-violet (UV) detection[16, 17, 18] methods have been developed which have detection limits of approximately 100 $\mu g \ell^{-1}$.

Two methods for the detection of acrylamide in aqueous samples have been developed during this project. Both of these methods have been combined and sent in draft to Mr L. Pittwell, Secretary of the Committee of Analysts for consideration as a "Standard Method". These methods include one with a detection limit of 0.25 $\mu g \ell^{-1}$ and the second with a detection limit of 5 $\mu g \ell^{-1}$. Gross pollution may raise the detection limit for certain samples. The former of these methods has been published in the "Analyst"[19]. This method utilises HPLC/UV to separate and quantify an acrylamide derivative. Ultra-violet detection has many advantages over ECD in that it has an extended linear range and cannot be contaminated. The only routine method capable of extracting acrylamide from water in order to achieve the desired sensitivity of 0.25 $\mu g \ell^{-1}$ was bromination by the Hashimoto procedure [14]. The α,β dibromopropionamide thus formed exhibited reduced sensitivity to UV detection and therefore required considerable concentration. Strict adherence to cleanliness of glassware and purity of reagents, etc., is therefore essential to the success of this method. The derivatisation/extraction procedure was the major drawback of the method in that it was both time-consuming and inefficient. Precise, reproduceable results for acrylamide are obtainable, however, although the overall method is time-consuming.

In order to overcome this latter inconvenience a HPLC/UV direct injection technique was developed which has a detection limit of 5 $\mu g \ell^{-1}$ for most samples. Two major limitations needed to be overcome before this limit of detection was achieved. Firstly the acrylamide peak needed to be resolved from an unknown coeluting unresolved "hump". The Hypersil ODS is the only phase tested to date capable of such resolution. Secondly, in order to utilise the high sensitivity of acrylamide in the far UV (194-202 nm) it is necessary to remove UV-absorbing inorganic anions and polar UV-absorbing organic compounds from the solution to be analysed. Ideally, less-polar organic compounds should also be removed to avoid column contamination. These criteria have been satisfied by the passage of aqueous samples through a mixed bed of Amberlite XAD-2 (hydrophobic) and hydrogen and hydroxide (cation and anion) exchange resins. Thus, regardless of starting solution, (river water, raw sewage, etc.) one is effectively analysing the neutral polar acrylamide in an almost distilled water solution. This method was initially only designed for personal use to screen samples. At the recommendation of Dr. Stella Patterson South West Water Authority this rapid method (approximately 8-20 minutes) was included in the "Standard Method" draft.

The Fate of Acrylamide in Aqueous Environments

Laboratory Studies

1. Bacterial Degradation

Initial laboratory experiments[21] confirmed the findings of Croll *et al*[22] that acrylamide is degraded in river water and sewage samples. This work was extended to include a wide variety of water sources, i.e. river, estuarine, sea, peat bog, effluent and process waters from various industries etc. and showed that the ability to degrade acrylamide was a widespread phenomenon. Incubations in sterile, sterile spiked with unsterile, light/dark, aerobic/anaerobic conditions showed that various naturally-occurring photosynthetic/non-photosynthetic, aerobic/anaerobic bacteria possess the ability to degrade acrylamide. The sterilisation procedure for Plymouth tap-water reduced bacterial activity to a level whereby no loss occurred over a two-month period. Algal growths were, however, noted in the incubation vessels. The addition of chlorine to sterile tap-water samples at concentrations of 1 - 20 mgl^{-1} for one to twenty-four hours resulted in no loss of acrylamide (owing to formation of any halogenated derivatives) (see below). The occurrence of high levels of certain heavy metals in river waters contaminated with tin mine effluent effectively sterilise certain rivers with regards their capability to degrade acrylamide. The loss of acrylamide by bacterial degradation can occur in non- sterile, light/dark, aerobic/anaerobic conditions and the rate of degradation is likely to be dependent upon the numbers of bacteria per given water volume. Lag periods noted before the degradation of acrylamide in waters are therefore likely to be caused by the natural stock needing to attain numbers capable of effecting solution concentration rather than acclimatisation owing to changes in the metabolic activity to to accommodate a new energy source. The presence of an intensely active bacteria surface such as sewage filter bed clinker surfaces led to losses of acrylamide from solution with no obvious lag-phase. Such an effect was noted when investigating the loss of ammonium from river water incubated with and without rocks from an eutrophic river. The presence of carbon, hydrogen, oxygen and nitrogen should make acrylamide an ideal growth medium for bacteria. No inhibitory effects on bacterial degradation were noted at 8 $\mu g\ l^{-1}$ to 100+ mg l^{-1} concentrations.

The effect of temperature on bacterial degradation of acrylamide

Laude *et al*[25] incubated summer-collected acrylamide spiked samples at various temperatures and found the degradation rate to decrease with decreasing temperature. They inferred probable seasonal *in situ* variations in the acrylamide degradation rate. It is possible, however, for differing microbial populations with different metabolic rates to exist in streams in the summer and in the winter. Samples of summer and winter collected river waters from"unpolluted"and "polluted" reaches of four streams were incubated in aerobic conditions at their collection temperature with acrylamide. The results suggested increased degradation rates in the summer, but this effect was very variable and always less marked than suggested by Launde *et al*[25].

2. The chemical degradation of acrylamide

Croll *et al*[10] has shown that certain oxidising agents will degrade acrylamide, this project has also shown the same to be true for certain reducing agents (i.e. sodium dithionite and sodium thiosulphate)[21]. No other chemical degradation was noted for any sterilised samples for the pH range 4 to 10. Solutions of 0, 5, 50, 500 μgl^{-1} acrylamide in Plymouth tap water were dosed with 0, 0.5, 3.0, 6.0, and 20.0 mgl^{-1} chlorine. A Lovibond 1000 comparator using DPD No 4 tablets was used to check the total chlorine concentration (after dilution as necessary). The acrylamide concentration was assayed by direct solution injection after 1, 5 and 24 hours. Samples were maintained in the dark at a temperature of 17 ± 4°C. No loss of acrylamide was noted from any of the samples tested[26].

3. Adsorption Studies

No acrylamide loss, other than that likely to be caused by bacterial degradation, was noted from solutions in contact with natural sediments, soil, sewage sludge, kaolinite, montmorillonite, peat, anionic, cationic or hydrophobic resins[27]. Activated carbon was found to have a limited affinity for acrylamide which was not affected for the pH range 4 to 10. Losses of acrylamide from water are therefore likely to be as a result of bacterial degradation rather than adsorption on to solid surfaces[21,27]. Entrainment of acrylamide on to solid surfaces when paper, industrial effluents, etc., are treated with polyelectrolytes, however, occurs[26]. This is presumably as the acrylamide is in the polymer matrix and therefore co-adsorbed. If the polymer/acrylamide/solid matrix is left in contact with water then acrylamide will leach into the water[26]. Should insufficient time be allowed for the acrylamide to leach out (as in the use of cationic polyacrylamide retention aids in paper-making) then acrylamide will remain with the solid. This may present a source of concern when large amount of waste paper are recycled in closed-system digestors. The use of polyacrylamides to flocculate biologically active solids might lead to no obvious water pollution as the entrained acrylamide may be rapidly degraded. This project has shown bacterial film associated with certain solid surfaces to be capable of very rapid degradation of acrylamide[28].

Metabolic pathway

It was considered that loss of acrylamide would be either by acid formation or reactions involving the double bond. Considerable time was invested in the development of a suitable method for acrylic acid[20]. No acrylic acid was, however, then detected for acrylamide incubations. Lack of time prevented further consideration of the degradation pathway.

In Situ Studies

It was not considered practical to attempt an extensive random survey given the considerable limitations in personnel and the time needed for analysis. Survey results were therefore conducted on a selective local basis. The criteria for selection were i) to obtain a variety of water types, and ii) data on sites known to be using polyacrylamides. Survey results are detailed in Table 1. Acrylamide was only detected in Plymouth Tapwater and one of the tapwater sources (i.e. the River Tavy) during the initial study in June 1978. A later more detailed study of the River Tavy and subsequent examinations of Plymouth Tapwater could detect no acrylamide, thus the earlier source could not be identified.

Sewer repairs were known to be in progress at the time of the original contamination. From conversational information supplied, it was inferred that no grouts based on acrylamide were used. Given the Japanese incident[3] we tried to pursue possible acrylamide pollution from grouting on several occasions. Freely available information was given by polyacrylamide manufacturers[11,12] on their other products. No information was ever obtained on British uses of grouts utilising acrylamide and other materials. DOW Chemical Co. Ltd. appear to be the main likely producer of such products. This therefore may still be an area of concern, but without some persuasion, information is unlikely to become available.

No significant acrylamide pollution (greater than 0.25 - 1 $\mu g l^{-1}$) was detected at sites using polyacrylamides which was directly attributable to their usage[27]. Financial limitations prevented proposed investigations of mining areas and polyacrylamide manufacturers. Indirect pollution resulting from polyacrylamide use occurred when waste paper was pulped[27] (see below). The absence of acrylamide at the English China Clay, Blackpool Works, St. Austell was considered encouraging as a proportion of the process water is recycled[19,21,27] (see below). It should be noted, however, that action by the South West Water Authority had resulted in the use of potable water quality polyacrylamides.

Case Studies

The China Clay Industry[27]

The English China Clay, Blackpool China Clay Pit, St. Austell, Cornwall, used polyacrylamide, instead of the starches previously used, to flocculate the clay pumped from the pit during the study period. A potable water grade polymer is used. Much of the water used in the mining of china clay is recycled. As the degradation of acrylamide in the process waters is longer than the residence time of the system[21], a potential for accumulation existed. Analysis of the various process waters and effluents after several months polymer usage could detect no acrylamide with a detection limit of 0.2 $\mu g l^{-1}$,[19]. The overdosing of clay slurry with one hundred times the normal polymer dosing on a laboratory scale resulted in an acrylamide concentrations of 11.2 $\mu g l^{-1}$ in water after filtration.

The Water Industry

Saltash Sewage Works[27] used polyacrylamides for sludge conditioning during this study. No acrylamide could be detected in process waters before or after polymer addition. The extremely high levels of dissolved organic matter in the sludge resulted in the need for six clean-up stages. The clean-up used consisted of: a hexane extraction (20 ml) followed by an ethyl acetate extraction (20 ml). The sample was then made alkaline (pH10) by the addition of sodium hydroxide (IM) and extracted with hexane and ethyl acetate as before. The sample was finally acidified (pH1 - 3) by the addition of hydrobromic acid (sp.gr. 1.48) and extracted as above. Even with this clean-up the levels of interference prevented acrylamide determination at less than 4 $\mu g l^{-1}$.

Avon Waterworks[27] used polyacrylamides for effluent treatment (i.e. precipitation of humic materials in backwash waters) during this study. No acrylamide could be detected in process waters before or after polymer addition with a detection limit of 0.2 $\mu g l^{-1}$. To assess the effect of overdosing of polymer on the monomer level, one of the three 70,000 gallon settlement tanks was emptied and was washed free of sludge. One backwash, 10,000 gallons, was spiked with one hundred times the normal polymer dosage and discharged into the final settlement tank. (The extreme viscosity of the polymer made handling difficult. Such an overdose would be extremely difficult to effect accidentally.) Samples were collected from the tank after 3, 30 and 60 minutes respectively and immediately filtered. Another backwash, plus one hundred times the polymer concentration was then added to the tank and the combined effluent sampled after,settling,prior to discharge to river. This second backwash was required as the tank would not discharge all of its contents to river. Ten thousand gallons of the tank were then discharged into Bala Brook over a period of two hours. River samples were taken downstream of the discharge and downstream of the confluence of Bala Brook and River Avon at appropriate times. The dilution of the effluent by Bala Brook, was approximately fourteen times and by the combined flows of Bala Brook and River Avon approximately forty times. A finite time was required for the acrylamide to diffuse out of the polymer matrix and become uniformly distributed in the settlement tank. The dilution afforded by River Avon reduced the monomer content below the detection limit of the method available. No adverse effects on the river biota were noted during this experiment.

The Paper Industry[27]

Three different paper mills were studied. Although these firms produced different grades of paper from different pulp sources, all used the same polyacrylamide retention aids and effluent flocculants during the study period. The samples taken on 5th June, 1979, showed no detectable acrylamide in the process waters or the effluents after polymer addition in either Mill A or B. Acrylamide was, however, detected in both process and effluent waters at Mill C. As all the mills used the same polymers it seemed unlikely that this acrylamide had derived directly from the mills' use of polymers.

Mill C was the only mill pulping waste paper during the study period. Between the two visits to this mill it shut down to renew both the pulping and dyeing recycling systems. On second visit samples were collected of the fresh-water intake, pulping recycle waters, dying recycle waters, final effluent and river below the discharge.

All dye process waters and effluents were treated as were the sewage sludge samples. The detection limit for process waters and effluents was 1.0 μgl^{-1}.

No acrylamide was detected in the freshwater intake, dye recycling, final effluent or river water. As the pulp recycling water had just been renewed none was discharged as effluent, although there was some carry-over from the pulping to the dyeing cycle. The presence of acrylamide only in the pulping recycling (pulping is only mechanical) suggests that the monomer was derived from the paper being pulped. It is known that paper filters could leach acrylamide[11], thus it would appear that acrylamide contained in the retention aid may be co-absorbed onto the paper with the polymer and that there may be insufficient time between the addition of polymer and drying for all the acrylamide to leach. The pulping of large quantities of waste paper may then concentrate the acrylamide in the pulping water which is recycled.

A mass flow study of acrylamide degradation in artificially spiked rivers/ estuaries[28]

The application of laboratory studies to environmental situations are often tentative. An *in situ* study was therefore designed to see if acrylamide would be degraded in a river/ estuarine situation and if continual exposure would result in acclimatisation. Acrylamide was continuously introduced into Tory Brook (Fig II) (into which acrylamide had not previously been discharged) during the period 9th October to 22nd December 1979. Sufficient acrylamide was added to raise the river concentration to approximately 40 μgl^{-1} for the first six-hour period. The river concentration was then reduced to approximately 5 μgl^{-1} for the remainder of the first week. This cycle of acrylamide exposure was maintained weekly for three weeks and then approximately monthly until the 22nd December 1979. After each six-hour exposure, water samples were collected at each river sampling station (Fig II) and analysed for acrylamide (Brown and Rhead, 1979). The mass flow of acrylamide was calculated from the concentration and river/tributary flow data. On the 29th October 1979 the acrylamide concentration was maintained at approximately 40 μgl^{-1} for twenty-four hours prior to analysis and additional samples were collected from Plym Estuary. Before the addition of acrylamide and at approximately monthly intervals after the first addition, river samples were collected and their ability to degrade acrylamide in the laboratory noted. The effect of temperature was also assessed by collected river samples from four rivers (Fig I). Samples were collected in the summer and again during the winter and their ability to degrade acrylamide in the laboratory assessed. The samples were maintained at temperatures appropriate to their collection date.

No loss of acrylamide occurred from Tory Brook. The residence time of this river was approximately four to five hours. Acrylamide was detected at Station IV in the Plym Estuary at both high and low tides on the 29th October 1979 but not at Station VII. The seawater dilution at Station VII had probably lowered the acrylamide levels to below the detection limit. Analysis of collected Tory Brook samples before addition of acrylamide infer that the degradation potential of acrylamide increased downstream probably reflecting the increased microbial activity of the lowland areas as compared to the upper catchment. Comparison of the degradation rates at the various sampling stations before and after acrylamide addition to that during the addition of acrylamide suggest that some increase of degradation potential had occurred whilst acrylamide was being added. The degradation rates of acrylamide from summer and winter collected river samples did not vary by as much as suggested by laboratory degradation experiments in which the incubation temperature of summer collected samples was changed (Lande *et al*, 1979).

The Toxicity of Acrylamide to the Fauna of an Artificially Spiked River 28

As with chemical degradation studies the application of laboratory toxicity studies to environmental situations are also often tentative, owing to the complexities of real habitats as opposed to controlled conditions. A biological appraisal of Tory Brook was therefore undertaken concurrently with the degradation study. A qualitative aquatic insect survey of Tory Brook before and after exposure to approximately 40 $\mu g l^{-1}$ acrylamide for six hours on the 9th October 1979, showed a decrease in the population size and diversity of species. No aquatic insects were found when a drift net was submerged for three six-hour periods prior to the addition of acrylamide. Examples of *Chironomidae* sp, *Baetis rhodani* and *Amphinemura sulcicollis* were found after six-hour exposure to approximately 40 $\mu g l^{-1}$ acrylamide. Following the six-hour exposure, the acrylamide concentration was reduced to approximately 5 $\mu g l^{-1}$ and maintained at this concentration for one week. This cycle of acrylamide exposure was maintained weekly for three weeks and then approximately monthly until the 22nd December 1979. At the end of the first week's cycle *Hydropsyche instabilis* was the only aquatic insect unaffected by the acrylamide addition, and with the exception of a much depleted *B.rhodani* and *Chironomidae sp* populations no other species were noted. Both of these latter groups were absent by the end of the third cycle, whereas the H.instabilis population showed an apparent increase.

Chironomidae sp., B.rhodani and A.sulcicollis were again found when the river was examined four and eight weeks after the final acrylamide addition but at very low population densities.

An electro-fishing survey of the Tory Brook catchment was carried out during the week beginning 21st August 1978 by a local mining firm during a baseline environmental study of the Hemerdon area. Salmo trutta (trout) was found in Smallhanger Brook and Nicholl's Farm Brook (Fig II), Cottus gobio (Bullhead) was found in Nicholl's Farm Brook, but Anguilla anguilla (Eel) was found in Smallhanger and Nicholl's Farm Brook and a few in Tory Brook downstream of the Smallhanger Brook confluence. No fish were found in Tory Brook above this confluence. It was considered that those eels found in Tory Brook were probably migrating. Lack of facilities prevented any appraisal of the effect of acrylamide addition on any fish which might have been present in Tory Brook. No obvious fish kills were noted or reported.

A mass flow study of acrylamide degradation in artificially spiked sewage works

The ability of activated sludge and filter sewage plants to degrade acrylamide was assessed by artificially dosing a known quantity of acrylamide continually into the inlets of Camel's Head (activated sludge) and Torpoint (filter) sewage works for 48 hours. This period was chosen after the use of the colouring agent Bromophenol Blue to quantitatively monitor solute mobilites, basin retention characteristics etc. in these sewage works. Both works were shown to have overall retentions of equal to or less than 12 hours. Flow was continuously recorded throughout all studies.

During the acrylamide dosing experiments samples were collected in triplicate at 30 minute intervals at relevant positions in the sewage works after 24 hours and again after a further 24 hours. Sampling sites chosen were; inlet, after primary settlement tanks, after activated sludge tanks/filter bed, after final settlement. The substantial flow variations both diurnally and in the short term meant that given a constant dosing apparatus it was impossible to maintain a constant acrylamide concentration in the inlet. A dosing apparatus linked to the flow recorder to compensate for this was initially to be used for this study. This would have overcome the above problem. Strict financial constraints prevented application of this ideal solution.

Inlet acrylamide variations were aggravated by the complex solute movements both within and between the component basins of the sewage works as shown by previous colouring agent studies. The mass flow balances were therefore somewhat more imprecise than had been initially envisaged but infinitely preferable to an industrially polluted situation.

Given the above limitations the triplicate results were in good agreement. From initial laboratory studies[27], it was considered that acrylamide would not be lost in the primaries as it should not be associated with particulate matter. The in situ results confirmed this inference with no significant loss of dosed acrylamide in the primaries.

(The Camel's Head works has 2 batteries of 8 upward-flow sedimentation tanks[29], the Torpoint works has two rotating bridge radial flow tanks although at the time of sampling only one was in use).

At Camel's Head Sewage Works effluent from the primaries is mixed with activated sludge (normally 3:1, but 4:1 during the investigation) and split between 2 batteries of 6 hopper bottomed tanks. These tanks are aerated by Simplex high intensity surface-aeration cone, gearbox and 5.6 kW electric motor. Designed flow characteristics do not agree with actual flow characteristics as shown by the Bromophenol Blue study. The supposed retention was 6.25 hr with plug flow, 95% of a Bromophenol Blue dose was lost within 3.5 hours and the flow was shown to be VERY diffuse plug flow.

Approximately 50% of the acrylamide (dosage approximately 200 $\mu g l^{-1}$) was lost in the activated sludge tanks.

The Torpoint Sewage Works filter beds (3) were approximately five foot deep. The clinker had an average diameter of ½ inch. Normally a proportion of the final settlement effluent is recycled through the filters. This facility was switched off during the experiments to facilitate interpretation of the results. Supposed water retention on the filter was between 20 and 30 minutes. This seemed strange considering it represents water falling by gravity only 5 foot through a coarse matrix. During the Bromophenol Blue study the retention in pipework between the primary tanks to the filter beds (via proportionating manifold) ranged from 20 to 25 minutes. Intense blue colouration was noted at the base of the central core approximately five minutes after the first passage of blue "labelled" water onto the surface of the bed.

For the acrylamide degradation experiment water was collected from the supply arm and approximately 6 minutes later from the appropriate position at the base of the central core. (Mass flow balances were therefore considered more precise for filter beds than the other water basins). This procedure was repeated 4 times at 30 minute intervals after 24 hours and again after a further 24 hours. An acrylamide loss of 50 ± 7% was found.

Final settlement tanks for both sewage works were of the radial-flow type. Given the difficulty of lag periods between basins and mixing within basins, mass flow balances for the final settlement tanks was again imprecise. The loss ranged from 0 to 10% with an average of 2%. Given experimental error this is probably not significant. Incubations of influent and settled effluent dosed with acrylamide during these experiments showed no loss of acrylamide after 24 hours storage at ambient temperature and light conditions when maintained aerobic.

A series of laboratory studies were implimented to confirm the field data. Of particular interest has been the loss of acrylamide in the filter bed with such a short retention time, though as mentioned previously it has been shown that stable solid surfaces may support bacterial population with immense degradation capacity[23,24]. Sterile Plymouth Tapwater (100 ml) PT, PT: activated sludge (Camel's Head Sewage Works 1:1, 3:1 and 5:1), PT: activated sludge (1:1) i) heated to 70°C, ii) poisoned with mercuric chloride, PT: clinker (Torpoint Sewage Works) 2 and 30), PT: clinker (30) i) heated to 70°C.

ii) poisoned with mercuric chloride were aerobically incubated with $200\ \mu g l^{-1}$ acrylamide (Table II).

No acrylamide loss occurred for the tapwater control. Acrylamide was neither lost from heated or mercuric chloride treated sewage sludge/clinker. All the remaining solutions degraded acrylamide. Increasing the numbers of bacteria i.e. sludge dosing or numbers of clinkers increased the rate of acrylamide removal. Unlike other incubations no extensive lag periods (days) were noted. The extremely rapid loss of acrylamide from the filter bed as opposed the laboratory simulation is likely to be as a result of bacterial biomass to bulk water volume ratio in the bed being far greater than 100 ml of solution containing 30 clinkers (i.e. the water probably flows through the filter as a thin surface film).

It is considered that with redesign considerable improvements could be envisaged in the potential of sewage works to remove acrylamide. This could be achieved both by increasing the retention times of water in the biologically active zones and increasing the numbers ofbacteria present within these zones. If this research has a more general application and primary and final settlement have minimal importance for dissolved organics removal, settlement retention times in sewage works could be reduced to minimum and retention in more biologically active zones increased. Some support for this may be gleaned from initial Bromophenol Blue studies of the primaries at the Camel's Head works. Initially over 95% of dosed Bromophenol Blue was removed within 15 minutes for the complete tank assembly because of blockage of the proportionating manifold. Flushing of the manifold resulted in a loss of 95% of the Bromophenol Blue over a period of 4 hours. Effluents from the tanks and final effluents were satisfactory on both occasions.

Arranged studies at mining sites and at a sewage works which has received a concentrated acrylamide discharge for ten years had to be cancelled because of lack of funding. The latter was considered of considerable importance, and initial studies had shown promise.

Summary

1. Analytical methods for the analysis of acrylamide and acrylic acid (a possible degradation product) have been developed and published. The method capable of detecting acrylamide at trace (0.2 $\mu g \ell^{-1}$) levels is somewhat time consuming owing to the derivatisation and extraction procedures. To partially alleviate this difficulty an additional rapid (8-20 minutes) screening method with a detection limit of 5 $\mu g \ell^{-1}$ acrylamide, was developed.

2. Owing to its neutral polar nature acrylamide was not significantly adsorbed onto solid surfaces other than activated carbon during laboratory experiments.

3. A wide variety of aerobic/anaerobic, photo-synthetic/non-photosynthetic microheterotrophs which occur in nature and polluted aqueous and sediment environments, possess the ability to degrade acrylamide. Seasonal variations in the rate of degradation occur owing to temperature differences. This effect is, however, variable and cannot be predicted from basic temperature kinetics without knowledge of microheterotroph community composition etc. Chlorination and heavy metal pollution may prevent acrylamide degradation for in excess of two months.

4. Strong oxidising and reducing agents may degrade acrylamide, but neither pH variation between 4 and 10 or the chlorination procedures used in tapwater preparation change acrylamide.

5. For the sewage works studied (activated sludge and biological filter bed) no acrylamide loss was noted during primary settlement, confirming the laboratory studies that suggested that acrylamide would not be adsorbed onto solid surfaces. An approximate 50% loss of acrylamide was noted for both the activated sludge tanks and biological filter beds. A loss of 0 to 8% was shown for the final settlement tanks. Laboratory studies on collected sewage samples showed the <u>in situ</u> acrylamide loss to be a biological process. As rapid degradation of acrylamide was associated with biologically active surfaces, it is possible that when polyacrylamides are used to dewater sludge, that the acrylamide which is initially entrained in a polymer/sludge matrix might be degraded before diffusing into the water.

6. Degradation/adsorption studies using a river continuously artificially dosed with acrylamide for three months could not demonstrate any <u>in situ</u> mass loss of acrylamide. This further supports the inference that acrylamide is not significantly adsorbed onto solid surfaces. For the residence time of the stream studied (4 - 5 hours) the continuous dosing of acrylamide was insufficient to acclimatise the microheterotrophs sufficiently to effect any <u>in situ</u> degradation. Laboratory incubation of collected river samples showed that prior to acrylamide exposure there was an increase in degradative rate with river maturing. The continuous dosing of acrylamide appeared to cause some additional increase in microbial activity as shown by increased degradations rates.

7. _In situ_ exposure of aquatic insects to low levels of acrylamide (5-40 $\mu g \ell^{-1}$) caused mass mortalities, but the effect appeared to be species selective.

In conclusion it is considered that the improvements in polymerisation procedures, which have lowered the acrylamide monomer levels to less than 0.3% for many commercial products, has eased the likelihood of serious acrylamide contamination of water through the use of polyacrylamides. The use of high monomer content polymers, the manufacture of polymers from monomer (either at factories or _in situ_, as for sewer grouts, etc) and the recycling of waste paper might still lead to significant acrylamide levels in potable waters. The most common forms of sewage treatment seem to only remove approximately 50% of the acrylamide input, although acclimatisation might improve this figure. A one day preliminary survey at a Yorkshire sewage works (which has received acrylamide discharges for several years) showed that levels of acrylamide in the effluent were comparable to the inlet levels. As acrylamide is not adsorbed or chemically degraded in rivers, and microbial activity is unlikely to remove a significant proportion in less than a day, dilution must be relied upon to protect water supplies. Potable water treatment processes, other than activated carbon, do not remove acrylamide. The sterilisation procedures for potable water preparation appear to stabilise acrylamide in tapwater for in excess of two months. These factors combined to make it imperative that preventive measures are used to ensure that water sources are not contaminated. It is not considered feasible to develop a technique with a detection limit of 0.2 $\mu g \ell^{-1}$ acrylamide that is rapid enough for the screening of large numbers of samples (i.e. 50 + per day) as such detection levels require derivatisation and extraction procedures, which are of necessity, time consuming. A rapid direct injection technique which has a detection limit of 5 $\mu g \ell^{-1}$ acrylamide has been developed at this laboratory. It is suggested that a suitable means of monitoring water supplies would be infrequent selective analysis for 0.2 $\mu g \ell^{-1}$ and routine analysis at the 5 $\mu g \ell^{-1}$ level.

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FIGURE I

Sample Stations in the South West of England

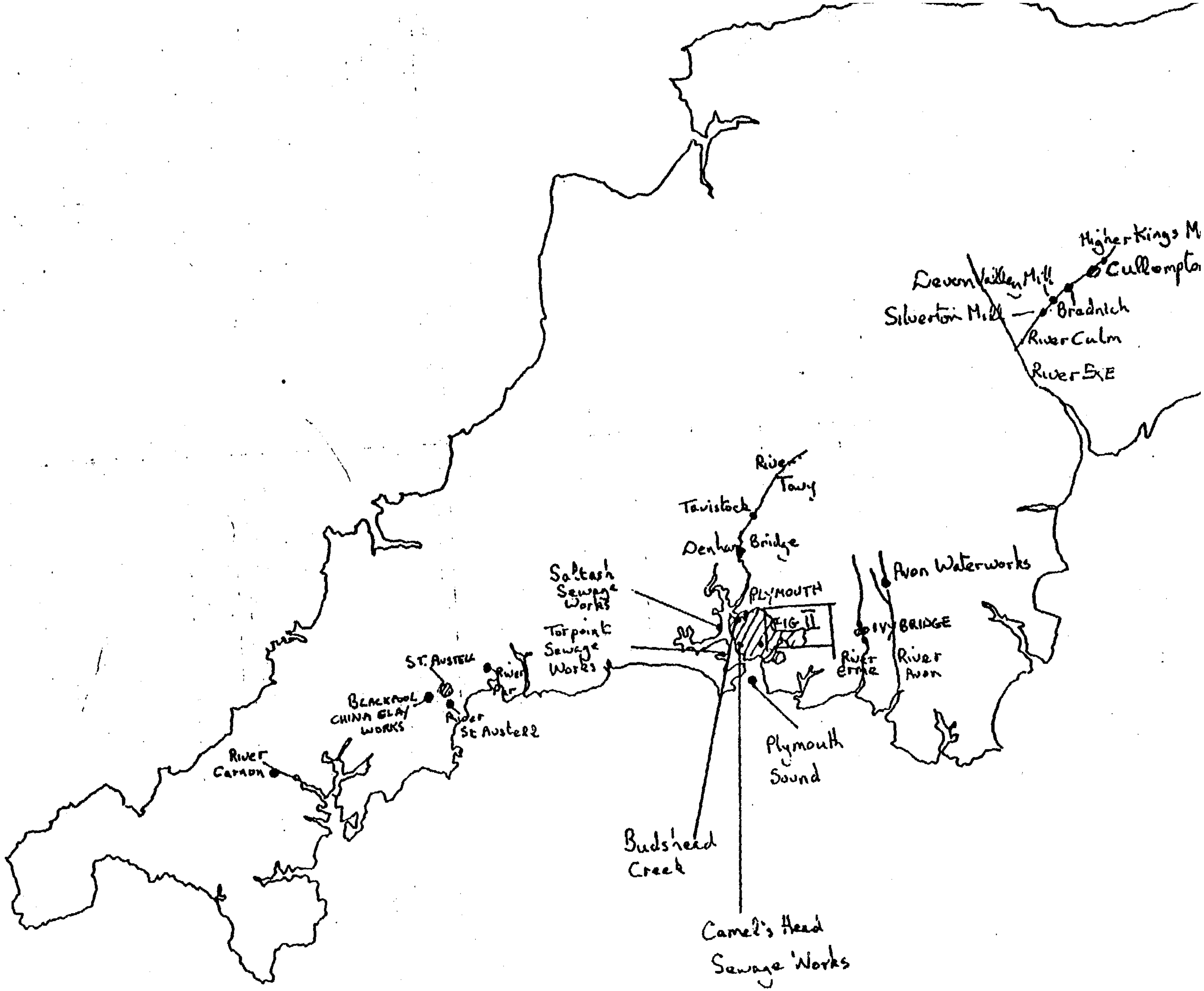
Higher Kings M
Cullompto
Devon Valley Mill
Bradnich
Silverton Mill
River Culm
River EXE
River Tavy
Tavistock
Denham Bridge
Saltash Sewage Works
PLYMOUTH
FIG II
Torpoint Sewage Works
Avon Waterworks
IVY BRIDGE
River Erme
River Avon
Plymouth Sound
Budshead Creek
Camel's Head Sewage Works
ST. AUSTELL
River Par
BLACKPOOL CHINA CLAY WORKS
River St Austell
River Carnon

FIGURE II

The Tory Brook Catchment

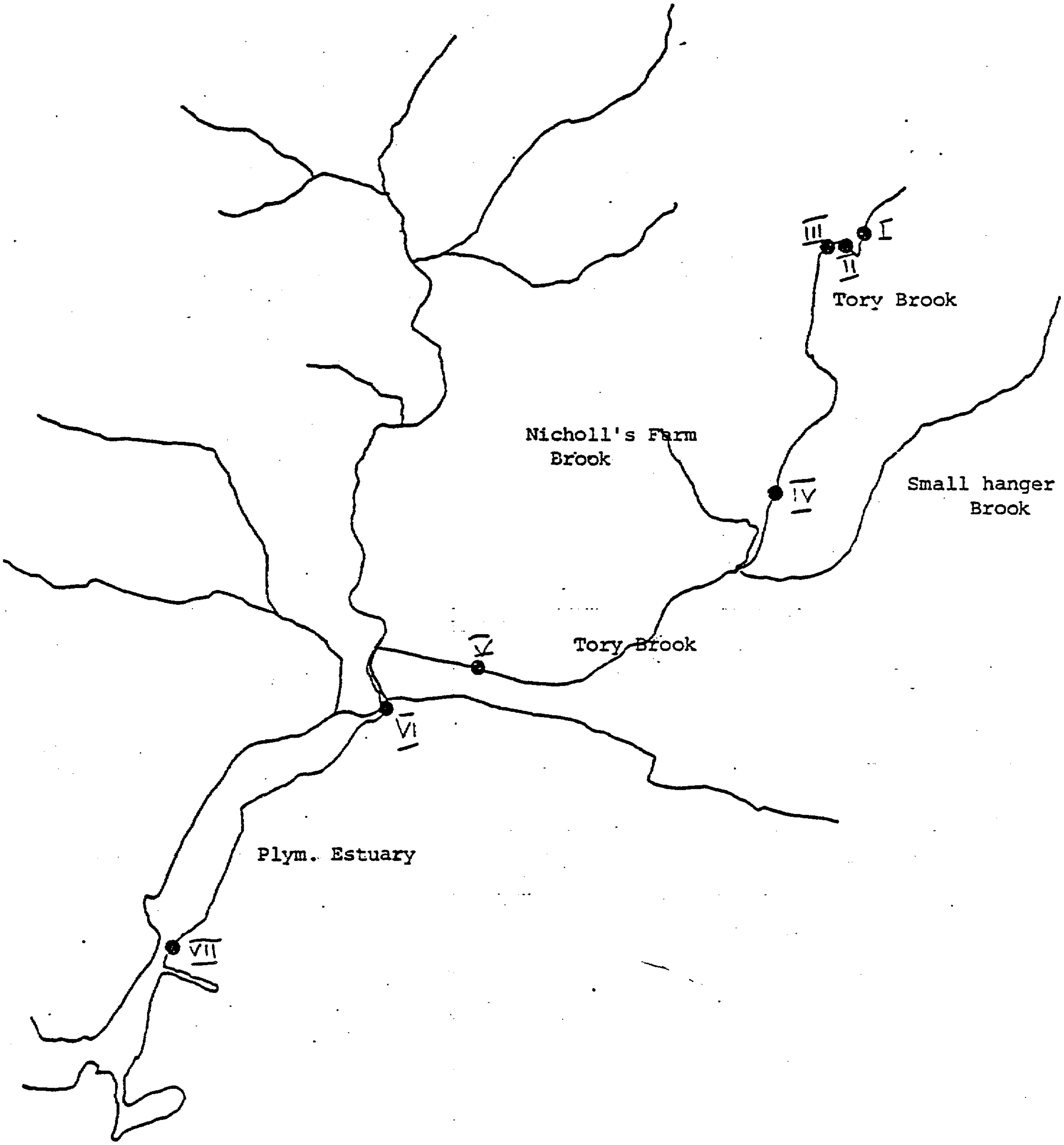
I
II
III
Tory Brook
Nicholl's Farm
Brook
IV
Small hanger
Brook
V
Tory Brook
VI
Plym. Estuary
VII

FIG II

Table I

The acrylamide survey of natural and polluted waters

Table I Concentration of acrylamide = $\mu g l^{-1}$

Sample Station	Acrylamide
19.6.78	
River Tavy	3.4
Plymouth Tapwater	4.5
Camel's Head Sewage Effluent	2.3
5.7.78	
Ivybridge Tapwater	<0.2
River Erme above Paper Mill	<0.2
River Erme below Paper Mill	<0.2
Plymouth Tapwater	0.75
14.7.78	
Ivybridge Tapwater	<0.2
Budshead Creek (Estuarine)	<0.2
Plymouth Tapwater	<0.2
Camel's Head Sewage Effluent	17.4
19.7.78	
English China Clay, Blackpool Clay Pit St. Austell	
i Kernic Mica Dam	<0.2
ii Hosepool	<0.2
iii Final Effluent	<0.2
iv 140' Thickener Basin	<0.2
River Calm above Paper Mill	<0.2
River Calm below Paper Mill	<0.2
St. Austell Tapwater	<0.2
Bradnich Tapwater	
Plymouth Sound Seawater	
9.10.78	
English China Clay, Blackpool Clay Pit St. Austell	
i Kernich Mica Dam	<0.2
ii Final Effluent	<0.2
iii Par Buelles	<0.2
Plymouth Tapwater	<0.2
8.5.79	
Plymouth Tapwater	<0.2
Saltash Sewage Works	
i Influent	<1.0
ii Effluent	<1.0
iii Sludge	<10.0
22.5.79	
Avon Waterworks	
i Sludge backwash before settlement	<0.2
ii Sludge backwash after settlement	<0.2
iii Tapwater	<0.2
Bala Brook below effluent	<0.2
5.6.79	
Silverton Paper Mill (A)	
i Process Water	<1.0
ii Effluent	<1.0

Table I cont.

Sample Station	Acrylamide
Devon Valley Paper Mill (B)	
i Process Water	<1.0
ii Effluent	<1.0
Higher Kings Paper Mill (C)	
i Process Water	45.4
ii Effluent	14.4
13.6.79	
Higher Kings Mill (C)	
i Freshwater Intake (River Calm)	<0.2
ii Pulping recycling water	10.5
iii Dying recycling water	<1.0
iv Final Effluent	<1.0
v River Calm 600m below effluent	<0.2
19.6.79	
Avon Waterworks	
i Sludge backwash	<0.2
ii Sludge backwash + 100γ polymer	8.5
a) 3 mins	<0.2
b) 30 mins	8.6
c) 60 mins	8.3
Bala Brook above effluent	<0.2
Bala Brook below effluent	<0.7
River Avon below Bala Brook confluence	<0.2
20.7.79	
R. Carnon (Hale Mills)	<0.2
23.7.79	
R. Tory (below Mica Dam)	<0.2
25.7.79	
R. Par (St. Blazey	<0.2
R. St. Austell (St. Austell)	<0.2
9.10.79*	
R. Tory (below Mica Dam)	<0.2
(* Start of artificially dosing of Tory Brook continued for next 3 months)	
16.10.79	
R. Tavy (Tavistock)	<0.2
Tavistock Sewage Effluent	<0.2
R. Tavy (Denham Bridge)	<0.2
19.5.80	
Plymouth Tapwater	<2.0
Camel's Head Sewage Influent	10.0
3.6.80	
Bingley Works (Yorkshire) Concentrations <u>mgl</u>$^{-1}$ Influent	
10.00 am	15.2
12.00 am	0.2
4.00 pm	6.2
Effluent	
10.00 am	0.3
12.00 am	7.0
4.00 pm	0.6