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The effects of surfactants in the Rivers Exe and Creedy

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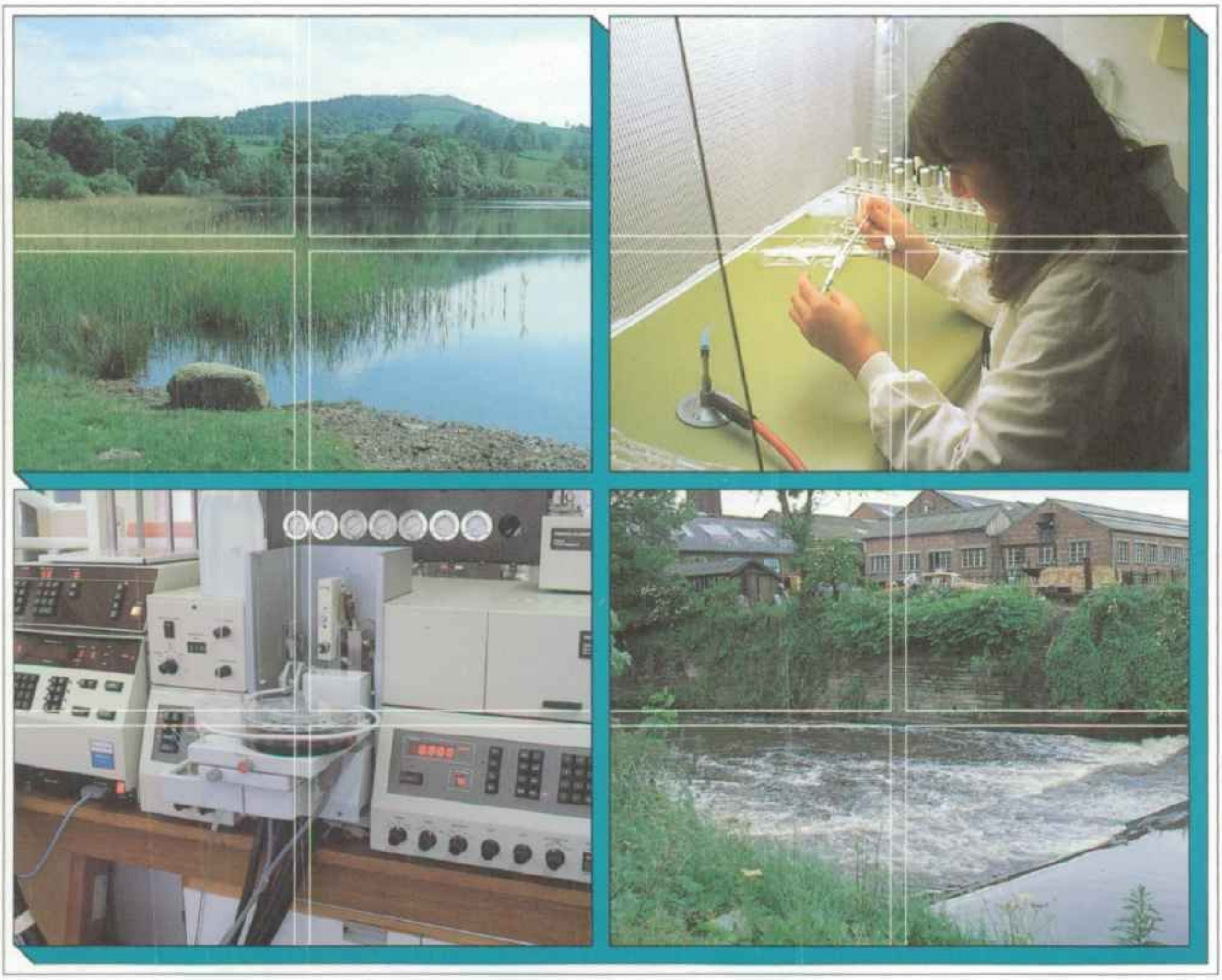

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Project leader:	W.A. House
Report start date:	01.11.92
Report end date:	01.03.93
Report to:	South West Water plc Peninsula House Rydon Lane Exeter EX2 7HR
IFE Report Ref:	RL/T11053n1/1
TFS Project No:	T11053n1

The Institute of Freshwater Ecology is part of the Terrestrial and Freshwater Sciences Directorate of the Natural Environment Research Council.

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SUMMARY

Foaming on the rivers Exe and Creedy has been a nuisance and cause of public concern. Local fishing organisations have also complained of "exceptional incidences" of fungal infections on salmon over and above that considered to be normal. Unfortunately, little research has been done to provide a quantitative assessment of the problem so that appropriate remedial action can be taken. This study was undertaken to evaluate the extent of the problems associated with the discharge of detergents, examine data that is available from the NRA on the concentrations of detergents in the rivers and effluent discharges and to summarize our state of knowledge of the acute and chronic toxicity of the most important classes of detergents, the linear alkylbenzene sulphonates, alkyl ethoxylates and alkylphenol ethoxylates.

Overall, the information concerning the measured concentrations of detergent residues in water is poor with none concerning residues in suspended solids, river bed-sediments or the biota; funding was not available for independent measurements. In view of this, estimates have been made of the concentrations of the anionic and nonanionic compounds in the water based on the available information for the catchment, the literature of incidence at other sites and our own field studies on a previous project. In view of recent measurements by the NRA of anionic surfactants in effluents, these are likely to underestimate the concentrations in the rivers.

A summary of the toxicity data does indicate that concentrations which affect algae, invertebrates and fish are likely to occur in both rivers; there is some evidence of changes in skin morphology of fish subject to both anionic and nonionic detergents. However it is important to appreciate that the toxicity of the residues depends on the detailed composition of the detergent, the occurrence of contaminants in the formulations which may reach the final effluent discharge and the degradation products. The nonylphenol residues from some nonionic compounds are identified as problematic although again, no information is available about their occurrence in these particular rivers.

It is concluded that an assessment of the concentration of detergent residues in water, suspended solids and bed-sediments at impacted sites on the rivers Exe and Creedy, including those sites where foaming has been a problem, is necessary for further ecotoxicology reviews or studies. This would enable a better evaluation of the toxicity data for algae, invertebrates and fish. It is also evident that a long-term chronic toxicity test with fish is desirable with an assessment of both behavioral and physiological responses in conditions appropriate to the rivers Exe and Creedy.

GLOSSARY

AEO	alkyl ethoxylate
APEO	alkyl phenyl ethoxylate
AS	alkyl sulphate; anionic surfactant
C10	alkyl chain of 10 carbons
dm^3	SI unit of volume equivalent to 1 litre
EC_{50}	effect concentration to achieve some effect on 50% of test species
FAB-MS	fast-atom-bombardment with mass spectrometry; used for specific analyses of detergent molecules
GC	gas chromatograph; analytical method
hplc	high performance liquid chromatograph
LAB	linear alkyl benzene
LAS	linear alkylbenzene sulphonate, a major anionic surfactant
LC_{50}	lethal concentration for 50% mortality
LOEC	lowest observed effect concentration
MBAS	methylene-blue active substance; analytical method to determine total anionic detergents
NOEC	no observed effect concentration
NP	nonylphenol; a degradation product from APEOs
NRA	National Rivers Authority
ppb	parts per billion equivalent to $\mu g\ dm^{-3}$ or µg/l
STW	sewage treatment works
SPC	sulphophenyl carboxylic acid

1. INTRODUCTION

There has been concern about the impact of pollutants in the rivers Exe and Creedy and particularly the effects of low flow and concomitant decreasing dilution of sewage and industrial wastes during the summer months. Although a considerable amount of data is available concerning the chemical composition and biological diversity at particular sites in the Exe catchment, this is not generally targeted at pollutants which are of importance locally. This is particularly true of the occurrence of detergent residues and industrial organic compounds in the Exe and Creedy. When measurements have been made, they have been restricted to determinations of the concentration of compounds in water samples and have not examined other aspects such as the suspended sediments, bed-sediments, algae, invertebrates and fish. This is partly because of the lack of resources for the relevant analyses and also the lack of research to evaluate the impact of point-discharges, such as waste-water effluents, on the ecology and general health of the aquatic life in the rivers.

The rivers Exe and Creedy have been well documented in terms of the potential sources of pollution in the catchments (Halcrow, 1989). These will not be considered here but include large fish farms, waste disposal sites, manufacturing industry, water treatment works, poultry processing plants, agricultural stores, sewage treatment works, animal feed factories and food processing plants.

This report is a small study to examine information on detergent residues in the rivers. The funding was insufficient for any independent chemical analyses by the Institute and relies on the limited amount of data available from the National Rivers Authority (NRA). In this respect the assessment of the impact of detergents is limited although, from the information available, it is possible to draw some worthwhile conclusions.

The extent of the foaming problem is illustrated in Plate 1 for a site near Exwick Weir in the summer of 1991. Other photographs have been taken by Mr I. Cook, River Exe Riparian Owners Association, to document the foaming problems associated with the river Exe. Local fishing organizations have also been concerned about the incidence of fungal growth of fish in the river Exe (see Plate 2 as an example).

It is not possible in the confines of this study to examine the river fish in more detail or investigate links between the water quality and fish ecology. However, the results of this pilot study do indicate areas of concern which have a relevance to the biological diversity and health of these rivers.

2. MAIN DISCHARGES TO THE RIVERS EXE AND CREEDY

The rivers Exe and Creedy are both softwater rivers; their general inorganic composition will not be examined in detail although a cursory glance is worthwhile to provide some general background information. The NRA, as requested, have provided details of the composition of the rivers at five sites on the river Exe from the Pynes intake (NGR SX93009710) and upstream at Bickleigh castle (NGR SS93700680), Ashley (NGR SS95300990), Collipriest (NGR SS95201170) and Tiverton (NGR SS94901310). Data were also obtained from the river Lowman, upstream of Tiverton (NGR SS95701260) and the river Creedy downstream of the Newton St Cyres sewage works (NGR SX90109680). The locations of the sites are shown in map 1. There is limited information at the sites concerning trace metal concentration, e.g. Zn, Cd, Pb, Ni and trace organic compounds, e.g. total dissolved phenols and pesticides including the triazines and organochlorine insecticides. Chemical information on pH, electrical conductivity, water temperature, dissolved oxygen, BOD (Biological Oxygen Demand), total organic carbon, ammonia, nitrate, nitrite, total oxidized nitrogen, suspended solids, alkalinity, chloride, phosphate, silicate and sulphate are available at about monthly intervals for the above sites. These are single-spot samples. The changes in pH, conductivity and total organic carbon along the river Exe are shown in Figure 1. The pH values are in the region of 7.7 with similar variability for all the sites. The vertical bars shown do not reflect the changes during spates or indeed reflect the diurnal variations in the river. The increase in pH, conductivity and inorganic carbon at Collipriest (see Figure 1) may be caused by the dilution of the river Lowman water or the impact of discharges in the Tiverton area. The river Lowman is more alkaline and has a higher calcium concentration compared with the river Exe, indeed the major-ion composition is similar to the river Creedy. The total organic carbon concentration tends to increase downstream of Tiverton but it is noticeable that both the river Lowman and Creedy have higher mean values of both conductivity and organic carbon than any of the sites on the Exe.

Only single measurements of the total dissolved anionic surfactants are available for most sites during 1992. On 5th October 1992 a sample from Oakford farm on the river Creedy had a concentration of 120 $\mu g\ dm^{-3}$ anionics compared with 90 $\mu g\ dm^{-3}$ in a sample from the river Lowman at Tiverton and 60 and 80 $\mu g\ dm^{-3}$ in samples from river Exe at Tiverton newbridge and Ashley respectively. Three samples were analysed from the intake at Pynes and gave 60, < 50 and 70 $\mu g\ dm^{-3}$ total anionics in January, April and July 1992. No measurement are available about the concentration of other detergent classes, e.g. nonionics or cationic compounds.

The main discharges addressed here are:

R. Exe	(a)	Tiverton sewage treatment works (STW)
	(b)	John Heathcoat & Co. Ltd at Tiverton
R. Creedy	(a)	Sewage at Newton St Cyres, Crediton, Yeoford and smaller works

The detailed statistics of the dilution of the various effluents are not available. However, it is possible to estimate dilution ratios from the consent limitations and river flows. For the Exe this leads to dilution factors from *ca* 10 to 200 with typical values estimated at John Heathcoat & Co. Ltd of 1:40 in the summer months. For the Tiverton STW the ratio drops to *ca* 1:10 at very low flow. On the R. Creedy, with its much lower flows, the dilution is expected to be relatively low at *ca* 1:13 (based on a total sewage effluent of 220 $m^3\ d^{-1}$ and low flow 95% quartile, of 28000 $m^3\ d^{-1}$) with values reaching *ca* 1:4 during low summer flows. The dilution ratios are obviously variable; the concentration of any chemical in the effluents will probably change on dilution with the river water but without information from measurements downstream of the discharge, it is difficult to predict the concentration after dilution. This is because:

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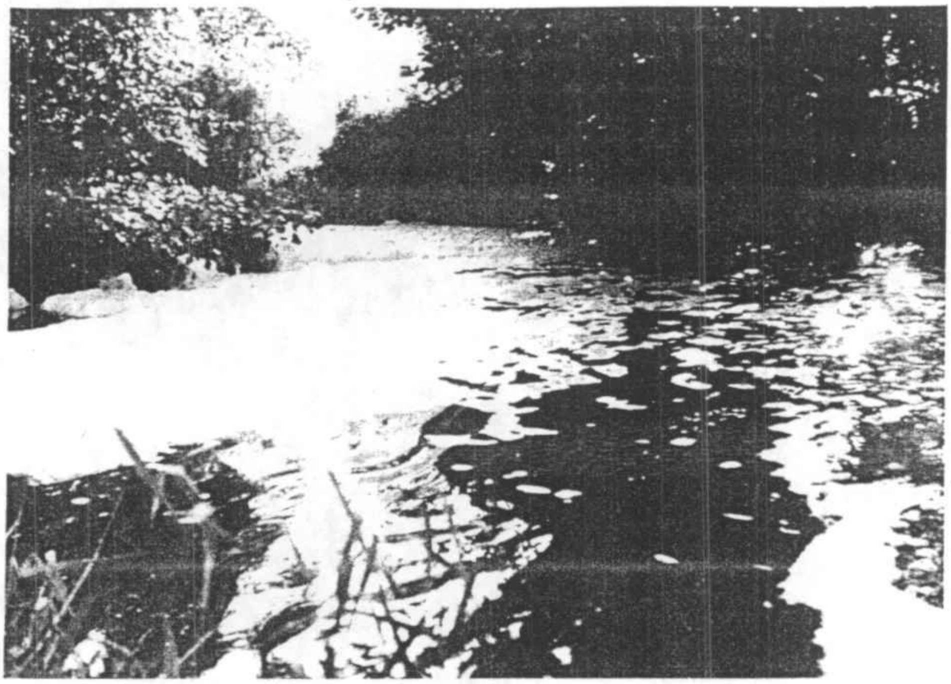


Plate 1. Foam on the river Exe at Exwick weir in the summer of 1991.

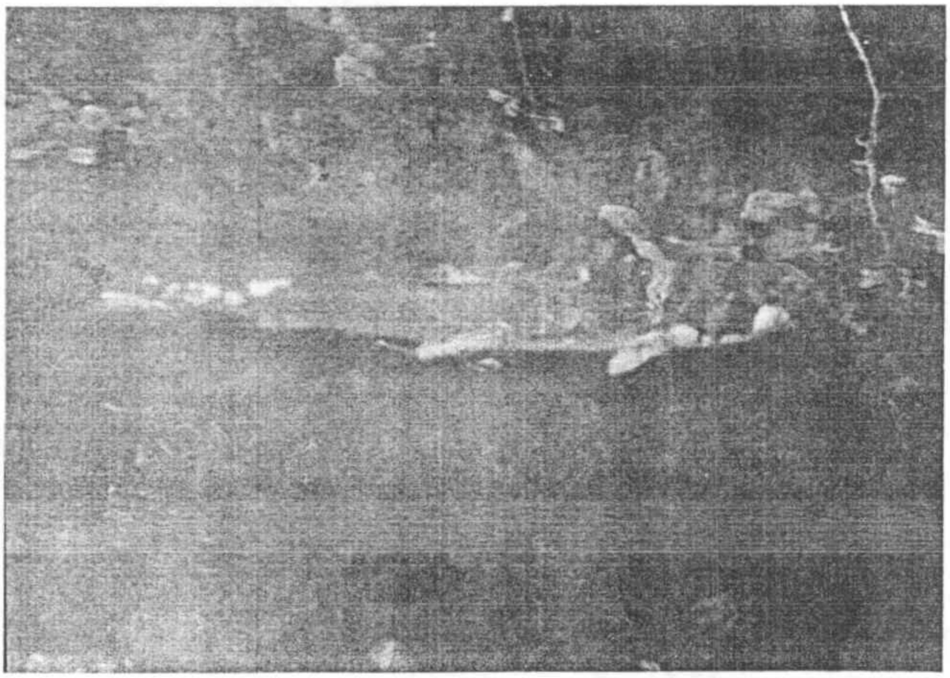
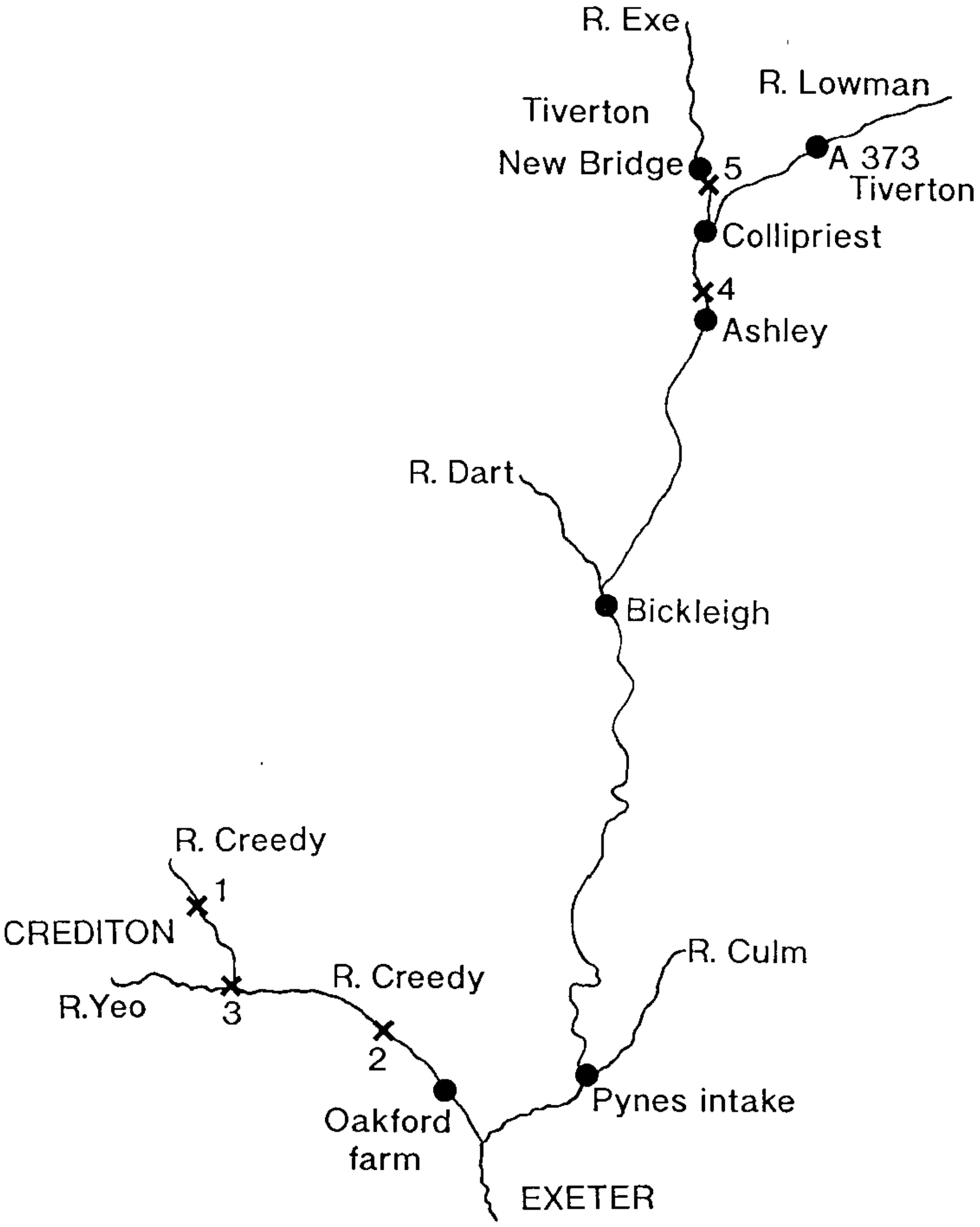


Plate 2. An example of Saprophytic infection evident on some fish in Exe and Creedy (taken in April 1991).

Photographs supplied by courtesy of Mr I. Cook, River Exe Riparian Owners Association.



Map 1. Location of sampling sites for which chemical data were examined (Figure 1) on the rivers Exe and Creedy.
Key: 1, 3: Crediton STW; 2: Newton St Cyres STW; 4: Tiverton STW; 5: John Heathcoat Co. Ltd discharge

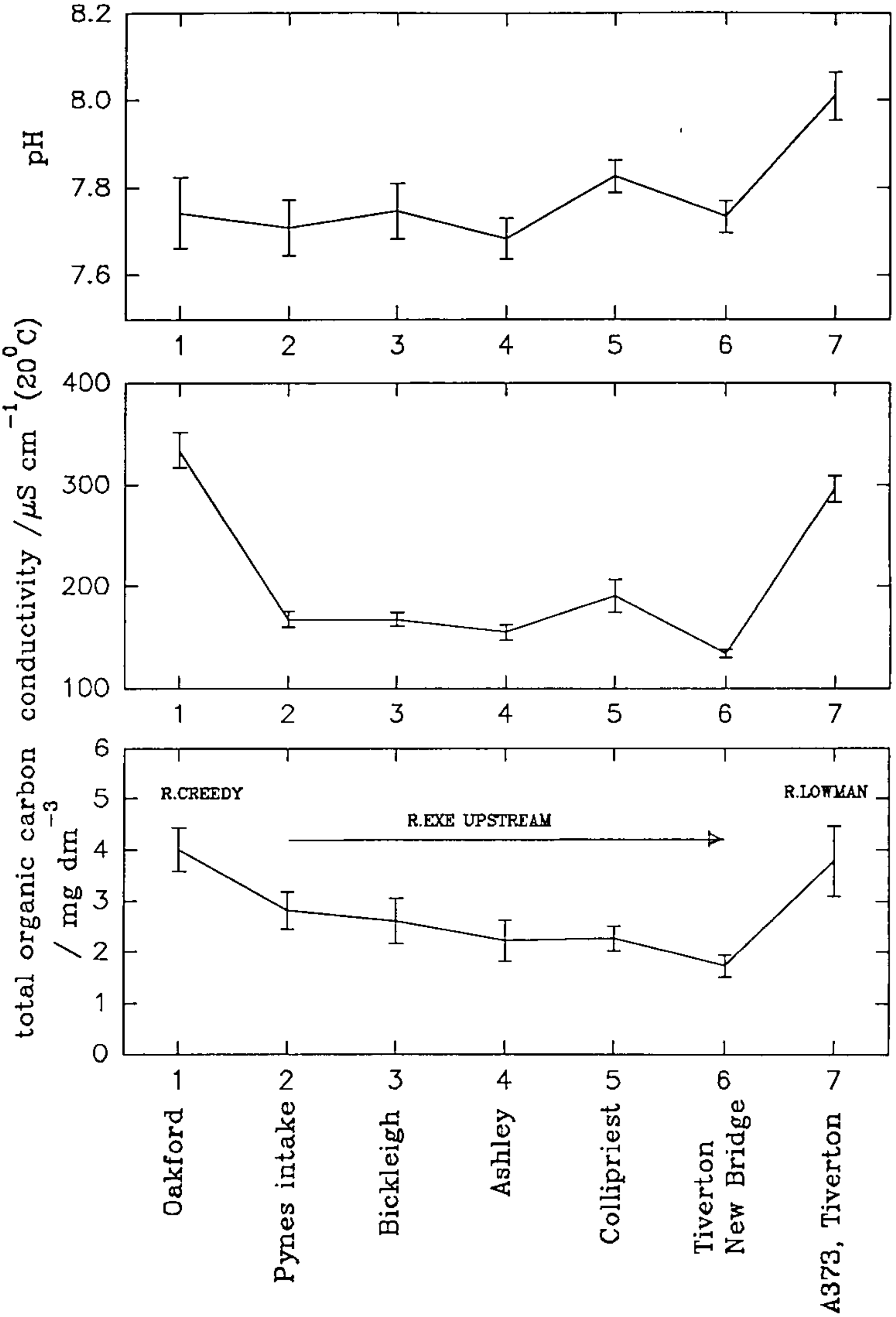


Figure 1. Examples of the changes in water composition at 5 sites on the R. Exe and sites on the rivers Creedy and Lowman. The solid lines pass through the mean monthly values with the standard errors (99% confidence limits) shown as vertical lines.

(a) A straightforward calculation of the concentration after dilution viz

$$C_{river} = C_{effluent} \times dilution\ factor$$

assumes that the chemical is conservative and in a truly dissolved form. This then excludes those contaminants associated with colloid material (i.e. particles or macromolecules <0.2 µm) and suspended solids or sediments. These particles may release contaminants into the river water, thus increasing the dissolved concentration above the value expected from eqn [1], i.e. straight dilution. Alternatively, the particle may aggregate and settle on the bed-sediment and effectively reduce the concentration measured in "whole water" samples, ie samples analysed without filtration.

(b) Contaminants will interact with the river bed-sediments and suspended sediments in the river. This may be through adsorption or release of the contaminant and will therefore affect the concentrations that are truly dissolved.

As far as I am aware, no measurements have been made of the concentration of contaminants associated with suspended solids in any of the effluents or receiving waters. It is also unclear whether the existing data include contaminants associated with suspended solids and colloids. The analytical procedures for the determination of the soluble fraction of the contaminants are usually not efficient at extraction of the solid-bound fractions.

3. CONCENTRATION OF ORGANIC COMPOUNDS IN THE EFFLUENTS AND WATERS

Only limited information is available concerning the occurrence of dissolved organic contaminants in these rivers. Halcrow (1989) listed over 56 compounds occurring in composite samples obtained over 24 h in November 1988. The samples were from:

(a) Upstream of the Tiverton, STW on the R. Exe.
(b) Effluent from the Tiverton, STW.
(C) Downstream of the Tiverton, STW at Bickley bridge.

Detailed analysis of detergent residues was not attempted although alkylphenol ethyoxylates (nonionic detergents) were detected, the method employed for the analysis (gas chromatography, GC) is not well suited for these compounds. The estimated concentration at 50-100 µg dm^{-3} suggested a source of pollution in the river. Other compounds of note include biphenyl (*ca* 5 µg dm^{-3}) and diphenyl ether (*ca* 5 µg dm^{-3}). Anionic surfactants such as alkyl sulphates (AS) or linear alkylbenzene sulphonates (LAS) were not determined. These compounds occur in all domestic sewage effluents including biologically treated sewage. Concentrations vary according to the composition of the raw sewage and treatment plant operation. Typical values for raw sewage or sewage after primary settlement range from 2 up to *ca* 30 mg dm^{-3} as methylene-blue active substances (MBAS) or chromatographic analysis by hplc. The MBAS method is not specific to AS or LAS but to any compound which forms an extractable complex with methylene blue. However, the research of Osburn

(1986) has shown that MBAS values for raw sewage are usually very similar to those from gas chromatography analysis for LAS. The concentrations of LAS in treated sewage are less with values ranging from 0.02 to 0.6 mg dm^{-3} (LAS) from studies in USA, Canada, Germany, UK and Switzerland (de Henau *et al*, 1986; Holysh *et al*, 1986; Osburn, 1986; Rapaport *et al*, 1987; Giger *et al*, 1987; Matthjis & de Henau, 1987; Wagner, 1978 and Waters & Garrigan, 1983). Using the dilution factors given in section 2 and with a concentration of LAS of 0.5 mg dm^{-3} in the effluent, i.e. upper-limit expected for a treatment plant, then concentrations in the river after dilution calculated from eqn [1] are 3-50 μg dm^{-3} (ppb) for the R. Exe and 40-130 μg dm^{-3} for the R. Creedy.

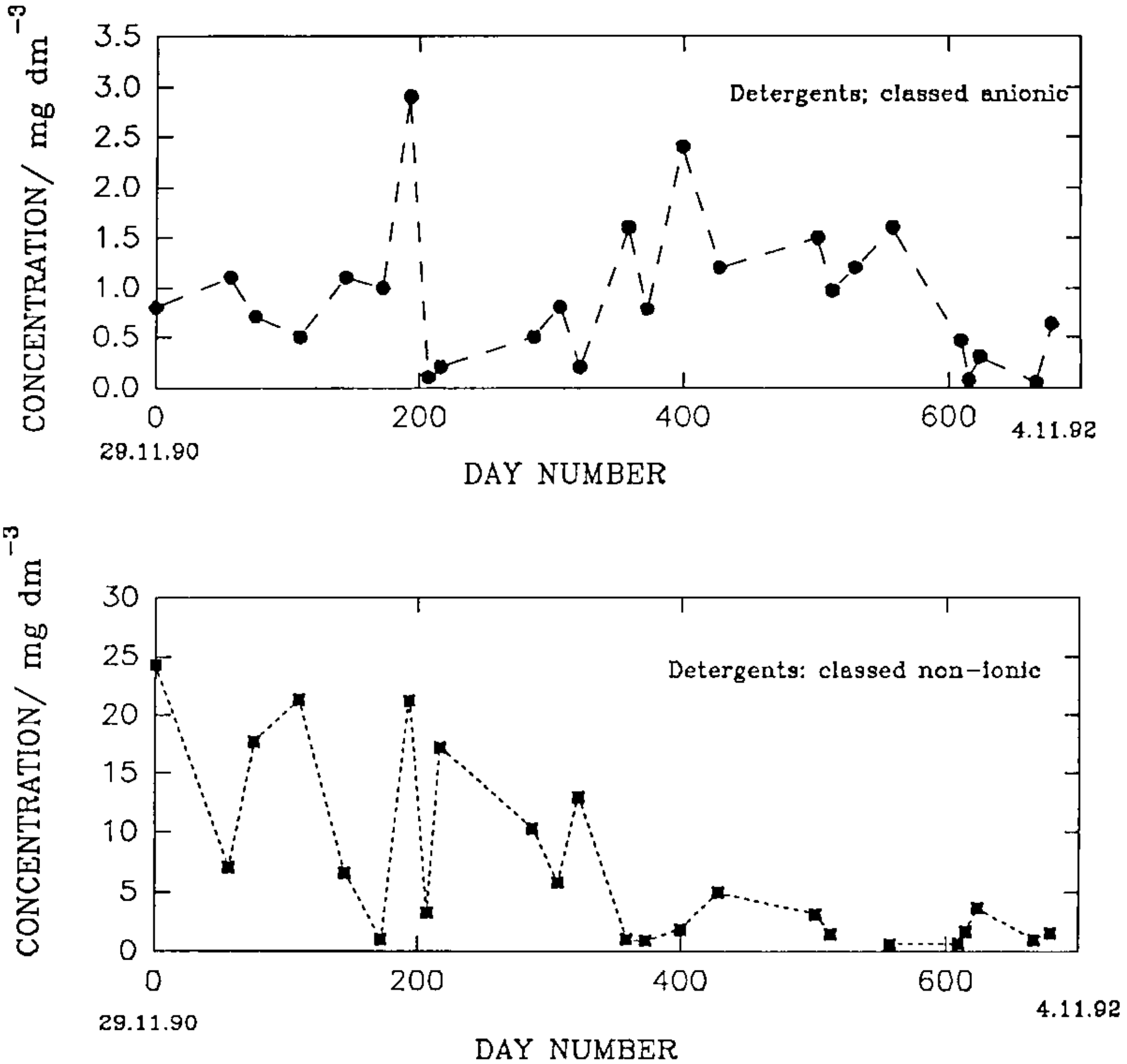


Figure 2. Concentration of two classes of detergents determined in the process wastes from J. Heathcoat & Co. Ltd by single analysis between the period from 29 November 1990 to 4 November 1992.

The concentration of anionic surfactants in the effluent from John Heathcoat & Co Ltd have been monitored at about monthly intervals since November 1990. A summary of the available information is shown in Figure 2 (NRA, analysis of the process waste with concentrations expressed as Manoxol OT for anionics). The results illustrate large variations in the concentration of both compound classes in the process waste. No systematic change in the concentration of anionics occurs over the period with values from *ca* 3 mg dm^{-3} to less than 0.1 mg dm^{-3}. Generally the concentrations are higher than might be expected from a sewage treatment plant. It is not possible to estimate the total load of anionic detergents to the R. Exe because of the large variability in the concentrations and infrequency of the analyses. Neither is information available about the homologue distribution of the anionics including LAS compounds. This is important in view of the greater toxicity of the higher chain homologues of LAS (see section 5 for further details of the toxicity of LAS). With an effluent concentration of 3 mg dm^{-3} river water concentrations in the range of 15-300 µg dm^{-3} can be expected.

The results for the nonionic detergent class, Figure 2, indicate much higher concentrations in the effluent with values often exceeding 15 mg dm^{-3}. However, there is a gradual decrease in the concentration with values <5 mg dm^{-3} in recent months. Assuming that the method of analysis for the compounds was the same throughout the study so that the data are directly comparable, this trend is encouraging. The range of concentration expected in the river by straight dilution is 75-1500 µg dm^{-3} although values of *ca* 400 µg dm^{-3} are predicted during typical low summer flow. The estimates are summarized in Table 2. Again it must be reiterated that these concentrations do not take into account the uptake and release of the surfactants by suspended solids or river bed-sediments.

Table 1. Estimates of the concentration of anionics and non-ionic classes in the rivers Exe and Creedy.
All concentrations in µg dm^{-3} or ppb.

Location	Anionics	Nonionics
John Heathcoat & Co Ltd	15-300	75-1500
Tiverton, STW; downstream	3-50	-
Creedy, STW; downstream major sewage inputs	40-130	-

Note: estimates based on dilution factors of 10 and 200 for the river Exe and 4 and 13 for the river Creedy.

There is evidence from a recent survey by the NRA (personal communication) that the concentration of anionics in some sewage effluents are higher than 0.5 mg dm^{-3} used in the calculations for Table 1. These include small treatment works feeding streams to the river Creedy, e.g. at Knowle (NGR SS78310159) an effluent concentration of 6.8 mg dm^{-3} was recorded with a downstream value of 4.6 mg dm^{-3}. Upstream of the STW at Newton St Cyres on the river Creedy the concentration of anionics was recorded as 0.63 mg dm^{-3} which is well above the range noted in Table 1. At Brampford Speke (NGR SX93009710) the final effluent from the STW was measured as 1.25 mg dm^{-3}. Other high concentrations of anionics were noted in discharges to Thorverton stream and at Dulverton. Most of the high concentrations were recorded in feeder streams to the main rivers and their impact on the Exe and Creedy is therefore difficult to assess without more detailed information and further studies. An independent survey of the catchment is needed.

4. TECHNICAL PRODUCTS USED BY JOHN HEATHCOAT & CO LTD

Products in use at John Heathcoat & Co Ltd are likely to include the following:

Table 2 Detergent compounds and classification.

Product	Classification
Hostapol SVX	non-ionic
Tanaterge CFP	non-ionic
Tanaterge CSU	non-ionic/anionic
Sandoclean PC	non-ionic
Tanaterge 9060	anionic
Sandopur SR	anionic
and prior to 1990 Kieralon jet	anionic/nonionic
Lyogen WD	cationic

Information on the product safety sheets concerning ecological effects is in most instances absent. Data for Lyogen WD gives LC_{50} (48 h) of 10-100 mg dm^{-3} and Sandoclean PC EC_{50} (24 h) of 0.4-0.8 mg dm^{-3}. All the products are given as miscible with water. Very little information is produced on the composition of the products. The marketing companies have been helpful in supplying additional general information on the active ingredients. These companies included Sybron Cherrie Nederland B.V., Sandoz Chemical (UK) Ltd, Hoechst UK Ltd. Although the details of the formulations are not available the major ingredients in the formulations currently in use at John Heathcoat & Co Ltd are:

linear alkylbenzene sulphonates (LAS)
naphalene sulphonate formaldehyde condensate
α-olefinsulphonate
alkylsulphonates
C9-C11 alkyl ethoxylates
polyglycol ethers
diethylene glycol monobutyl ether
aliphatic alcohol ethylene oxide condensate (alkyl ethoxylates)
poly (propylene/ethylene) glycol ethers

The relative occurrence of these compounds in the effluent is unknown and is likely to vary considerably both during plant operation and as products change. As determined in the analysis by the NRA, the effluent contains both anionic (LAS, olefinsulphonates and alkylsulphonates) and nonionic detergents, e.g. alkyl ethoxylates. Polyglycol ethers are also likely to occur in the effluent. All of the formulations consist of a mixture of different chain length homologues and unspecified impurities from the manufacturing process. Apart from the most researched compounds such as LAS, it is unlikely that specific toxicity information is available about individual homologues. There is some information on the acute toxicity of the polyethylene glycol ethers to fish indicating LC_{50} (24 h) of 8.5 mg dm^{-3} (Muller, 1980).

In view of the complex nature of the effluents and range of detergents discharged, a summary of the toxicity and information on sub-lethal effects is given for the two main detergent classifications. This will be discussed in terms of the observed and predicted concentrations appropriate to the rivers.

5. IMPACT OF LINEAR ALKYLBENZENE SULPHONATES, LAS

The literature on the analysis, occurrence and impact of LAS is enormous. A review of the environmental safety of LAS has been completed by Painter & Zabel (1988) and more recently this has been extended to include a literature review of the degradation of LAS and other synthetic sulphonates under anaerobic conditions (Painter & Mosey, 1992).

The chemical structure of LAS is $C_nH_{2n+1}C_6H_4SO_3Na$ where the integer, n, is usually between 10 and 14 although higher values have been reported in river waters, e.g. n = 15,16 (Baker *et al*, 1991). The total LAS concentrations in the various regions of England (Northumbria, North-West, Severn-Trent, Southern, and Yorkshire) were reported from the analysis by fast-atom-bombardment (FAB) mass spectrometry (MS) or FAB-MS. This technique enables detailed information about the homologue distributions which is particularly useful for environment impact assessment. Unfortunately only two samples were analysed from the south of England with the majority of results obtained for the midland and northern regions at sites identified as having "foaming problems". Overall the results indicate the occurrence of LAS at concentrations classified as "medium", 40-80 µg dm^{-3} or "high", >80 µg dm^{-3} with only a few samples in the classification of "low", i.e. 1-40 µg dm^{-3}. The "medium" concentrations are consistent with effluents of 0.5 mg dm^{-3} LAS and a dilution factor of 10. The concentrations of LAS predicted in Table 1 are in the range detected in the classification 40-80 and 80-500 µg dm^{-3} given by Baker *et al* (1991). It is also noteworthy that the concentrations reported by Baker *et al* (1991) for some locations are likely to represent a "best case" because of the heavy rainfall prior to sampling. The concentration of LAS homologues associated with suspended solids or sediments were not studied. However, information reported by Ladle *et al* (1989) gave total LAS in the surface sediments of up to 40 mg kg^{-1} (dry sediment) representing a concentration from the water of about 80 times. This concentration of LAS homologues on suspended and bed-sediments has been studied in more detail by House & Farr (1989) and Marchesi *et al* (1991). They found the adsorption of LAS and alkylsulphate surfactants increased with increasing alkyl chain length. The effect was greatest for LAS surfactants with approximately 15 fold increase in the bed-sediments for the C10 homologue compared with 24,000 fold for the C13 homologue. This behaviour is supported by the results from field studies where the concentration of the C13 and C12 LAS in the surface bed-sediments is greater than the C10 and C11 components (Ladle *et al* (1989). This means that although the higher chain-length constituents are a relatively small percentage of the detergent product, they are the most abundant components adsorbed to river sediments. The implication of this partition for the toxicity of the contaminated sediments is not understood; existing studies, e.g. Ladle *et al* (1989) and Woltering *et al* (1987), have attempted to make an assessment of the effects using either field monitoring of the invertebrate community or the results of toxicity screening tests together with expected environmental exposures. The screening tests do not always include sedimentary materials or invertebrates that are likely to ingest particulate matter. Field monitoring studies are particularly difficult because the effluents usually include other organic contaminants and nutrients making it difficult to separate the changes in the ecology of a site caused by detergent impact. In general, it is likely that the major invertebrate community differences are caused by the impact of nutrients and waste of a high biochemical oxygen demand (Maki & Rubin, 1979). Pittinger *et al* (1989) have reported a chronic "no observed effect concentration" (NOEC) for *Chironomus riparius* to be 319 mg kg^{-1}. Their study indicates that when LAS is adsorbed on sediment, only a fraction is biologically available to benthic organisms.

Although total LAS concentrations in the rivers Exe and Creedy sediments have not been measured, data from various sources, as well as our own, for marine and freshwater sediments indicate values in the range of *ca* 1-300 mg kg^{-1} (Kimerle, 1989), i.e. below the NOEC reported above. Obviously, in view of the paucity of chronic toxicity data concerning sediment bound LAS, no firm conclusions can be made at the moment.

The hazard assessment of acute and chronic toxicity data for LAS in surface waters has been conveniently summarized by Kimerle (1989). Figure 3 shows the range of values for the acute EC_{50} LC_{50} for algae, daphnids, invertebrates and fish together with the range of chronic toxicity (NEOC) for invertebrates and fish. This is compared with the concentrations of LAS determined for natural waters. The concentrations of LAS in water varied as shown with 70% of all data between 10 and 50 µg dm^{-3} and 85% below 100 µg dm^{-3}. Kimerle (1989) excluded all chronic toxicology data for LAS homologues with a chainlength higher than an average of 13 carbons on the basis that these do not occur in surface waters.

The results illustrate that if all the anionic surfactants in the rivers Creedy and Exe are of the LAS type, then the predicted concentrations are in the range where effects might be expected. This is more likely in the river Creedy at periods of low flow and hence lower dilution of the effluents from STW in the receiving waters. The anionic compounds from the industrial manufacturing, although containing LAS (see Table 2), are likely to have a wider range of constituents.

It is now worthwhile examining some of the details of the aspects of toxicity broadly presented in Figure 3. A recent review has highlighted some of the problems of the evaluation of the risk assessment of surfactants to algae (Lewis, 1990). As shown in Figure 3, the reported range of concentrations over which effects were observed is particularly large. Few generalizations are possible concerning the toxicity to algae as reported in the literature. The laboratory results depend on the type of surfactant used and in the case of LAS, on the

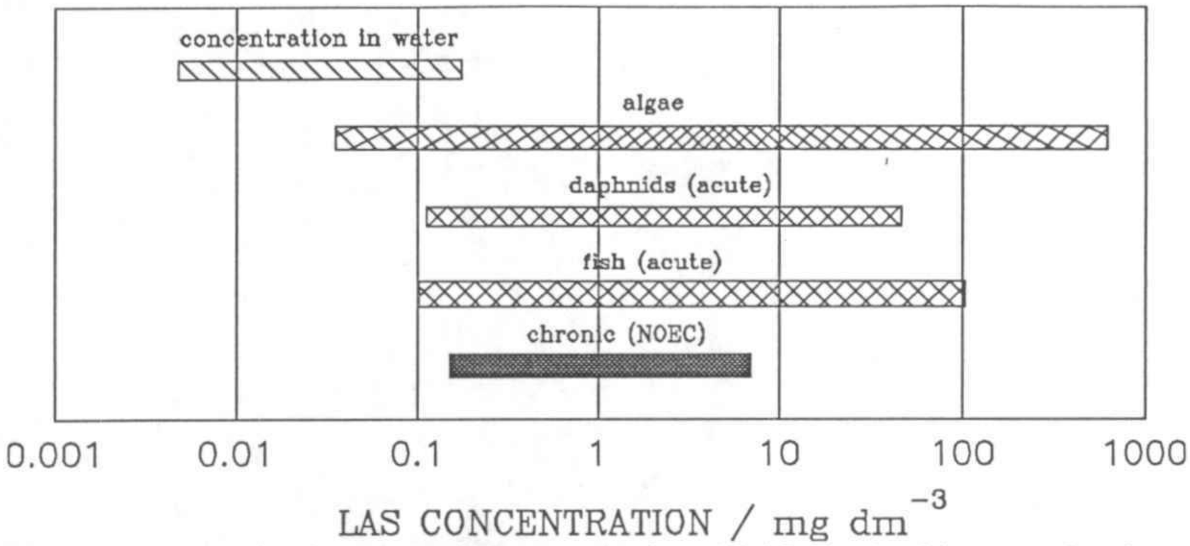


Figure 3. Schematic of the hazard assessment of total LAS dissolved in water for algae, daphnids and fish (acute LC50, EC50) and chronic, NOEC, for invertebrates and fish. Taken from Kimerle (1989).

homologue distribution, i.e. relative amounts of the different alkyl chain components. They also depend on the test species of algae and the conditions of the test, e.g. the water temperature, composition, hardness and suspended solids or colloid concentrations. In most of the toxicology studies, the concentration of surfactant is a nominal value, i.e. as calculated from the amount of surfactant added to the test chamber and volume of water in the chamber, and not the concentration analysed in the water at the time of the test. Lewis (1990) noted that differences in experimental approach have resulted in part in the wide range of reported effect levels for algae beyond the limits given in Figure 3, e.g. the effect concentration of C13 LAS on *Gymnodinium breve* was 0.025 mg dm^{-3}. Lewis also concluded that most of the toxicology studies used only a few freshwater species and noted that the toxicity of most surfactants is less when determined for natural algal communities under natural conditions.

The results for daphnids are shown in Figure 3; these invertebrates encompass the range of sensitivities for many other invertebrate species (Kimerle, 1989) and are the most common test species (Lewis, 1991). The effect concentrations for *Daphnia* and LAS cover a range of 0.005 to >10.0 mg dm^{-3} which, as expected, is shifted to lower concentration compared with the acute data (Figure 3). Again, it is important to consider the composition of the LAS formulation, as the toxicity increases with increasing chain length of the alkyl group. An example of this behaviour is shown in Figure 4 for acute toxicity tests. LAS surfactants having a chain length greater than 13 or 14 are not likely to be discharged into rivers. It is also interesting to note that the longer chain homologues have reduced toxicity in the presence of clay, presumably because of the reduction in the dissolved LAS caused by the adsorption onto the clay. Similar results are also expected for other types of suspended solids particularly those rich in organic matter thus promoting the hydrophobic interaction of the detergent with the surface (House & Farr, 1989).

The chronic effects that have been monitored for the studies using *Daphnia* include: survival, reproduction (Taylor, 1985; Canton & Sloof, 1982 and Maki, 1979). The range of first effect concentrations (this is the geometric mean of NOEC and lowest observed effect concentration, LOEC) was determined by Taylor (1985) as 1.7-3.4 mg dm^{-3} for LAS of mean composition $C_{11.8}$ LAS for a 21 d test of survival and reproduction. The NOEC ranged from 1.3-3.3 mg dm^{-3}. A LOEC for *Ceriodaphnia dubia* exposed to $C_{11.8}$ LAS over 7 d was <0.32 and 0.89 mg dm^{-3} has been reported by Masters *et al* (1991). The results of LAS, LOEC determination on other invertebrate species have been summarized by Lewis (1991); they support the conclusion that the majority of chronic effect concentrations exceed 100 µg dm^{-3} which is similar to that for other anionic surfactants including alkyl sulphates.

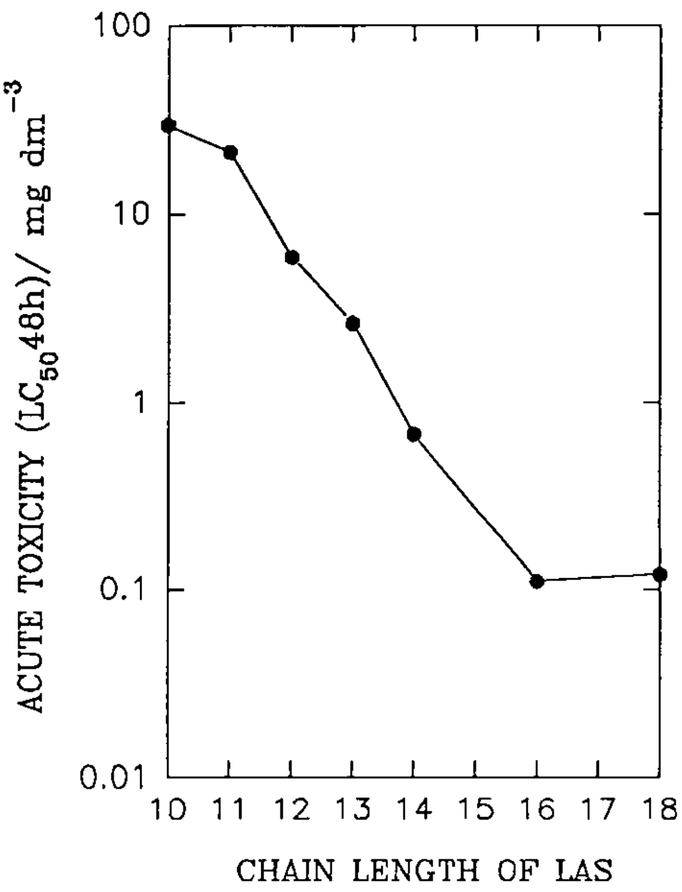


Figure 4. Variation in the acute toxicity of LAS to daphnia magna, LC_{50}(48h), with alkyl chain length. Data from Maki and Bishop (1979)

The acute toxicity data for fish (see Figure 3) encompasses a similar concentration range as that for daphnids. Most of the chronic data have been obtained from tests with fathead minnow. The first effect concentrations for fathead minnow vary with the LAS chain length. This is illustrated for the data of Macek & Sleight (1977) in Table 3.

Various physiological responses have also been recorded for fish and have been reviewed recently by Lewis (1991). The effects studied include olfaction, respiration and gill physiology. Most observed effects occurred at concentrations exceeding 0.1 mg dm^{-3} but LOEC of 0.005 ~ 0.015 mg dm^{-3} have been reported for LAS for changes in gill and skin morphology after 30 days exposure (Misra *et al*, 1985; 1987). Behavioural responses have also been used to evaluate possible effects on fish. Avoidance of several anionic surfactants, including LAS and alkyl sulphates, by a variety of fish species has been observed at concentrations in the range of 2 to 400 µg dm^{-3} (Tatsukawa & Hidaka, 1978). Other aspects of behaviour, such as swimming activity and feeding, tend to be affected at higher LAS concentrations, typically between 200 and 500 µg dm^{-3}. Studies have included the effects on trout, goldfish, cod and carp.

Table 3. Effect concentrations for 28 d duration tests of survival and hatching of fathead minnow (Macek & Sleight, 1977).

LAS chain length	first effect concentration /mg dm^{-3}
C10	14-28
C11	7.2-14.5
C12	1.08-2.45
C13	0.12-0.28
C14	0.05-0.1

The recent report to the NRA (Baker *et al*, 1991) also lists chronic toxicity data from the literature for bluegill (*Lepomis machrochirus*), fathead minnow (*Pimphales promelas*), fingerlings (*Cirrhina mrigala*), guppy (*Poecilia reticulata*) with effect concentrations between 5 and 10,000 µg dm^{-3}.

Other aspects of LAS impact on rivers have only recently been studied in any detail. These include the occurrence of the metabolites sulphophenyl carboxylic acids (SPCs) (Field *et al*, 1992; Marcomini, 1992), linear alkylbenzenes (LAB), e.g. see Takada & Ishiwatari (1987), and tetralin and indane sulphonates (DATS) which occur as minor components or impurities in LAS formulations. The details of LAS biodegradation are available elsewhere (Schoberl, 1989). Under aerobic conditions, SPCs are formed with various alkyl chain lengths. In anaerobic conditions, i.e. in the absence of oxygen, the evidence indicates that LAS is **not degraded** and remains persistent (Painter & Mosey, 1992). Many river sediments, especially in the vicinity of sewage discharges, are anaerobic below the surface. The SPCs detected in sewage effluents possess carbon chains of between 3 and 10 atoms with concentrations in the effluents reported by Field *et al* (1992) of 51 ± 5 µg dm^{-3}. The main homologue components in the effluent were the C6 and C7 components; once the alkyl chains are reduced by microbial degradation to 4-5 carbon atoms, the benzene ring oxidation and desulfonation begins leading to complete mineralization and loss of toxicity, i.e. the formation of sulphate and carbon dioxide/water.

The LABs, used in the manufacture of LAS, are more persistent than LAS such that the ratio LAS/LAB decreases from *ca* 550 in sewage effluents to close to unity in sediments downstream of discharges (Takada & Ogura, 1992; Takada & Ishiwatari, 1987). The impact of LABs associated with suspended solids and sediments on the aquatic fauna is uncertain. No attempt has been made here to examine the toxicology of LABs or indeed the other groups of compounds mentioned above, i.e. DATS and SPCs. However, the indications are that few studies of the toxicity have been made and certainly not at the chronic effect level.

6. IMPACT OF NONIONIC SURFACTANTS, ALKYL ETHOXYLATES AND ALKYL PHENYL ETHOXYLATES

Nonionic detergents are the second most important class of surfactants after the anionics with the two most used members comprising about 80% of the use of nonionics in Europe. These are the alkyl ethoxylates (also called alcohol ethoxylates) of general formula:

$$C_n H_{2n+1} - 0 - (C_2H_4O)_m - H$$

AEO

with n = 8 to 18 and an average of 4-20 ethylene oxide (EO) units, and the alkyl phenol ethoxylates (APEOs) of general formula:

$$R - C_6H_4 - 0 - (C_2H_4O)_mH$$

APEO

with $R = C_nH_{2n+1}$, where n = 8 or 9, i.e. octyl or nonyl, and m = 4 - 17 EO groups.

The occurrence of these compounds has been determined for the NRA (Baker *et al*, 1991) in different regions of England. There was frequent occurrence of the two groups in the survey with the majority of determinations in the concentration range of 1-40 µg dm^{-3} and a few in the band of 40-80 µg dm^{-3}. For the AEOs, n was determined as 16 or 17 and the APEOs were the octylphenol ethoxylates or nonylphenol ethoxylates; information on the ethoxylate chain lengths was not given. Only two samples of river water were analysed from the south of England (locations not given). One of these contained 1-40 µg dm^{-3} of nonylphenol ethoxylate. No information is available about the concentrations of AEOs or APEOs in the rivers Exe and Creedy. As mentioned in section 2, nonionics may reach concentrations of 75-1500 µg dm^{-3} depending on the dilution of the effluent from John Heathcoat Co. Ltd and the composition of the effluent. The information about the formulations (see section 4), suggest that the nonionics are mainly AEOs. No further information is available from the water companies or NRA concerning the composition of the nonionics in the effluents or receiving waters.

An examination of the acute and effect toxicity data for the nonionic detergents reveals the same type of problems mentioned for LAS. Acute toxicity tests with *Daphnia magna* using AEO with n = 14 and m between 1 and 9 demonstrate a greater than one order of magnitude decrease in toxicity with increasing ethoxylate composition. It has also been noted by Maki & Bishop (1979) that AEOs are more toxic to *Daphnia* in softwater compared with hardwater. Hence, differences in effect concentrations and acute toxicity data may reflect variations in the chemical composition of the nonionic surfactant, the water composition and species/life-stage of the organism.

Lewis (1991) has made a comprehensive survey of toxicity data for invertebrates and fish. There are less data available concerning AEO/APEO compared with LAS although in general, the reported NOECs are similar in magnitude to the anionic compounds discussed in section 5. The NOECs and first-effect concentrations vary between *c.* 0.2 to 2.5 mg dm^{-3} for invertebrates for the AEOs. The effects monitored included: reproduction, larval growth and development. Few chronic data are available for APEOs; Hidu (1965) gave a first-effect concentration of 2.4 mg dm^{-3} for *Mytilus edulis* (mussel) which compares with 0.05 mg dm^{-3} for LAS. The data on fish are sparse with NOEC quoted for C_{12-13}AEO and C_{14-15}AEO and fathead minnow of 0.32 and 0.18 mg dm^{-3} respectively. These data are based on growth, hatching and larval survival (Maki, 1979). Behavioural responses have also been studied but the effect concentrations are typically the same order of magnitude for the chronic effects (Lewis, 1991). Since the data are based on relatively short laboratory tests, i.e. 21 days duration or less, the extrapolation of the results to field conditions is difficult, particularly when predicting the more subtle ecological changes.

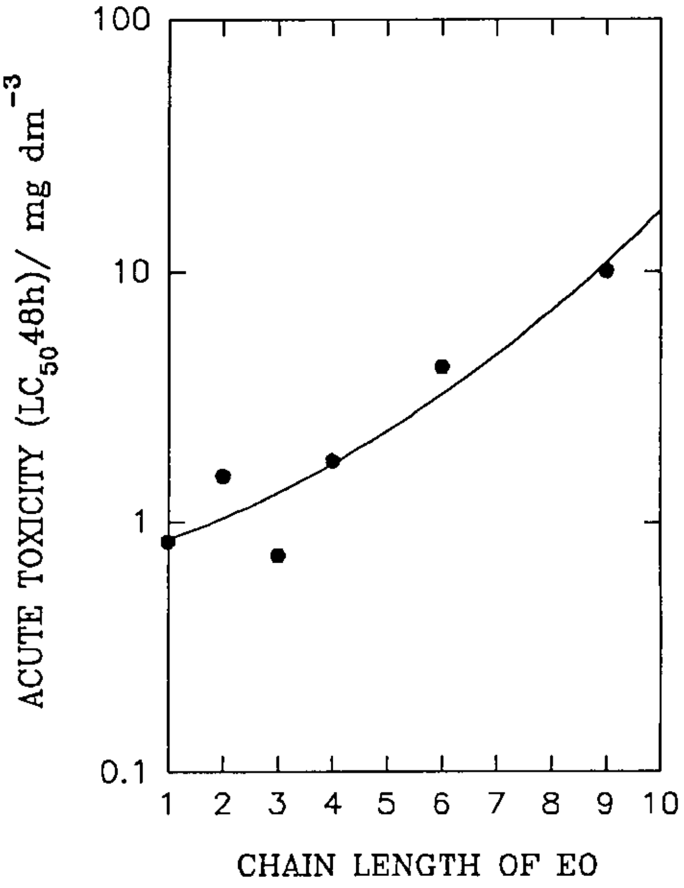


Figure 5. Variation in the acute toxicity of AEO's to daphnia magna, LC_{50}(48h), with chain length of the ethoxylate, $C_{14}AE_1$ to $C_{14}AE_9$ (Maki and Bishop, 1979)

Acute toxicity data for brown trout (*Salmo trutta*) yield LC_{50} (96 h) of 1.8 mg dm^{-3} of AEO similar to that determined by harlequin fish (*Rasbora heteromorpha*) of 1.6-2.8 mg dm^{-3} (Reiff *et al*, 1979). Experiments with rainbow trout (*Oncorhynchus mykiss*) gave a LC_{50} (24 h) of 8.5 mg dm^{-3}. No other data have been found for trout and Chattopadhyay & Honar (1986) found values of LC_{50} (24 h) of 163.9 mg dm^{-3} for the fish *Tilapia mossambica* for a commercial AEO detergent. However, important effects on the feeding and growth rate were noted at a concentration of 3.9 mg dm^{-3}. It was noted that the fish became lethargic and stayed near the bottom and corner of the tank. The nonionic surfactants accumulate in the intestine, gall bladder and the liver of fish and also damage tissue (Kuchi *et al*, 1980). Chattopadhyay & Honar (1986) noted that the maturity of the fish was greatly affected by the detergents (AEO) resulting in low fecundity; at a concentration of 10.59 mg dm^{-3} no fish were found to be mature enough to lay eggs.

The effects of nonionic detergents on algae are variable depending on the specific structure of the compound in test species (Lewis, 1990). Effect concentrations vary from approximately 2 to 50 mg dm^{-3} for AEO with few values for APEOs. For nonionic surfactants in general, toxicities range from 3 µg dm^{-3} to 17,784 mg dm^{-3}. Comparisons of the relative toxicity of cationic, anionic and nonionic detergents to algae indicate that cationics are more toxic than the other two classes, with the relative order of the anionic and nonionic depending on the test species and no doubt conditions of the test.

The degradation of the APEOs has also been a subject of some controversy. The degradation proceeds by progressive attack on the ethoxylate chain leading to alkylphenol polyethoxy carboxylic acids and alkylphenol mono- and di-ethoxylates (AP1EOs and AP2EOs) which are resistant to biodegradation. The latter compounds are hydrophobic and tend to adsorb to suspended matter. The hydrophilic carboxylic acids are more water soluble but of low aquatic toxicity compared with the parent detergent molecules. The AP1EOs and AP2EOs further degrade in anaerobic conditions to nonylphenol (NP) which is more toxic than the corresponding APEO detergent (Varma & Patel, 1988-89; Ankley *et al*, 1990; Lewis, 1991). Giger *et al* (1984), found NP concentrations of between 450 and 2530 mg kg^{-1} in anaerobically digested sludge samples from European waste-water plants. Studies of STW and rivers in Switzerland have shown that the AP1EOs, AP2EOs and NP are the major refractory constituents in mechanically/biologically treated sewage effluent (Ahel *et al*, 1984). NP has been found at concentrations of between 1 and 40 µg dm^{-3} in the Delaware river in U.S. during the summer months, with lower concentrations during the winter, viz 1-2 µg dm^{-3}. In view of these results and the increasing toxicity of the ethoxylates with decreasing alkyl chain length (Figure 5), toxicity studies have been reported for NP. The LC_{50} (96 h) and lethal thresholds for shrimp, salmon and trout are reproduced from Varma & Patel (1988-89) in Table 4. These authors concluded that NP poses a considerable threat to aquatic fauna.

DoE (1992) have included an appendix E in a document from the technical committee on detergents and the environment (DoE, 1992) which examines a value of NOEC for NP of <0.6 mg dm^{-3} for *Daphnia magna* reproduction. They quote a LC_{50} (24 h) and LC_{50} (48 h) for *Daphnia* of 180 mg dm^{-3} and suggest a "viable offspring" NOEC of 24 mg dm^{-3}. In the same report (DoE, 1992), Brown tabulates a LC_{50} (24 h) of 0.2 mg dm^{-3} for *Daphnia magna*. Ankley *et al* (1990) give a mean LC_{50} (48 h) for NP of 0.47 mg dm^{-3} for *Ceriodaphnia dubia* compared with 1.04 mg dm^{-3} for nonylphenol ethoxylate in the same test conditions. In both tests, the concentrations are the nominal values and not directly measured; with lipophilic compounds such as NP, the adsorption to the container is likely to reduce the concentration dissolved in solution.

Table 4. Acute toxicity data for nonylphenol, NP, for fish. From McLeese *et al* (1981) and Bringmann & Kuhn (1982).

	Daphnia magna	salmon	brook trout	rainbow trout
LC_{50} (96 h) /mg dm^{-3}	0.3	0.13-0.19	0.145	0.230
lethal threshold /mg dm^{-3}	0.15-0.32	0.18-0.19	-	-

There is little doubt that the biodegradability of APEOs is a major issue because of their impact on the environment. In general they fulfil the biodegradability requirements of the EEC Directive (EEC, 1982) but it is known that the APEOs' primary degradation, i.e. breakdown of the parent molecule, falls during winter temperatures so that the final effluent may be sufficient to cause foam in receiving waters. Foaming has been a localized problem in several NRA regions (Baker *et al*, 1991) and the analysis of the water has revealed concentrations of surfactants at some sites sufficient to cause ecotoxicological effects.

7. CONCLUSIONS

(a) There is a clear indication that the concentration of surfactants in the effluents to the rivers Exe and Creedy have been high enough to cause foaming and ecotoxicological effects on algae, invertebrates and fish in the river. Unfortunately, no data are available concerning the actual concentration of surfactant groups in the river water, suspended solids or bed sediments. Hence it is only possible to estimate concentrations from the likely dilution factors appropriate to the rivers.

(b) The chronic toxicity data and effect concentrations are similar for the nonionic and anionic detergents. Chronic effects are expected for the surfactant concentration estimated for the rivers Exe and Creedy (Table 1).

(c) There is a lack of information on the toxicity of chemicals associated with detergent formulations and degradation products. Of particular note are the alkylphenols contaminants from alkyl phenol ethoxylate degradation.

(d) It is clear that the consent to discharge limits are not based on current information on the ecotoxicology of the surfactants or their degradation products. There is no evidence of an environmental assessment of the impact of the discharges on rivers or indeed any available information of the concentration of particular components in the river. The estimation of the concentration of contaminants in the receiving waters from dilution factors is problematic and ignores the influence of sediments.

8. RECOMMENDATIONS

(a) Measurement of surfactant concentrations in the rivers is necessary to compare with available ecotoxicology data. This could include anionics, nonionics and cationic detergents as well as contaminants and degradation products identified in this report. The measured concentrations could then be related to the expected concentrations and the ecotoxicological data available for algae, invertebrates and fish.

(b) Longer-term chronic toxicity tests with fish need to be performed to assess effect concentrations associated with behavioural and physiological responses with particular attention to the occurrence of changes in skin morphology or fungal growths. Some reports of changes to skin morphology have been noted in sections 5 and 6.

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