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**PAH in Drinking Water - Investigation of
Leaching (DWE 7102)**

*Final Report to the Department of the Environment
December 1992 to November 1993*



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DOE Research Contract: PAH in Drinking Water - An Investigation of Leaching

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PAH IN DRINKING WATER - INVESTIGATION OF LEACHING (DWE 7102)

Final Report to the Department of the Environment
December 1992 to November 1993

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PREFACE

Elevated levels of polycyclic aromatic hydrocarbons (PAH) can occur in certain distributed water supplies in the UK. The source of these substances in drinking water is the coal-tar pitch linings which were applied to the internal surfaces of cast iron watermains before 1977.

The Department of the Environment placed a contract (PECD 7/7/422) with WRc in December 1992 to conduct, under the supervision of the Drinking Water Inspectorate, a study into the leaching of PAH from coal-tar pitch coatings and into possible ways to reduce leaching.

This final report presents the work undertaken.

SUMMARY

Exceedances of the PCV for polycyclic aromatic hydrocarbons (PAHs) are recorded occasionally in some water supply zones in England and Wales. The exceedances are generally due to the presence of only one of the six PAHs which make up the PAH parameter, namely fluoranthene. The cause of these exceedances is believed to be leaching from the coal-tar pitch linings applied to the majority of iron water mains. This process appears to be prevalent in systems used to supply hard groundwaters.

The purpose of this project was to find factors linked to water quality parameters, including water temperature, and the design features of distribution systems such as the age of the linings, pipe size, retention times and location of sample points, which affect the levels of PAH leaching. To this end data from two Department of the Environment surveys and from two water undertakers were examined by statistical methods. In addition, laboratory experiments were carried out to test the effects of temperature, exposure time, surface area of lining to volume of water ratio and acidity on the leaching of PAH into water from samples of coal-tar pitch applied to metal plates.

Also investigated in laboratory tests was the possible effectiveness in reducing the rate of leaching of fluoranthene of a number of techniques which might be more readily applicable in practice than relining or replacing mains.

The main conclusions and recommendations arising from our investigations are:

- The rate of fluoranthene leaching has a positive correlation with temperature, surface-to-volume ratio and retention time.
- The retention time result can be linked to the finding of higher levels of fluoranthene in samples taken at sampling points near dead-ends on distribution systems. Therefore it is recommended that ways of eliminating dead-ends be investigated.
- Of the remedial measures investigated only the partial covering of the lining material with woven nylon hose was shown to be effective. Thus it is recommended that ways of applying this technique, and similar techniques with other absorptive materials, in practice be investigated.
- Similar tests using PVC and MDPE pipe materials, for which in real-life systems there is some evidence of their ability to absorb PAHs, failed to reduce fluoranthene leach rates.
- It is thought that the possible effectiveness of forming phosphate and silicate deposits on coal-tar pitch lining material failed to be demonstrated because the tests were too short to allow the formation of deposits.
- A change of pH from slightly acid to slightly alkaline and changes of the level of carbon dioxide had no demonstrable affect on fluoranthene leach rates.

1. BACKGROUND

1.1 Introduction

Polycyclic aromatic hydrocarbons (PAH) are a group of several hundred organic chemicals many of which are found widely in the environment. Their presence is of concern since some PAHs have been shown to be carcinogenic.

PAHs are formed during the combustion of organic materials and, according to some inconclusive evidence, some are produced by bacteria and fungi. The PAHs present in fossil fuels were formed by the long-term transformation of the organic chemical components of dead plants and animals. Different ranges of PAHs are formed by the various processes. Of primary concern to the current study are the PAHs found at up to percentage levels in coal-derived products.

Some drinking water supplies have been found to contain PAHs. In virtually all cases, an increase in PAH levels has been found in distributed supplies compared to levels in the water leaving the treatment works (Crane *et al.* 1981). Thus, the source of these PAHs is within the distribution system. The obvious potential source is the internal coal-tar pitch linings applied to cast iron pipes before 1977; these contain high levels of PAH (Fielding and Crane 1988). After 1977, pipes were lined with cement or bitumen. PAH levels in bitumen are extremely low and the range of PAHs is different from that present in coal-tar pitch.

Coal-tar pitch and anthracene oil, used in the manufacture of some coal-tar based coating materials, have long been associated with the occupational incidence of skin and lung cancer (IARC 1973). In particular, benzo(a)pyrene and dibenz(a,h)anthracene, both of which occur in coal-tar (Lijinsky *et al.* 1963), are described as local and systemic carcinogens to test animals. Both produce tumours after oral administration.

In Great Britain, 60 to 70% of the length of pipes used for the distribution of drinking water is iron and a significant proportion of this are mains dating from before 1977. A survey published in 1977 estimated the length of water mains in the UK at that time as approximately 318 000 km. It is thought that the length of mains with coal-tar pitch linings is likely to be around 70% of the total 1977 length, i.e. 223 000 km, although the length will be steadily diminishing with large-scale relining activity by some of the water undertakers.

Two potential issues related to possible health effects arise from the use of coal-tar pitch linings:

- the leaching of components into drinking water;
- the exfoliation of the linings producing particulate coal-tar pitch-type material in tap water.

The Water Supply (Water Quality) Regulations (1989) stipulate a maximum Prescribed Concentration or Value (PCV) of 200 ng l^{-1} for the sum of six indicator PAH, namely fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene for water samples drawn from consumers' taps. Additionally, benzo(a)pyrene is individually restricted: a PCV of 10 ng l^{-1} , on an annual average basis, is stipulated. Within certain distribution systems, non-compliance with the PCV has occurred. Therefore the Drinking Water Inspectorate required research to determine the factors influencing PAH levels in distributed water supplies and into remedies likely to be more readily applicable than replacement or relining of mains.

1.2 PAH research

To investigate the scale of the PAH problem, the Department of the Environment (DoE) in 1988 and 1989, conducted surveys of PAH concentrations in water supplies. The first survey involved random tap sampling in all water supply companies; the second concentrated on zones and locations believed to be at greatest risk from PAH contamination and involved downstream series sampling comprising repeated sampling from pre-defined sampling points. The results of the 1988 survey indicated that less than 1% of samples failed the 200 ng l^{-1} PAH standard prescribed in the EC Directive 80/778 relating to the quality of water intended for human consumption (which was the water quality standard applicable at the time of the surveys). The first survey was conducted in December and the results may therefore be considered optimistic because of the generally low temperature of the waters sampled and a possible correlation between PAH levels and temperature. The results of the 1989 survey, which targeted dead ends of distribution systems and was carried out in the summer, showed association between failures of the PAH standards and presence of coal-tar pitch lined mains at or near dead-ends of distribution systems carrying groundwater. However, considerable variations in PAH concentrations were reported and systems apparently equivalent in configuration and water source type frequently exhibited apparently unrelated patterns of PAH concentrations.

Following these surveys the DoE placed a research contract with WRc in December 1992. The major concern of the project is exceedances of the PCV due to leaching of the more soluble PAHs, notably fluoranthene. Specifically, factors affecting PAH leaching and possible measures to reduce leaching were investigated. Details of the investigative methods employed are presented in this report together with the project findings, conclusions and recommendations.

2. OBJECTIVES AND PROGRAMME OF WORK

The research project had the following objectives:

1. To study the possible association of PAH leaching with the conditions and characteristics of the distribution systems.
2. To study the potential physical and chemical techniques which might reduce PAH leaching without having to resort to disruptive mains renovation practices.

The programme of work as defined in Schedule 1 of the contract was:

1. To study the relationship between PAH concentrations measured in samples taken from sampling taps and the following factors: location of sampling point, lengths and diameters of coal-tar pitch lined mains serving sampling points, retention time of water within the distribution system, temperature of water, condition and integrity of coal-tar pitch lining and demand on the system at the time of sampling. For this purpose, the DoE survey data plus any other data obtained during relevant surveys of water company distribution systems were to be used.
2. To examine any tentative association of factors identified by the data study analysis using laboratory scale studies to isolate and confirm the nature of any association.
3. To assess potential non-disruptive techniques which might reduce leaching of PAH from coal-tar pitch linings. These techniques were to include: modifying flow patterns and residence times within distribution systems, *in situ* deposition of coatings or films from aqueous solution either in a continuous flow or static mode and modification of water quality characteristics. The potential effectiveness of any technique was to be studied by means of laboratory scale tests using samples of coal-tar pitch lined mains.

The work proposed was to be completed within a 12-month period.

When preparing the project plan in detail, it was recognised, from experience, that the suggested method for Step 3 involving the use of samples of coal-tar pitch lined mains could potentially introduce extreme variability. It was agreed that tests would be undertaken on coal-tar pitch coated coupons freshly prepared for the study.

3. METHODS

3.1 Review of historical data

To improve current understanding of coal-tar pitch based linings within potable water systems, a review of historical information on the type and application of coal-tar pitch based internal coatings for cast iron water mains was undertaken. The major UK manufacturers of cast iron water mains, namely Stanton plc of Nottingham, were approached and asked if they could provide any information on the historical development of the use and application of coal-tar based coatings. In addition information and experience available at WRc and in published literature were collated.

This information is presented in detail in Appendices A and B and in summary in Section 4.1.

3.2 Statistical analysis of PAH data

Data, obtained both from the two DoE surveys into PAH concentrations in distributed water supplies and from compliance and survey data from a small selection of water utilities were examined statistically for correlations between PAH concentrations and factors such as water quality characteristics, position in the distribution system, age and diameter of main. Full details of the data and the statistical assessment are given in Appendix C. Although originally specified in the programme of work, it was found that the data available for study were not suitable for an assessment of demand on the system at time of sampling or of retention time directly, although some assumptions could be made from relative position in the system. Similarly, information on lengths of mains was not available.

3.3 Laboratory leach tests

Leaching of PAH from coal-tar pitch was investigated by means of a series of laboratory scale tests comprising the exposure of coal-tar pitch coated coupons to water samples of differing quality. The first series of tests investigated the factors influencing leaching. Factors examined were pH, water temperature, exposure time and the ratio of the surface area of coal-tar pitch to volume of water (surface area factor). The testing of the effects of exposure time and surface area were carried out in the same experiment. The second series of tests was aimed at potential non-disruptive solutions to PAH leaching problems. Potential remedies investigated comprised woven nylon hose lining, dosing with silicates and polyphosphates, contact with plastic materials and control of carbon dioxide content in ground water supplies.

The procedures and work plan are detailed in Appendix D and a summary of the tests undertaken is presented in Tables 3.1 and 3.2.

Table 3.1 Summary of PAH leach tests - investigation of factors which may influence leaching

Parameter investigated	Test conditions	Samples per test run	No. of test runs	Coupons per sample	No. of blanks per run	Total No. of samples [^]
Temperature Series 1	25 °C	2	3	1	1	6
	5 °C	2	3	1	1	6
Temperature Series 2	25 °C	3	2	1	1 ⁺	6
	5 °C	3	2	1	1 ⁺	6
pH	pH 6.0	2(4)*	5	1	1	14
	pH 7.9	2(4)*	5	1	1	14
Surface area to volume/ exposure time	1 coupon/ 6 hours exposure	2	2	1	1	4
	1 coupon/ 18 hours exposure	2	2	1	1	4
	2 coupons/ 6 hours exposure	2	2	2	1	4
	2 coupons/ 18 hours exposure	2	2	2	1	4

[^] excluding blanks

* On the final two runs of the pH experiments, four samples were tested

+ one blank for two runs

Except where indicated, the standard procedure had an exposure time per run of 16 hours and the temperature was maintained at an ambient value using a water bath.

Table 3.2 Summary of PAH leach tests - investigation of potential non-disruptive solutions

Remedy investigated	Test conditions	Samples per test run	No. of test runs	No. of blanks (in total)	Total No. of samples [^]
Nylon Hose	Hose present	4	2	2	8
	No hose	4	2	2	8
Silicate dosing	5 g l ⁻¹	4	3	1	12
	No dose	1	1	0	1
	10 g l ⁻¹	3	3	0	9
	No dose	3	1	1	3
Phosphate dosing	0.6 mg l ⁻¹	3	3	2	9
	No dose	3	1	0	3
	2.1 mg l ⁻¹	3	3	1	9
	No dose	3	1	0	3
MDPE pipe	Present	6	1	1	6
	Absent	6	1	0	6
PVC pipe	Present	6	1	1	6
	Absent	6	1	0	6
CO ₂ stripping	High CO ₂	4	3	1	12
	CO ₂ stripped	4	3	1	12

[^] excluding blanks

Except where indicated, the standard procedure had an exposure time per run of 16 hours and the temperature was ambient.

4. RESULTS AND OBSERVATIONS

4.1 Composition and application of coal-tar pitch linings to pipes - historical information

The original coal-tar based coating material was Dr Angus Smith's solution. The patent specification was taken out in 1848 and stated 'coal-tar reduced by distillation or otherwise to a thick pitch-like mass'. There exist written records of the use of Dr Angus Smith's solution for pipes laid in 1856 and 1884 (Anonymous 1936).

For the protection of pipelines, certain physical properties are desirable. The recipes of the 19th century provided thin brush-applied coatings; the qualities of these coatings included:

- resistance and impermeability to water;
- adhesion to imperfectly prepared surfaces;
- immunity against biological organisms.

Further development of the physical properties formed the basis of much research from 1930 onwards. For many years, the coating was applied by dipping the pre-heated pipe into a tank of molten coating material and the coating was then solidified by immersion in a cold water bath. This process gave a hard, glossy black coating about 100 µm thick. Originally the coating material was conventionally the pitch produced by the high temperature carbonisation of coal. By 1949, dipping mixtures were also prepared by digesting powdered bituminous coal in a high boiling refined tar oil (anthracene oil) called 'coal-oil'.

The standard applicable to these coating materials is BS 4164. The two types are defined as follows:

- BS 4164 Type I - coal-tar pitch (by-product of coal gas production);
- BS 4164 Type III - modified pitch (produced by digesting small amounts of coal dust in anthracene oil).

Further details of Specifications and Standards relating to internal coating of water mains are included in Appendix A.

In the National Water Council (NWC) Bulletin No.5 of February 1976, the following note appeared as a preface to a list of protective paints and coatings which had passed the NWC tests of effect on water quality:

"In order to avoid the possibility of the presence of the carcinogenic polyaromatic hydrocarbons all bituminous paints and coatings should be specified as made from petroleum or asphaltic bitumen and not coal tar bitumen."

This effectively ended the predominance of coal-tar pitch as a pipe coating material and from August 1977 virtually no iron pipes produced in the UK for potable water use were coated with coal-tar in any form. Since 1977, alternatives, such as bitumen coatings and concrete linings, have been used to protect iron pipes from corrosive waters. Alternative pipe materials have also been used: asbestos cement (AC), MDPE and PVC. AC pipes commonly have an internal bituminous coating to prevent moisture loss during storage. Bitumen is exclusively of petroleum origin and normally contains much lower levels of PAH than coal-tar pitch (Crane *et al.* 1981).

Table 4.1 presents a comparison of the properties typical of coal-tar pitch and bitumen based coatings (Collins and Smith 1978).

Table 4.1 Comparison of coal-tar pitch (BS 4164 Type III) and bitumen (BS 4147 Type I) coatings

Property	Coal-tar pitch	Bitumen
Mechanical:		
- thickness	about 100 µm ,	about 100 µm
- appearance	hard, glossy black	slightly softer, gloss lost on exposure to atmosphere
- water permeability	very low	low
Toxicological:		
- 'Total PAH'*	about 4%	less than 5 ppm
- specific carcinogens	some present	very low, if any
Palatability	some risk of taste and odour, especially in chlorinated waters	no taste or odour
Microbiological infestation	No infestation risks	No risk with material in use, but possible with some bitumen types

* Definition in Section 4.2.1

A review of the historical development of coal-tar based coatings has been put together based largely on information kindly provided by the cast iron pipe manufacturers, Stanton plc of Nottingham. This review is presented in Appendix B.

It is evident that significant changes in the constituents and concentrations of coal-tar pitch coatings have occurred over approximately 150 years of use. Even for specific preparations, variations in composition were experienced as a result of a gradual loss of certain constituents from the dipping baths during their period in use. In addition, the coating process provided a degree of choice to the customer in terms of physical characteristics by means of bath composition control with a consequent effect on coating composition.

This all suggests that the composition of coal-tar pitch linings could, in practice, be very variable pipe section to pipe section, even for pipes of similar age and manufacturing origin.

4.2 Data analysis

4.2.1 DoE surveys

The details of the data examined and the statistical analyses undertaken are presented in Appendix C, Section C.1. Survey 1 involving all water suppliers, returned an MAC failure rate of 1% of samples. (The MAC, Maximum Admissible Concentration given in the Drinking Water Directive, was the standard then in operation and is 200 ng l^{-1} measured as the sum of the concentrations of six individual PAHs, namely fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene. These six PAHs were chosen for historical analytical reasons as indicators of the presence of PAHs in water. The MAC was adopted in the Water Supply (Water Quality) Regulations and became known as the PCV, Prescribed Concentration or Value. The sum of the concentrations of these six substances is referred to in the rest of this report as 'Total PAH'.) Because the sampling took place in December the water temperatures were likely to have been lower than the average values throughout the year and therefore the data for Survey 1 may not represent the true average level of the PAH problem. Survey 2 provided much more detailed information of the PAH problem nationally. Zones studied in DoE Survey 2 were areas highlighted by Survey 1 as potential trouble spots. The sampling for Survey 2 was undertaken during the summer months when PAH levels may be expected to be higher. Thus the 28% MAC failure rate (based on mean Total PAH levels of four samples from each site rather than individual results) for this survey might be regarded as unexpectedly low for an investigation of expected problem areas at the time of year when levels of PAH leaching would be expected to be highest. Thirteen of the 25 zones had average Total PAH levels less than 50 ng l^{-1} . Hence 52% of these potential trouble spots did not suffer from elevated PAH levels at the time of sampling. The data were examined for correlations between PAH levels and constituents and zone characteristics including water type, position in distribution system, site variability for individual results and water quality parameters. The findings are summarised below.

Water type

An examination of the Survey 2 data, as depicted in Figure 4.1, showed that the areas where elevated PAH levels are experienced are predominantly those supplied with hard water. Areas with a mean Total PAH concentration exceeding 200 ng l^{-1} had a mean total hardness greater than 90 mg Ca l^{-1} , with the exception of one zone. Figure 4.1 also shows that a proportion of areas supplied with hard water do not have a problem with PAH.

PAH constituents

Fluoranthene is the most water-soluble of the six PAHs specified in the 'Total PAH' group (Verschuren 1983). In Survey 2 the proportion of this compound was generally above 90% of the Total PAH concentration. Relatively higher proportions of the other five PAHs were registered in some areas with softer waters, Figure 4.2. A possible explanation for this is a difference in lining condition between soft water areas where corrosion can be a problem, resulting in deteriorating linings, and hard water areas where linings are often found to be intact after considerable periods of use. As well as experiencing a leaching effect, where fluoranthene would predominate, the linings in contact with soft water supplies may be subject to release of lining material, as particulate matter, which would contain a wide variety of PAHs.

Position in distribution system

For a number of zones in Survey 2 a pattern of increasing PAH concentrations as the distance from the point of input increased was evident. Examples of the trends observed are shown in Figure 4.3.

Variability for individual sites

The behaviour of PAH levels at individual sites was quite variable. In some cases PAH concentrations registered at a single site ranged from below the detection limit to well in excess of 200 ng l^{-1} (e.g. Figure 4.4). For other sites PAH concentrations were consistently low or negligible, or consistently high. Figure 4.5 is an example of a particularly consistent zone. For the zones represented in both Figures 4.4 and 4.5, fluoranthene was the only PAH of the six indicators to be detected.

Some variation in PAH levels is expected, caused possibly by flow disturbances in the main, as would occur at peaks in demand or during nearby hydrant flushing. This may influence leaching as a result of changes in opportunity for dissolution (e.g. from changes in retention time) and may encourage the suspension of sediments which may contain adsorbed PAH. However, the magnitude of variations brought about by these influences and the interaction of the various factors cannot be adequately quantified from the data currently available.

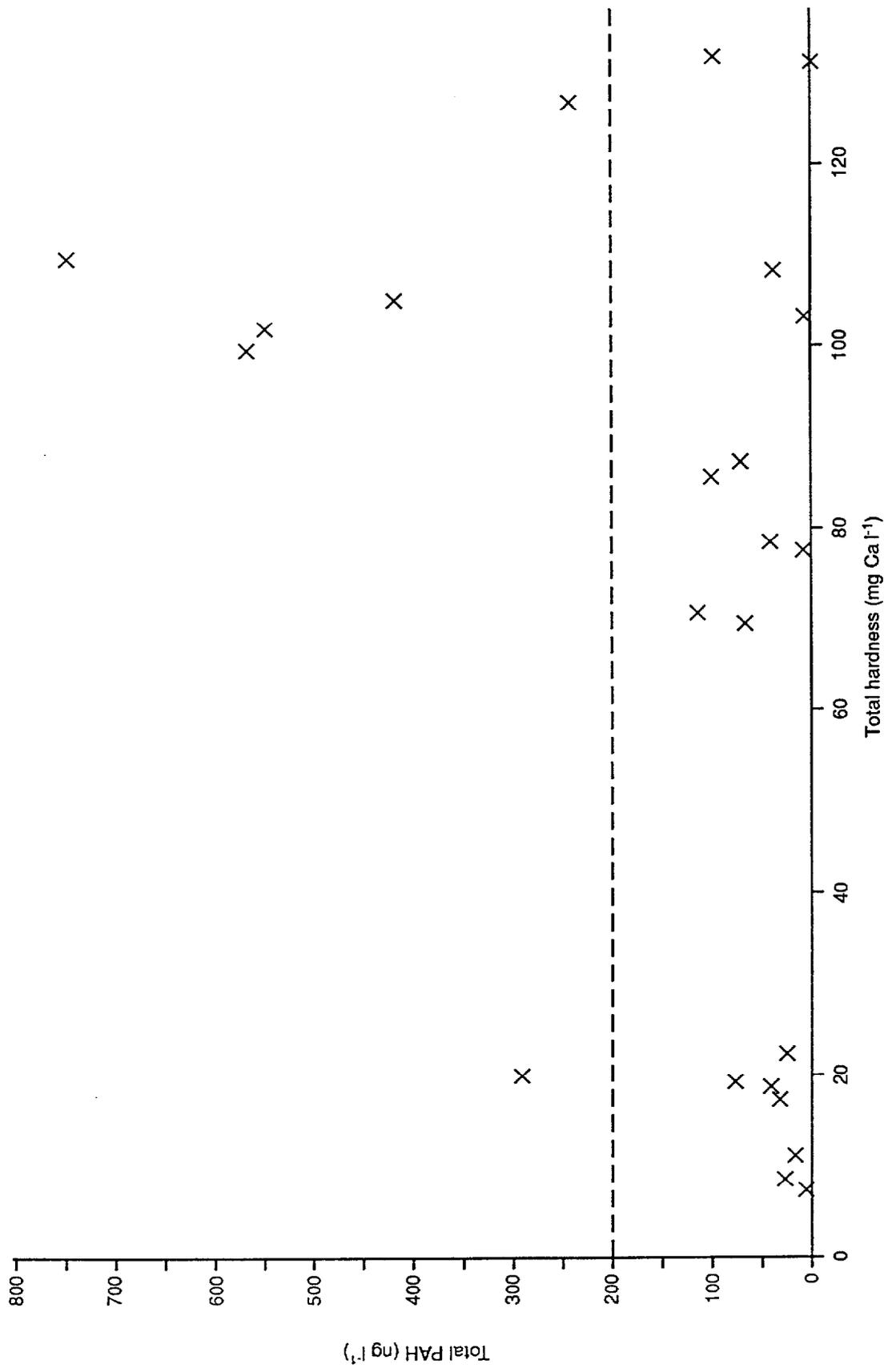


Figure 4.1 Relationship between Total hardness and PAH concentration

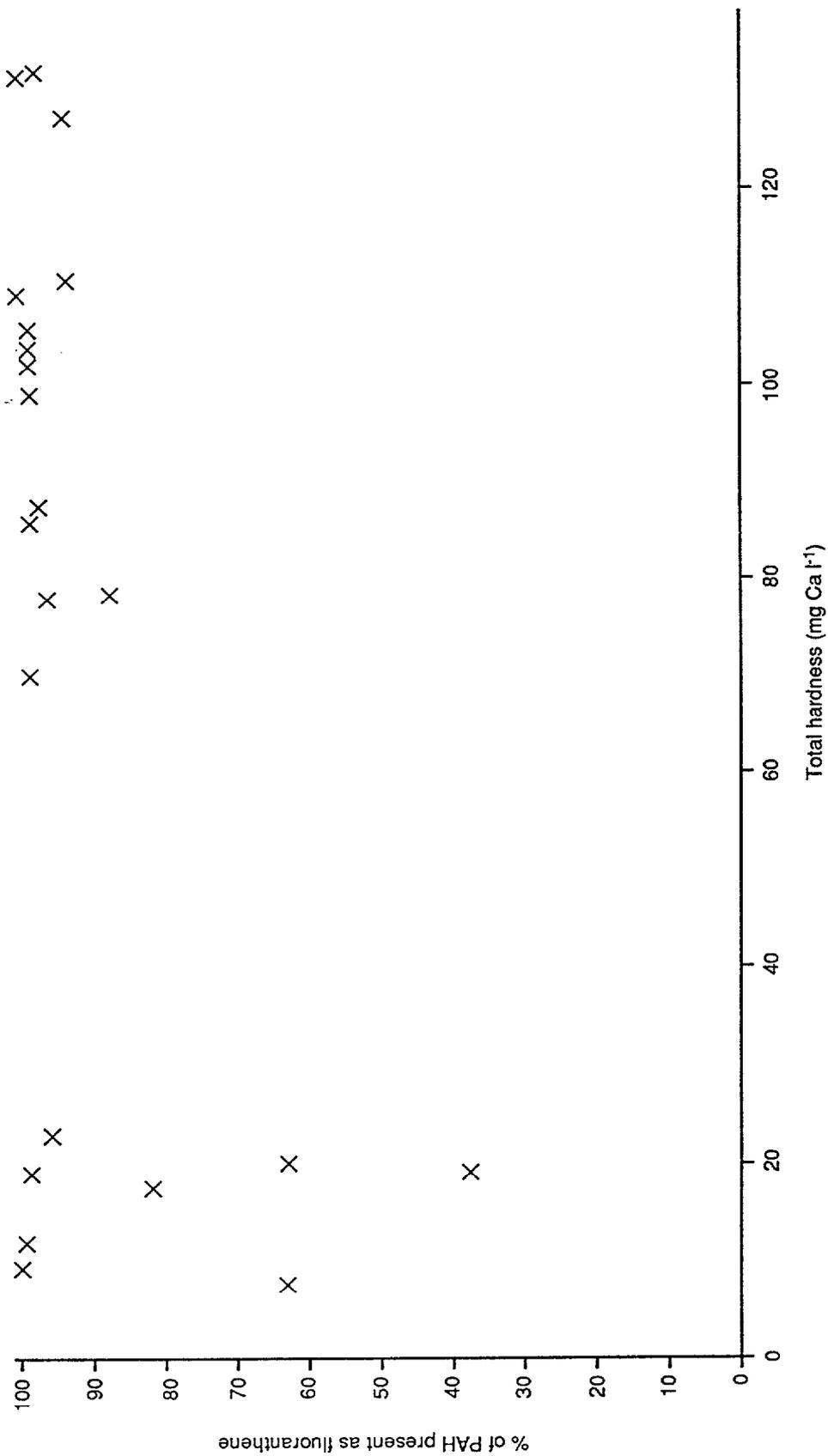


Figure 4.2 Fluoranthene proportion of Total PAH concentration in water of different hardness levels

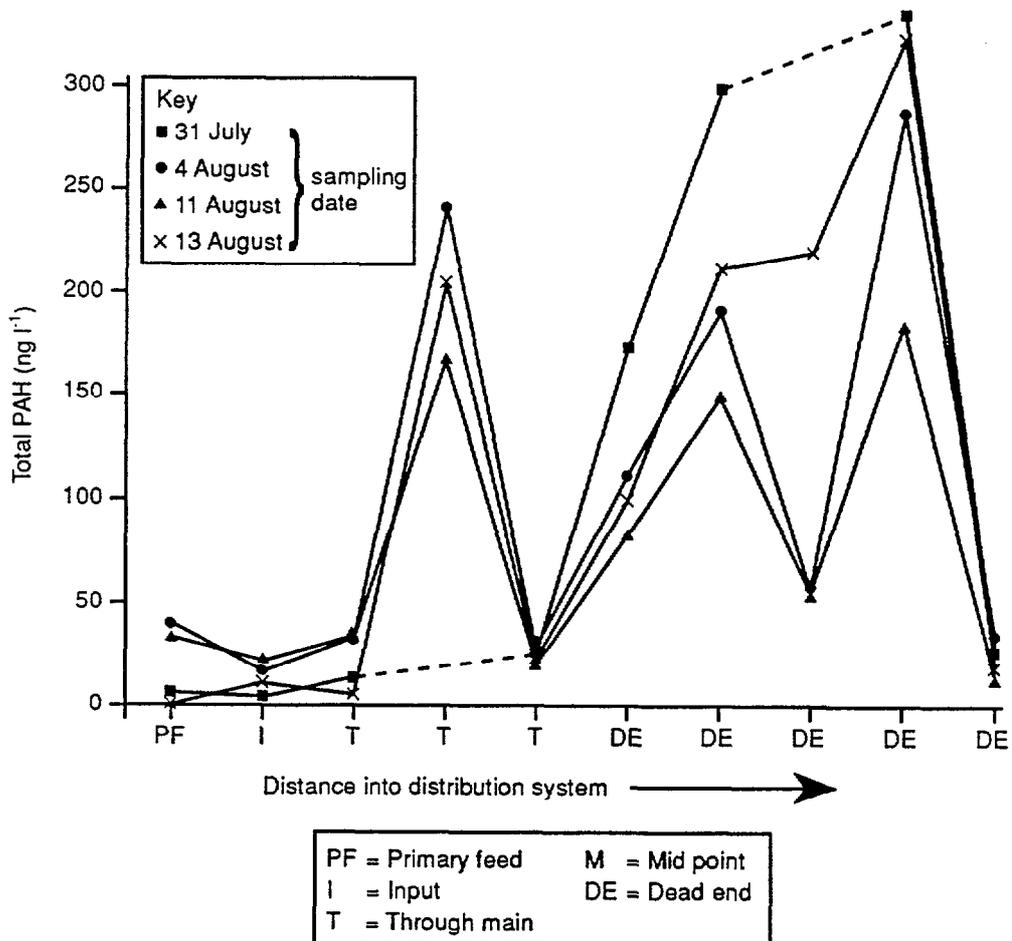
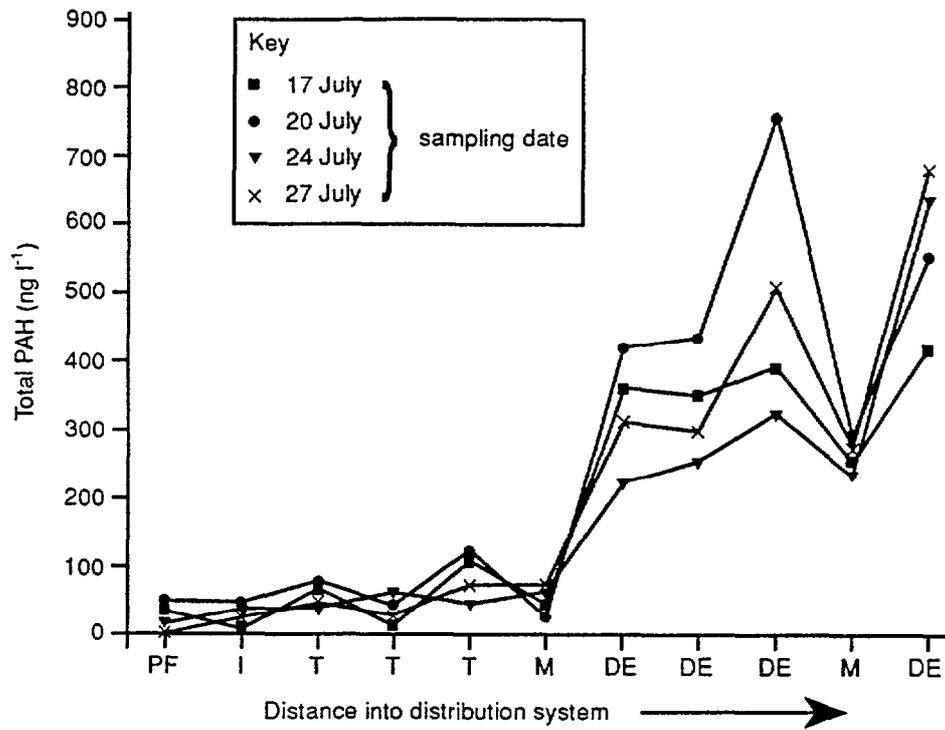


Figure 4.3 Typical results from DoE survey Part 2

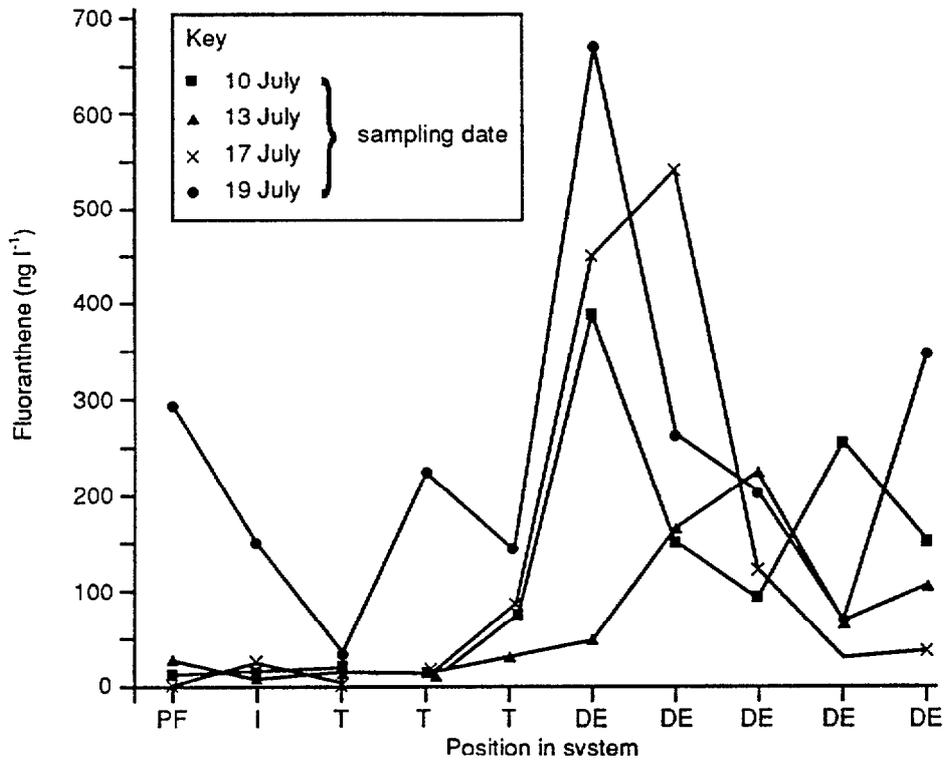


Figure 4.4 DoE survey Part 2 data - example unreproducible PAH concentrations

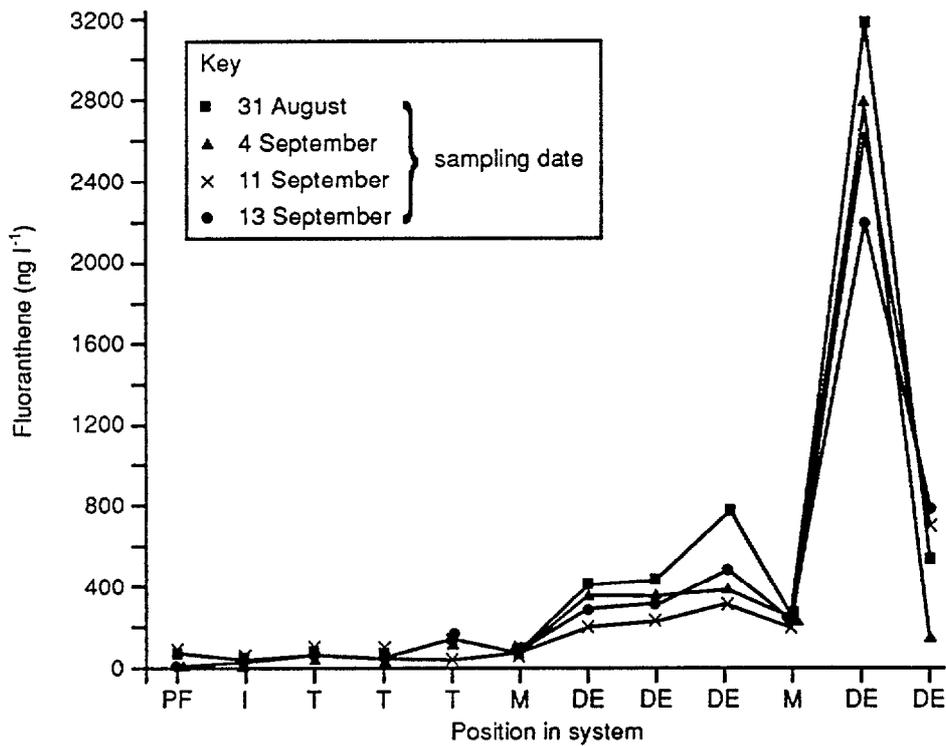


Figure 4.5 DoE survey Part 2 data - example of reproducible PAH concentrations

PF = Primary feed	M = Mid point
I = Input	DE = Dead end
T = Through main	

Water quality parameters

The data collected during DoE Survey 1 were examined for correlations between PAH and water quality parameters. Scattergraphs are presented in Figures 4.6 and 4.7 showing mean Total PAH as a function of mean levels of Total Organic Carbon (TOC) and turbidity respectively - parameters which an initial examination of the data suggested had a possible correlation with Total PAH. For all zones registering mean Total PAH levels above 100 ng l^{-1} , the mean TOC values were below $1.3 \text{ mg carbon l}^{-1}$. However, no consistent correlation was evident for zones registering low mean Total PAH. Similarly, Total PAH concentrations above 100 ng l^{-1} were associated with turbidity values below 0.42 NTU.

The absence of any marked association between Total PAH and water quality parameters in general may be due to interactions of numerous, and possibly counteracting, influencing factors. High TOC values are apparently beneficial in terms of being associated with low levels of Total PAH; yet the association of low TOC levels with low Total PAH levels in some zones indicates that other factors are operating. Thus the results for TOC and turbidity do not by themselves necessarily support possible associations of high PAH levels with hard groundwaters and clean main linings.

For Survey 2 data, a two-way analysis of variance examined the relationship between Total PAH levels and the water quality characteristics measured (iron, pH, turbidity and temperature) and distance from input. A positive correlation (95% confidence) was observed between Total PAH and the distance of the sample point from the input to the system. Iron and temperature were also found to increase with distance into the system, although their effects on Total PAH were not found to be statistically significant. No correlation between pH and PAH concentration was observed.

The two-week sampling period of the survey was probably not long enough to permit any conclusions on the existence or otherwise of a relationship of PAH with temperature. By conducting a survey over a longer time period a greater range in temperature than that experienced in Survey 2 would be provided.

4.2.2 Water Utility 1

Water Utility 1 provided water quality compliance data for the year 1990. Additional data, in particular descriptive of the distribution system, were supplied for sites where samples which had failed the Total PAH PCV of 200 ng l^{-1} had been taken. Statistical tests involving individual and stepwise regression analyses were undertaken, comparisons being made between mean parameter values for each compliance zone. Details of the data and the analysis are given in Appendix C, Section C2. A few cautionary notes regarding data interpretation are listed below, followed by a summary of the results.

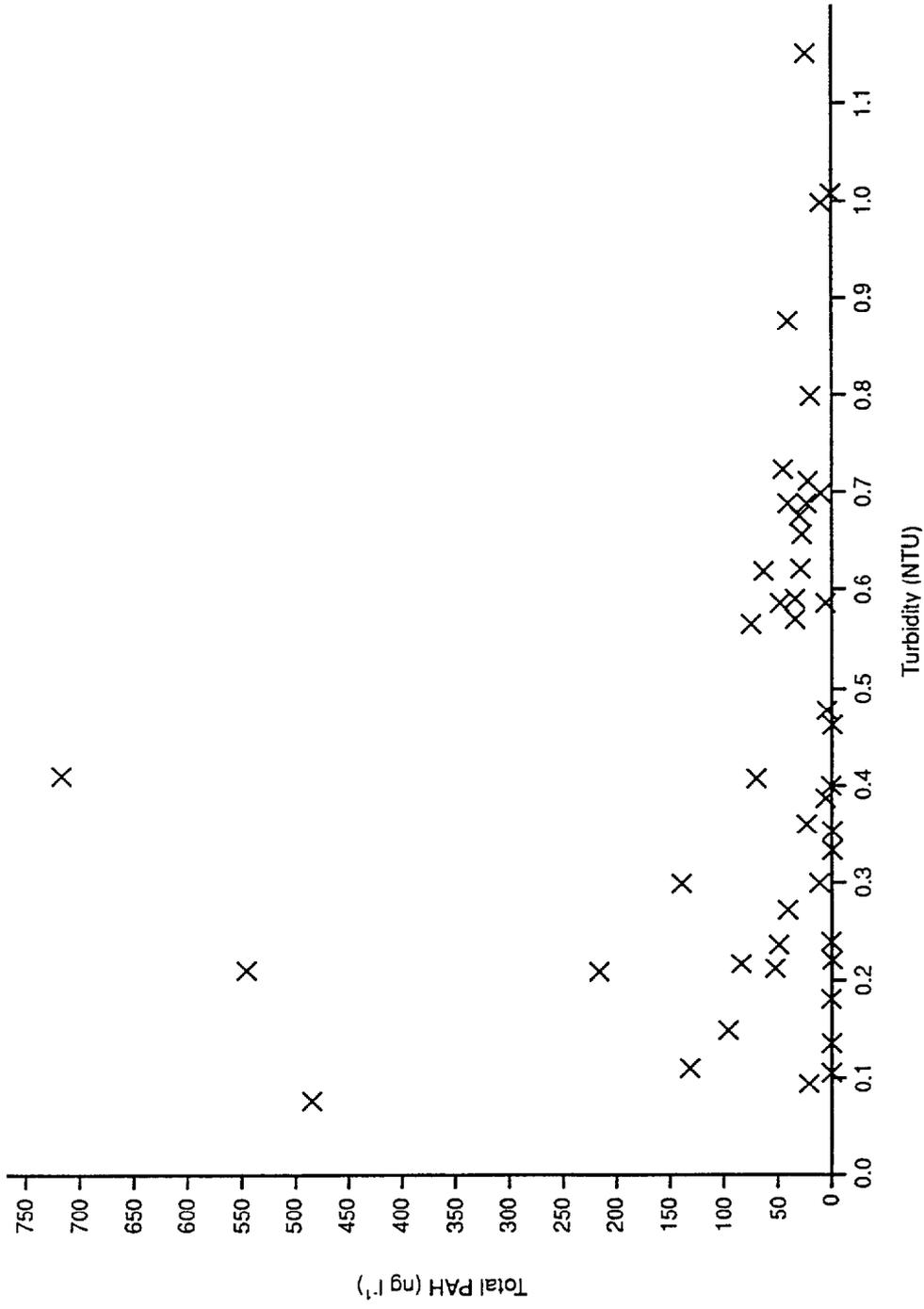


Figure 4.7 Scattergraph of mean Total PAH and mean turbidity values for a number of distribution zones

There are several reasons for interpreting the results presented with some caution:

1. Even where relationships were strongly indicated, visual examination of the graphs showed much scatter in the data. In some cases the slope of the relationship was strongly affected by a fairly small number of samples.
2. The possible intercorrelation of the explanatory variables made it very difficult to deduce which variables were having a real effect on PAH levels.
3. Comparison of parameters between the PCV failure data and the routine compliance data involved comparing two different data sets. This could have biased the comparisons.
4. Any relationships identified within the failure data set itself would apply only to failure data. They could not be applied to the majority of PAH samples which fall within the PCV.
5. The supporting data for the compliance results must always be treated with some caution: it is often the case that the nature of mains lining material is not known unless a section of the mains is actually removed - this would happen on only a small number of occasions.

Therefore it is recommended that the results be viewed primarily qualitatively. However, some potentially useful indications of the kinds of conditions affecting Total PAH have been gained from the analysis.

(a) Compliance data

The individual regression models showed significant variation in Total PAH for all of the explanatory variables, except temperature, when comparing mean Total PAH levels, Table 4.2.

Table 4.2 Individual regression models

EXPLANATORY VARIABLE	SIGNIFICANCE LEVEL Log(mean Total PAH)
Temperature	ns
pH	↓↓↓
Hardness	↓↓↓
log(TOC)	↓↓
log(turbidity)	↓↓

ns = not significant at a significance level of 5%
 ↓↓↓ = significant at 0.1% level with negative gradient
 ↓↓ = significant at 1% level with negative gradient

In the stepwise linear regression procedure applied to log(Total PAH) values only three of the variables appear significant.

- hardness - 0.1% increasing (↑↑↑)
- log(TOC) - 1% decreasing (↓↓)
- pH - 5% decreasing (↓)

Some intercorrelation of the variables is, however, expected with a consequent inability to fully isolate the effects. An apparently contradicting influence on PAH levels was indicated for hardness by individual and stepwise analyses. This may be a reflection of the limitations imposed by the use of zone mean values rather than individual sample values for the regression analysis.

(b) PCV failure data

Table 4.3 shows the number of samples and the mean value for each variable supplied corresponding to the Total PAH PCV failures in one area of Water Utility 1. Where the data were available, the number of samples and the mean value from the routine compliance samples for the same region are also given for comparison.

Table 4.3 Comparison of water quality parameters for Total PAH PCV failures with routine compliance data

EXPLANATORY VARIABLE	COMPLIANCE DATA		PCV FAILURES	
	No.	Mean	No.	Mean
PAH (ng l ⁻¹)	59	91	68	521*
Temperature(°C)	59	12.0	18	15.7
pH	59	7.42	17	7.43
Iron (µg l ⁻¹)	41	22.6	23	17.8
Aluminium (µg l ⁻¹)	41	11.7	17	16.9
Manganese (µg l ⁻¹)	41	7.0	17	5.3
Turbidity (NTU)	59	0.35	17	0.32
Free Chlorine (mg Cl l ⁻¹)	41	0.14	63	0.14*
Total Chlorine (mg Cl l ⁻¹)	41	0.18	62	0.21*
Diameter (inches)	-	-	62	4
Age (years)	-	-	54	25.4*

- information not available

* mean of individual values, all other means are means of supply zone means

These results suggest that the PCV failures are on average associated with higher temperatures and aluminium concentrations and lower concentrations of iron and manganese than the routine data. However, Student's t tests showed that only the differences for temperature and manganese are statistically significant, both at 0.1%.

No comparison was possible for the diameter and age of mains since these data were missing from the compliance data set.

In terms of PAH constituents, the results from Water Utility 1 indicated that of the six PAH determined, fluoranthene was the major constituent, mostly at nearly 100% of the Total PAH. In a small number of cases where the PCV for Total PAH was exceeded, fluoranthene was about 80% of the Total PAH concentration and for one high value of 1819 ng Total PAH l⁻¹, fluoranthene was 50%, although other high values were recorded which were almost 100% fluoranthene.

Regression analysis showed a significant relationship only between PAH and the explanatory variable, pipe age band (significance level 1%). The age bands 11-20, 21-30 and 31-40 all showed significantly lower PAH concentrations than the 0-5 year band and also the age bands representing pipes older than 40 years. The use of coal-tar pitch for internal pipe linings was stopped in 1977, thus pipes identified as between 0 and 5 years old should not generate PAH directly. It is likely in such cases that PAH generated upstream in mains which are coal-tar pitch lined act as the source of PAH in downstream sample points on non-iron mains. This is supported by the fact that only two out of the ten pipes which were 14 years old or less were not at dead end positions. The data permit no definite explanation as to why these recently laid mains are associated with higher levels of PAH than actual coal-tar pitch lined mains. Figure 4.8 shows the relationship between Total PAH and pipe age. The data show no obvious trends.

(c) Influence of water temperature on PAH levels

Subsequent to the analyses described above, a data set based on the results of compliance sampling and relating individual PAH levels with the parameters temperature, pH, alkalinity, hardness, TOC, turbidity and conductivity was provided by Water Utility 1. This data set permitted a more reliable assessment of the effect of temperature, previous data sets being limited to mean temperature values. Details of the data and the statistical analysis are presented in Appendix C, Section C.3.

A visual inspection of the graphs of mean temperature and PAH against month both showed similar patterns of higher values in summer (Figure 4.9).

The results of the ANOVA (analysis of variance) and simple linear and multiple regression analyses conducted on the data set are given in Table 4.4. They indicate that only month, zone and temperature are significant, with PAH increasing with temperature. The variables pH, alkalinity, hardness, TOC, turbidity and conductivity had no significant effect on PAH levels.

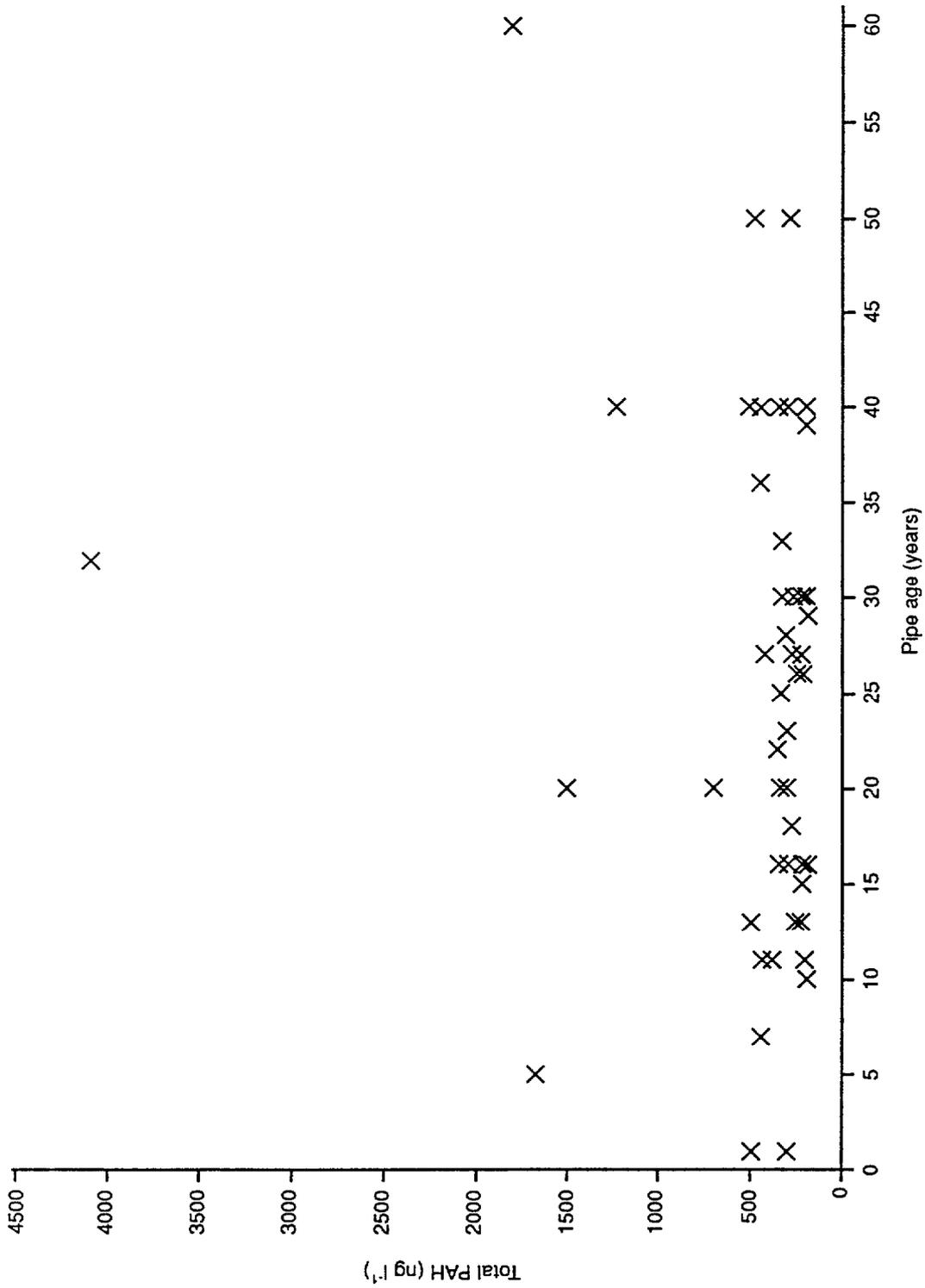


Figure 4.8 Relationship between Total PAH concentration of conveyed water and pipe age for a series of samples failing PAH compliance limits

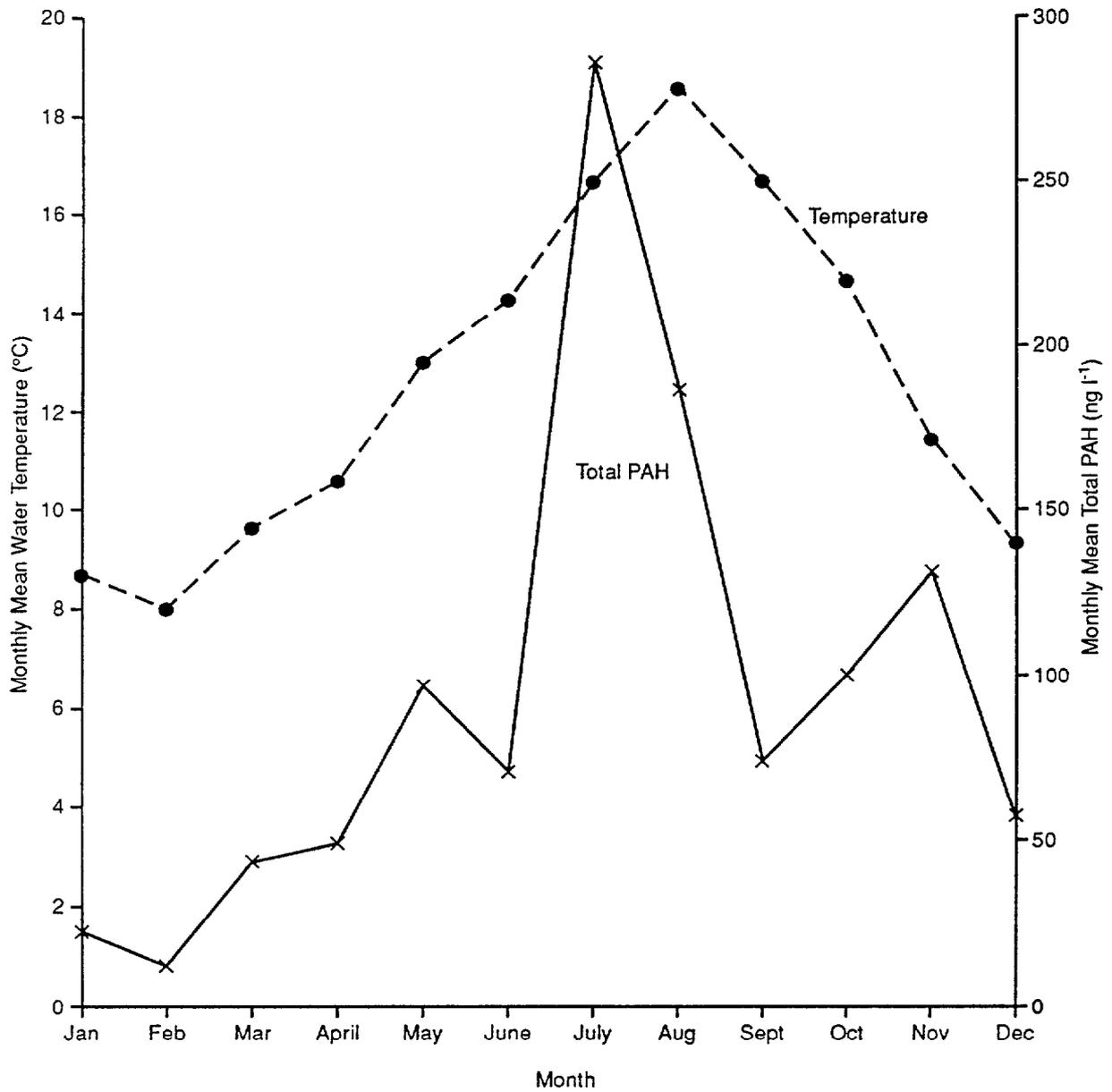


Figure 4.9 Variation of monthly mean water temperature and Total PAH concentration for compliance samples (Water Utility 1)

Table 4.4 Results of ANOVA and regression analyses of log (PAH)

Variable	ANOVA log(PAH)	ANALYSIS		Position in multiple regression
		Simple Linear Regression log(PAH)	Multiple Regression log(PAH)	
Zone	***		***	1
Year	ns			
Month	***		*	3
Temperature		↑↑↑	↑↑↑	2
pH		ns	ns	4
Alkalinity		ns		
Hardness		ns		
Turbidity		ns	ns	
Conductivity		ns	ns	
TOC		ns		

- * = significant at 5% level
- *** = significant at 0.1% level
- ↑↑↑ = significant at 0.1% level with positive gradient
- ns = not significant at 5% level

(d) Summary of Water Utility 1 data

Compliance data

There is evidence that PAH levels are higher where the pH is low. To a less significant extent this is true for conditions of low TOC and turbidity. The evidence for a relationship with water hardness was not consistent.

PCV failure data

There is some evidence that the Total PAH PCV failures are associated with higher temperatures and lower manganese concentrations than the routine compliance samples. There is also some evidence of a relationship between Total PAH and the age band amongst the PCV failures only, with higher Total PAH levels occurring in either fairly new (<5 years old) or fairly old (>40 years old) mains. Since pipes less than 5 years old (in 1990) would not be coal-tar pitch lined, the PAH would have arisen from older, upstream mains.

Effect of temperature

From another set of compliance data, a positive correlation between temperature and PAH concentration was indicated by simple linear and multiple regression analysis. The same data set showed zone and month of sampling also to be significant in terms of PAH concentrations recorded, but provided no evidence of correlations between PAH and the variables pH, alkalinity, hardness, TOC, conductivity and turbidity. It is, however, to be noted that the overall ranges of these variables were not particularly marked (details are provided in Appendix C, Section C3).

4.2.3 Water Utility 2

(a) Compliance data

Water Utility 2 provided water quality compliance data for the period April to October 1991. Statistical tests involving an analysis of variance were undertaken to test for significant variations in Total PAH and temperature from month to month. For other explanatory variables, a linear regression model of Total PAH against the variable in question was fitted. Details of the data and the analysis are given in Appendix C, Section C4. The results are summarised below.

A visual assessment of the data in the form of graphs, tables and histograms led to the following observations:

1. Mean temperature rose from about 10.5 °C in April to just over 17 °C in July and August before decreasing to 14.3 °C in October.
2. Monthly variation in mean Total PAH was less smooth. In July, Total PAH was at its highest concentration with a mean of 330 ng l⁻¹. The next highest mean concentration of 160 ng l⁻¹ was recorded in June. There was a large variation in Total PAH within each month.
3. The remaining graphs indicated that Total PAH might be increasing with temperature and decreasing with total chlorine.
4. The histograms indicated that the distributions of Total PAH and aluminium concentrations were rather skew. These variables were logged for all of the model fitting.

Figure 4.10 shows the monthly variations in mean temperature and mean PAH concentrations.

The analysis of variance showed that the variation in mean temperature over the different months was statistically significant (significance level 0.1%). However, the variation in mean Total PAH from month to month was not quite significant at a level of 5%.

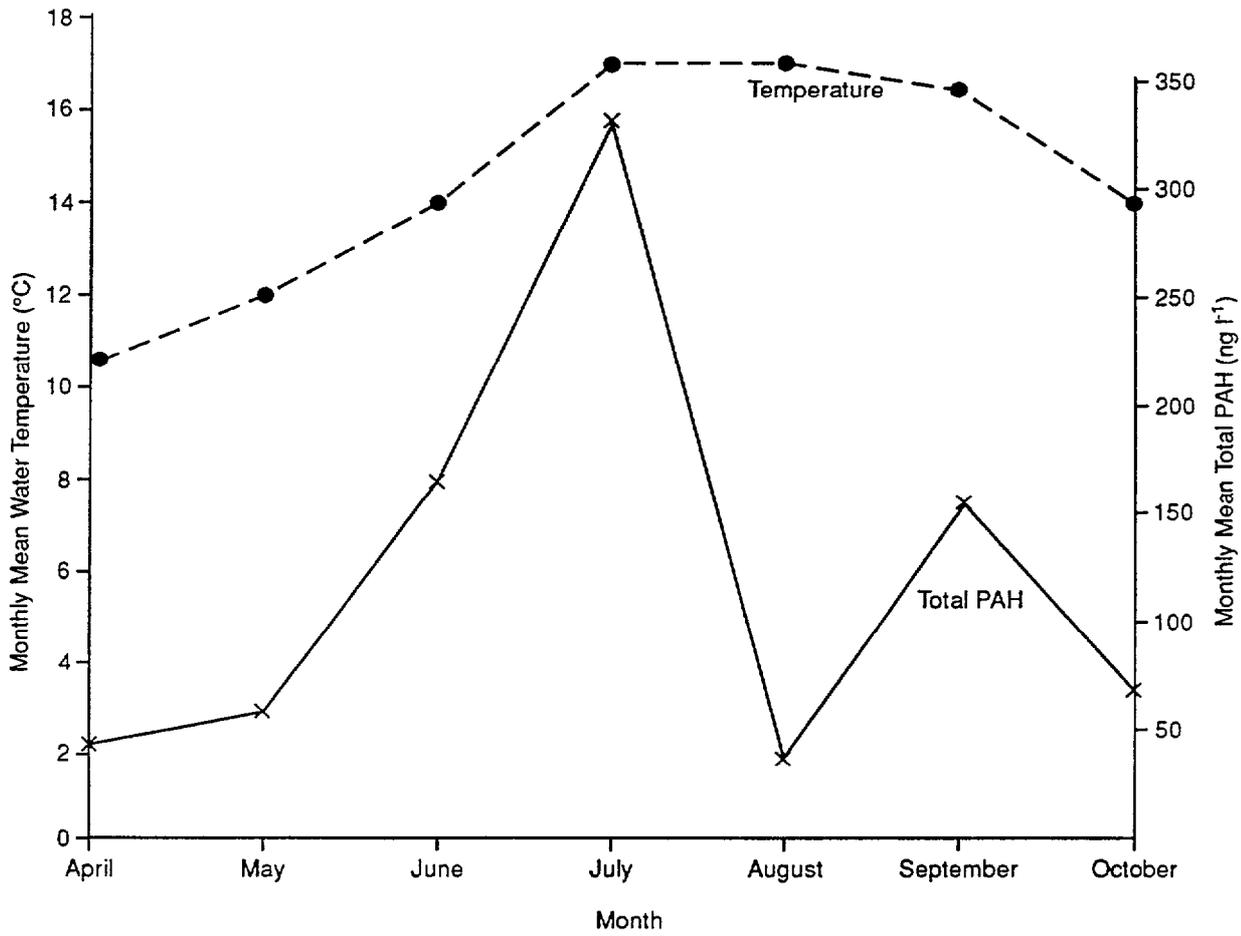


Figure 4.10 Variation of monthly mean water temperature and Total PAH concentration for compliance samples (Water Utility 2)

The only significant result obtained from fitting the linear regression models was an increase in log(Total PAH) with temperature (significance level 5%).

Therefore the results of the statistical assessment of the compliance data from Water Utility 2 can be summarised as follows:

- there is some evidence that Total PAH increases as temperature increases,
- no evidence was found of significant relationships between Total PAH and other explanatory variables studied, though the small numbers of data for total hardness, metals and TOC meant that it was difficult to draw any real conclusions for these variables.

(b) Specific study data

Water Utility 2 has undertaken extensive surveys in two study zones within its region and has kindly given their permission for the results of these surveys to be analysed and the findings presented. Details of the analysis are given in Appendix C, Section C5. The data sets permitted an examination for correlations between PAH concentrations and the variables: mains diameter, mains category (through, mid-point and dead end), temperature, free chlorine, total chlorine, pH, mains material, hardness and alkalinity.

Based on all relevant data from both zones, the graphs of PAH means and medians against month show that PAH concentration increases in the spring months with a peak in April then declines in June rising again to peak in September before again declining towards the end of the year. The temperature values had not been recorded for all samples and the spread of recordings throughout the year was very limited, being available only for the months of May, July and October. These findings are shown in Figure 4.11.

The results of the statistical analyses are shown in Tables 4.5 and 4.6.

All three simple regression analyses confirmed that PAH varies significantly by month. However, a negative correlation of PAH with temperature was identified for the combined data and Zone 1, yet a positive correlation for Zone 2, the latter on a small data set of only 10 points. Similar inconsistency was observed for hardness and alkalinity which did not vary significantly in the combined data analysis, nor for Zone 2 alone. However, in Zone 1, PAH levels rose significantly with both parameters, though the models contained only nine points each.

PAH concentrations were significantly higher for coal-tar pitch lined mains than for non-iron mains in the combined analysis. No such effects were evident in either of the individual zones, possibly as a consequence of the small number of mains falling into the non-iron category. In all three analyses, dead-end mains were shown to be associated with the highest PAH levels. The relative behaviour of mid-point and through mains was not consistent; for the combined data set and Study Zone 2, PAH concentrations at through mains exceeded those at mid-point sites, the reverse was recorded for Study Zone 1.

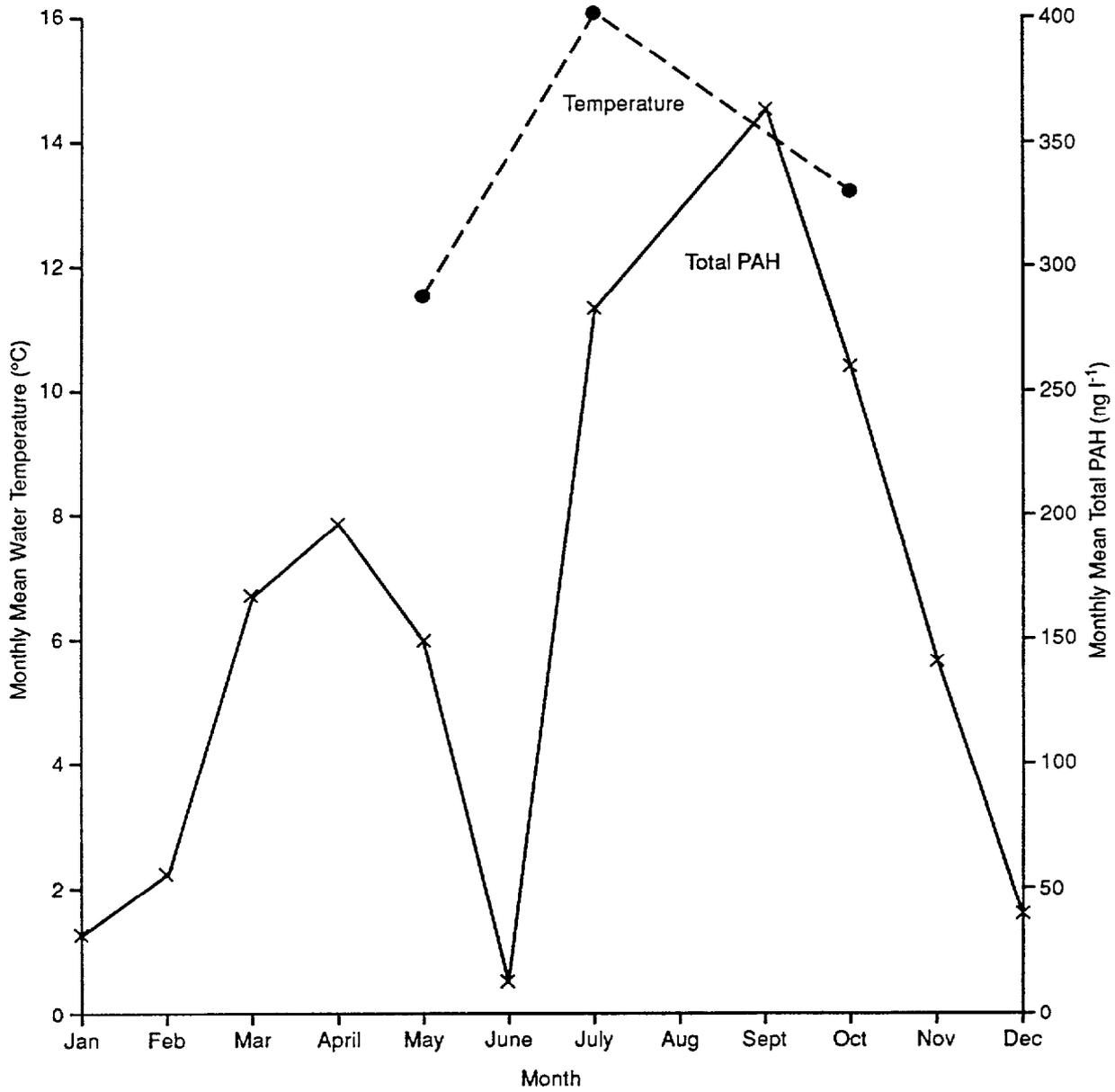


Figure 4.11 Variation of monthly mean water temperature and Total PAH concentration for survey samples (Water Utility 2)

Table 4.5 Results of Regression analyses of log (PAH) - specific study zones, Water Utility 2

Variable	ANALYSIS			
	Zones 1 and 2 combined		Zone 1	Zone 2
	Simple	Multiple	Simple	Simple
Mains diameter	↓↓		ns	ns
Month	***		***	*
Time of day	ns		ns	ns
Temperature	↓		↓↓↓	↑
Free chlorine	↓↓		ns	ns
Total chlorine	↓	ns(2)	ns	ns
pH	ns		ns	ns
Hardness	ns		↑↑	ns
Alkalinity	ns		↑↑	ns
Study zone (1 vs. 2)	↑↑↑		N/A	N/A
Mains material	↑		ns	ns
Mains category	***	***(1)	*	*

Numbers in parentheses indicate the position of the term in the multiple model

- * or ↑ or ↓ = significant at 5% level
- ↑↑ or ↓↓ = significant at 1% level
- *** or ↑↑↑ or ↓↓↓ = significant at 0.1% level
- ↑ = effect has a positive gradient
- ↓ = effect has a negative gradient
- ns = not significant
- N/A = not applicable

Table 4.6 Results of ANOVA by zone

Variable	ANOVA result
Free chlorine	↓↓↓
Total chlorine	ns
Diameter	↓↓

- ↓↓ = significant at 1% level, negative gradient
- ↓↓↓ = significant at 0.1% level, negative gradient
- ns = not significant

In the combined data set, mains diameter, free chlorine and total chlorine were shown to have a significant effect on PAH levels, lower PAH being recorded as diameter and free and total chlorine increased. These effects were not evident for either of the zones individually. Both free and total chlorine levels were higher in Study Zone 1 where the PAH levels were significantly lower than in Study Zone 2 (shown by ANOVA), it is therefore not certain whether it is chlorine levels or some other difference between the zones which is affecting PAH levels. The average mains diameters are not significantly different between the two zones.

Time of day and pH were shown not to be significant in any of the analyses. The samples were all taken between 9.00 and 15.00 hrs, so provide only limited information about diurnal variation. The stepwise multiple linear regression model added mains category as the only significant term. This suggests a high degree of correlation between the explanatory variables, making it difficult to infer which of the significant effects from the individual models have the most influence on PAH concentrations.

The results of the findings for the specific study zone data analysis can be summarised as follows:

- PAH varied significantly with month. Peaks in concentration occurred in April and September with a slump in June.
- Mains category had a significant effect on PAH concentrations. PAH values were higher at dead end sites than at mid-point or through main sites.
- Mains diameter, temperature, free and total chlorine, hardness, alkalinity and mains material were found to have some correlation with PAH levels but the findings were not consistent throughout the analysis.
- The variables time of day and pH had no effect on PAH concentrations.

4.3 Lining assessment

To permit comparison of the results obtained during the present investigation, previous work on lining composition was reviewed. Studies conducted by Crane *et al.* (1981) have established the concentrations of the six indicator PAH in typical coal-tar pitch lining samples. All formulations of coal-tar pitch examined were found to contain percentage levels of PAH. The levels of PAH did not appear to diminish appreciably as the lining aged. Bitumen was found to contain no measurable concentrations of any of the six PAH except fluoranthene, this being present at very low concentrations. Table 4.7 contains a summary of the findings from this work.

For the current study, a few exhumed pipe samples have been collected. Attempts were made to obtain associated data relating to the concentration of PAHs in water supplied by the main, of which the pipe samples are considered representative, the age of the main and the water quality characteristics of the conveyed water; such information being necessary to justify an analysis of the lining material. Unfortunately the data provided were extremely limited with the result that lining analysis was considered not to be worthwhile.

Table 4.7 PAH composition (% by wt)

Material	PAH ^(a)					
	F	B(b)F	B(k)F	B(a)P	B(ghi)Pe	InP
Coal-tar pitch Type I, BS 4164	8	0.6	0.4	0.8	0.8	0.4
Anthracene oil ^(b)	12	0.8	0.4	1.2	0.4	0.3
Coal dust ^(b)	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
BS 4164, Type III (unused pipe)	8	0.6	0.4	0.8	0.3	0.3
Lining 9" main, 20 years-old	4	0.6	0.4	0.8	0.6	0.3
Lining 3" main 20 years-old	1.6	0.1	0.1	0.2	0.1	0.1
Bitumen lining, potable water storage tanks	0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Lining on unearthed 18" steel pipe	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Lining unused AC pipe	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

(a) Abbreviations for the individual PAHs:

F = Fluoranthene B(b)F = Benzo(b)fluoranthene,
 B(k)F = Benzo(k)fluoranthene B(a)P = Benzo(a)pyrene,
 B(ghi)Pe = Benzo(ghi)perylene InP = Indeno(1,2,3-cd)pyrene

(b) Constituents of lining material to BS 4164 Type III

4.4 Laboratory tests

The methods used to conduct these tests on factors that may affect leach rates and potential remedial measures are described in Appendix D, Section D1.

4.4.1 Application of results

An analysis of the coal-tar pitch used to coat the coupons (Table 4.8) showed that this material was similar to that present on the internal surfaces of cast iron pipes laid before 1977 (reference Table 4.7).

Table 4.8 Composition of coal-tar lining on coupons (% wt)

Constituent	wt %	
	Sample 1	Sample 2
Fluoranthene	5.90	5.07
Benzo(b)fluoranthene	0.94	0.86
Benzo(k)fluoranthene	0.50	0.47
Benzo(a)pyrene	0.96	0.83
Benzo(ghi)perylene	0.55	0.47
Indeno(1,2,3-cd)pyrene	0.57	0.51
Naphthalene	0.16	0.19
Acenaphthene	0.71	0.66
Fluorene	0.65	0.73
Phenanthrene	5.95	5.20
Anthracene	0.98	0.95
Pyrene	3.74	3.37
Benz(a)anthracene	1.50	1.37
Chrysene	1.45	1.28
Dibenz(a,h)anthracene	0.14	0.13
Total PAH	9.42	8.21
Total 16*	24.70	22.09

* The 16 PAH are those PAHs on the US Environmental Protection Agency (EPA) indicator list. Acenaphthylene is included in the 16 PAH but, because of its relatively low level fluorescence emission, could not be determined by the analytical method used.

These results confirm that the coal-tar pitch used to coat the coupons is a suitable material for the investigation of PAH leaching. It is, however, important to recognise that the effects of deterioration or ageing of coal-tar pitch linings, of corrosion deposits and of

treatment-derived deposits which may affect PAH leaching from pipes in service will not be emulated in tests with new coupons. The direct application of the coupon test results is therefore inappropriate to predict actual levels in the field. The laboratory technique does however permit comparison of the effects of factors under controlled conditions.

4.4.2 PAH analytical method

An outline of the analytical method used in this work is included in Appendix D, Section D2.

Briefly, the method involved extraction of the test water samples with dichloromethane, concentration of the extract by evaporation, addition of an internal standard and analysis with high performance liquid chromatography (HPLC) using a fluorescence detector.

For about the first half of the tests quantitative results were produced for all six substances comprising the Total PAH parameter using a six-point concentration calibration curve. For most of the later work only the level of fluoranthene was assessed in this way. Chromatograms were inspected to see whether the sum of the concentrations of the other five PAHs were likely to exceed 10% of the Total PAH concentration. Where this was the case the levels were estimated against a single concentration calibration and therefore the concentrations recorded may be less precise than those for fluoranthene. In the tables in Appendix E these results are written in brackets. In the tables in the following sections, where this type of result was obtained for the non-fluoranthene PAHs, values for Total PAH are omitted and where the proportion of fluoranthene is less than 90% of the Total PAH an approximate value is indicated.

Assessment of control samples gave a relative standard deviation for the complete analytical process, including the extraction, of 16 to 20%, depending on the PAH. This result has been taken into consideration when evaluating the results of the factor and remedial measure tests.

4.4.3 Factor tests

The findings of the factor tests are summarised below. Where the proportion of fluoranthene in the test water at the end of a run was found to be 90% or more of the Total PAH concentration this is taken to indicate that the leaching process dominated the transfer of PAHs from the coupon to the test water. Where the proportion of the remaining five PAHs is higher, there is a possibility of particulate material, derived from flakes of coating, being present in the sample. Appendix E lists the test results in full.

(a) Temperature

The tests were carried out at 5 °C and 25 °C with three runs for each of two coupons at each temperature.

Table 4.9a contains a summary of the results of these tests. Each run was a sixteen hour exposure of a coupon to 2.5 litre of water. For the majority of samples, fluoranthene constituted 90% or more of the Total PAH detected, indicating a genuine leaching effect.

Table 4.9a Summary of leach tests investigating the effect of temperature - Series 1

Temperature °C	Coupon No.*	Run No.	Total PAH ng l ⁻¹	-----Fluoranthene-----		
				ng l ⁻¹	% Total PAH	Leach rate ng cm ⁻² h ⁻¹
25	2	1	40	40	100	0.18
		2	624	620	99	2.8
		3	527	470	89	2.1
25	17	1	35	35	100	0.16
		2	818	810	99	3.6
		3	634	630	99	2.8
5	15	1	300	290	97	1.4
		2	93	66	71	0.31
		3	27	27	100	0.13
5	16	1	938	930	99	3.7
		2	107	96	90	0.38
		3	99	94	95	0.38

16 hours exposure

* Each coupon was given an identification number so that the history of the tests in which it had been used could be reviewed and if necessary differences between coupons investigated to aid the interpretation of results.

The results for the second and third runs were as expected with the leach rates at 5 °C much lower than the values obtained at 25 °C. Excluding the first test run, the average leach rate for fluoranthene of the four tests at 25 °C (2.8 ng cm⁻² h⁻¹) was 9.4 times the average at 5 °C (0.3 ng cm⁻² h⁻¹) with a factor of 5.5 between the lowest rate at 25 °C and the highest rate at 5 °C. The results of the first runs were almost the exact opposite with low leach rates being found at 25 °C and high rates at 5 °C. The obvious explanation is that a mix-up occurred between the samples but it was noted that in the first runs at 25 °C a dull film had formed on the coupons. There were also some changes in water quality - notably in pH levels - between runs. (These changes were noted in blank samples kept under similar conditions. The changes were measured in blanks to avoid the risk of the taking of these measurements affecting the PAH concentrations in the real samples.)

Therefore it is considered that there is some doubt about these results. The tests were repeated using a different design where successive runs for each of three coupons were

carried out at low and high temperatures in alternating sequence repeated once. This design was adopted to reduce the uncertainty in interpreting the results introduced by between-coupon variations in leach rates.

A summary of the results of the second temperature series are shown in Table 4.9b.

Table 4.9b Summary of leach tests investigating the effect of temperature - Series 2

Temperature °C	Coupon No.	Run No.	-----Fluoranthene-----			
			ng l ⁻¹	% Total PAH	Leach rate ng cm ⁻² h ⁻¹	Mean leach rate
5	3	1	9	>90	0.04	0.16
	9	1	14	>90	0.07	
	14	1	86	>90	0.38	
25	3	2	30	>90	0.15	0.74
	9	2	163	>90	0.76	
	14	2	296	>90	1.3	
5	3	3	<5	>90	0.00	0.08
	9	3	28	>90	0.14	
	14	3	21	>90	0.09	
25	3	4	74	>90	0.37	0.82
	9	4	180	>90	0.89	
	14	4	276	>90	1.2	

16 hours exposure

The results for the second series were much more consistent. The average leach rates for fluoranthene were 0.12 ng cm⁻² h⁻¹ for 5 °C and 0.78 ng cm⁻² h⁻¹ for 25 °C. Only one relatively high value was recorded at 5 °C (0.38 ng cm⁻² h⁻¹ for coupon 14, run 1) but this behaviour was not inconsistent for the coupon, which gave the highest leach rates at 25 °C. For each coupon all the results at 25 °C showed higher leach rates than at 5 °C.

A graphical representation of the effect of temperature (Series 2 tests) is shown in Figure 4.12.

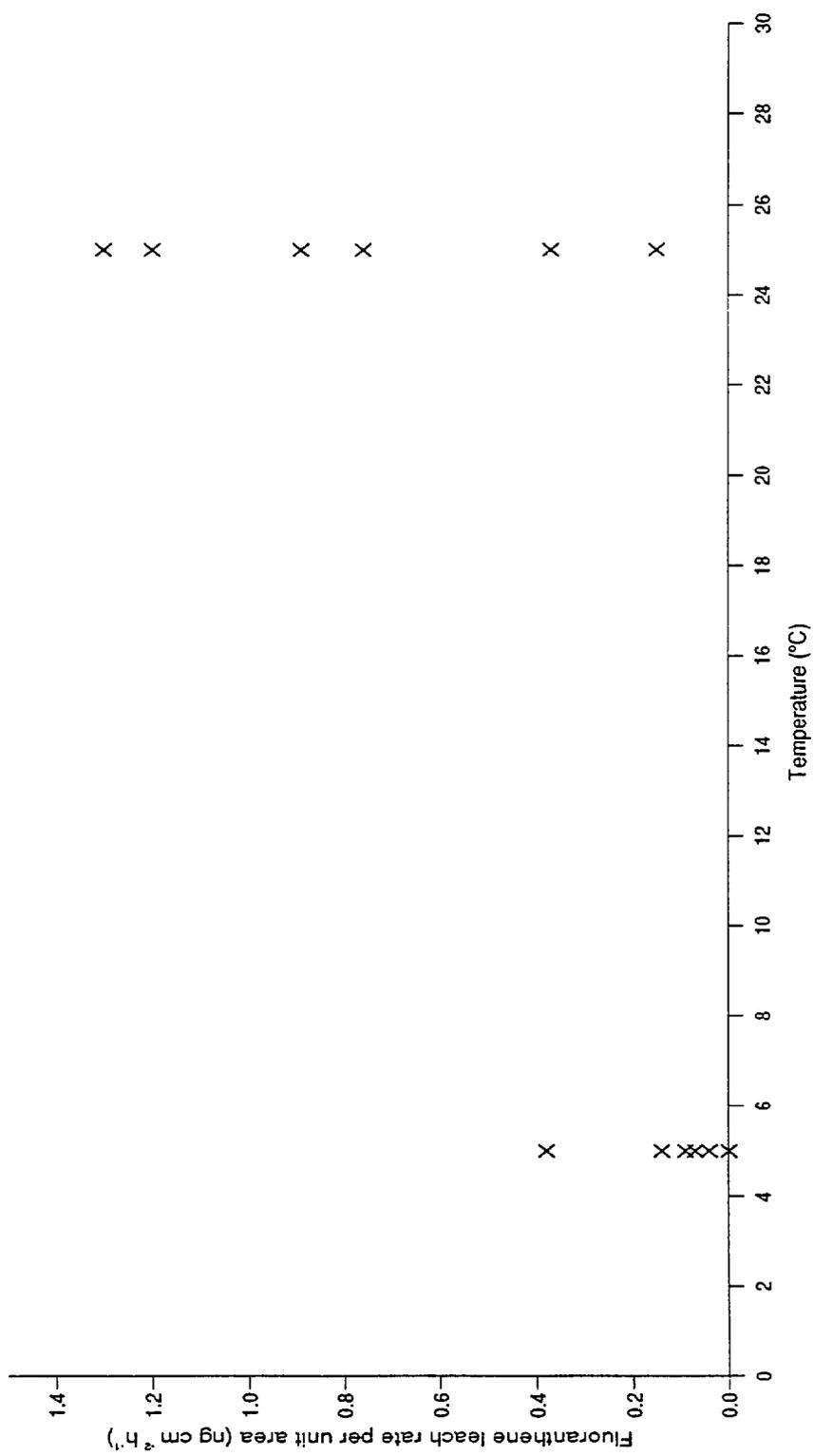


Figure 4.12 Fluoranthene leach rate per unit area with respect to temperature

(b) pH

The pHs chosen were a slightly acid pH 6.0 and a slightly alkaline pH 7.9. These values represent a nearly one-hundredfold difference in concentration of hydrogen ions. The pH-buffered solutions were prepared using mixtures of phosphoric acid and its salts. The test was carried out in two stages with, in the first stage, two coupons being exposed at each pH for a series of three runs. The second stage was an extension, because only marginal differences in leach rates had shown up in the first stage, with two further runs being done for each coupon plus two more coupons at each pH to give a total over both stages of 14 runs at each pH.

A summary of the results of these tests is shown in Table 4.10. The results are for 16-hour exposures. The high proportion of fluoranthene (>90%) relative to the other five indicator PAHs observed for the majority of these samples indicates genuine leaching.

A graphical representation of the effect of pH on fluoranthene leach rate per unit surface area of coupon is shown in Figure 4.13. The spread of leach rates at each pH was essentially the same, especially if the two samples which had more than 10% of the non-fluoranthene PAHs present were omitted from the calculations. Taking all the results the average fluoranthene leach rates were $0.59 \text{ ng cm}^{-2} \text{ h}^{-1}$ at pH 7.9 and $0.68 \text{ ng cm}^{-2} \text{ h}^{-1}$ at pH 6.0. Ignoring the one odd result at each pH, the corresponding average leach rates were 0.61 and $0.59 \text{ ng cm}^{-2} \text{ h}^{-1}$.

Table 4.10 Summary of leach tests investigating the effect of pH

Ph	Coupon No.	Run No.	Total PAH ng l ⁻¹	-----Fluoranthene-----			Leach rate ng cm ⁻² h ⁻¹	Mean leach rate
				ng l ⁻¹	% Total PAH			
6.0	1	1	175	170	97	0.78	0.68 (0.59*)	
		2	84	84	100	0.38		
		3	220	220	100	1.0		
		4	241	241	100	1.2		
		5	154	154	100	0.76		
6.0	3	1	73	73	100	0.33	0.68 (0.59*)	
		2	59	59	100	0.27		
		3	81	81	100	0.37		
		4	103	103	100	0.50		
		5	107	104	97	0.51		
6.0	34	4	181	181	100	0.87		
		5	454	388	85	1.9		
6.0	24	4	82	82	100	0.42		
		5	52	52	100	0.27		
7.9	14	1	81	81	100	0.33		
		2	138	130	94	0.53		
		3	110	110	100	0.45		
		4	181	174	96	0.76		
		5	142	137	96	0.60		
7.9	7	1	59	54	92	0.28	0.59 (0.61*)	
		2	50	47	94	0.24		
		3	68	59	87	0.30		
		4	79	79	100	0.44		
		5	152	152	100	0.85		
7.9	26	4	233	233	100	0.96		
		5	209	209	100	0.86		
7.9	28	4	246	236	96	1.0		
		5	153	153	100	0.67		

16 hours exposure

* mean values excluding results where fluoranthene is <90% of Total PAH

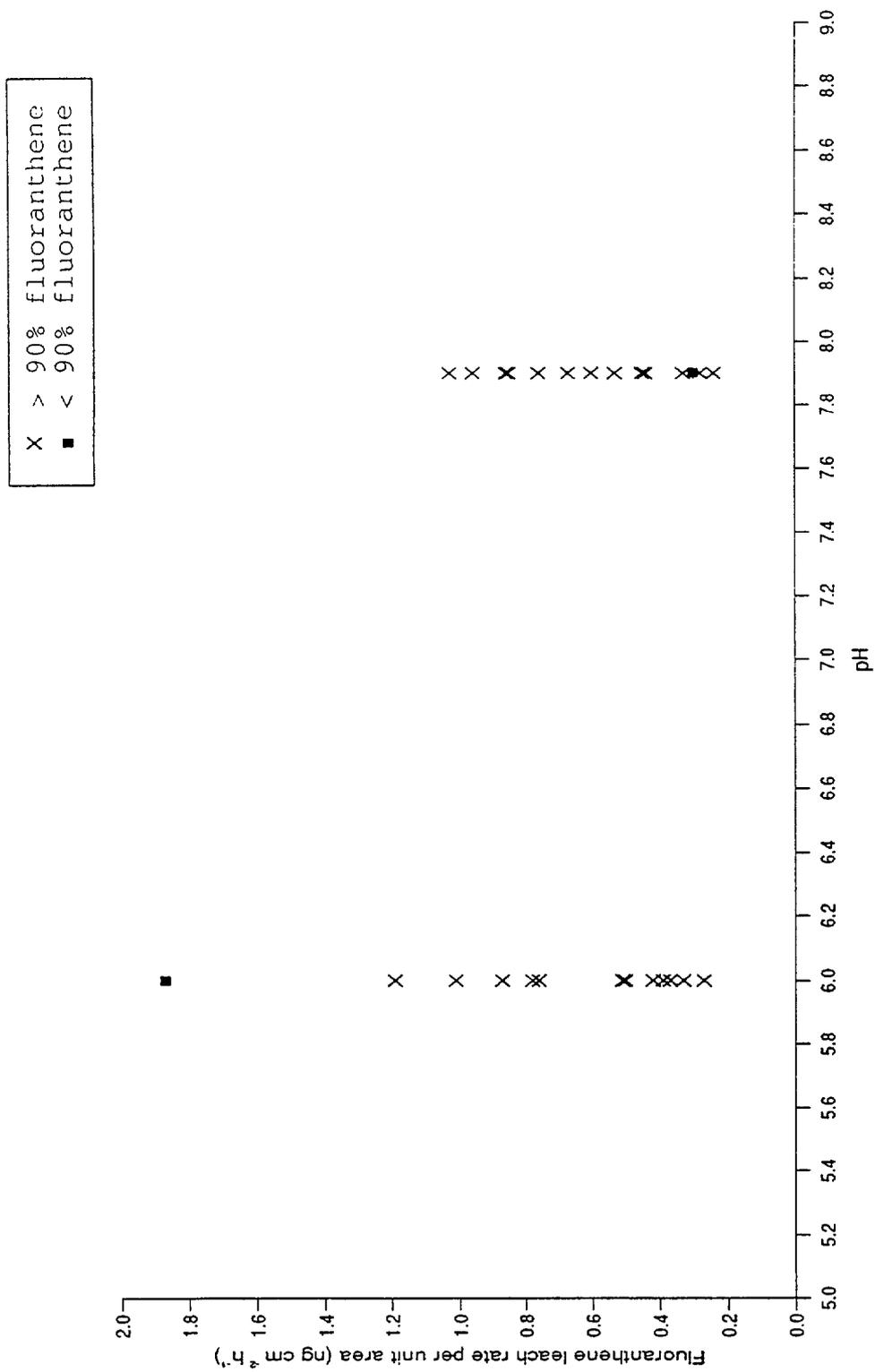


Figure 4.13 Fluoranthene leach rate per unit area with respect to pH

(c) Exposure time and surface area exposed

These two factors were investigated together. Runs were carried out with one coupon per bottle and two coupons per bottle for exposure periods of six and 18 hours. Tests were conducted in duplicate and each type of run was repeated once, to give a total of 16 runs, at:

- one-coupon/6-hour-exposure
- one-coupon/18-hour-exposure
- two-coupon/6-hour-exposure
- two-coupon/18-hour-exposure.

A summary of the results of these tests is presented in Table 4.11. For the majority of the samples, fluoranthene constituted more than 90% of the Total PAH detected, once again indicating a predominance of leaching.

To assess the effects of exposure time and surface area exposed on the leaching of fluoranthene, the results were calculated as ng cm^{-2} and ng h^{-1} respectively. Figures 4.14 and 4.15 show graphically the relationships. As expected for a dissolution mechanism, both factors showed a positive correlation with the quantity of fluoranthene leached. (The two samples containing over 10% non-fluoranthene PAH have been left out of the calculations.)

For the time factor, the average fluoranthene leach rates at 6 and 18 hours were 5.25 and 14.5 ng cm^{-2} , which is close to the expected result. The plot of the individual results, Figure 4.14, moderates this conclusion to some degree because of the scatter in the recorded leach rates. The results indicate that over this period of time it is unlikely that the level of fluoranthene in the water had reached a maximum.

For the surface area factor, average fluoranthene leach rates for the one-coupon and two-coupon runs were 33 ng h^{-1} and 65 ng h^{-1} respectively, indicating the expected result. Although the plot of the results for individual runs, Figure 4.15, shows that this conclusion can be generally supported by the scatter of the results, there is some overlap between the two classes, so the averages represent an over-optimistic interpretation.

The average rate of fluoranthene leaching over 18 hours (0.80 $\text{ng cm}^{-2} \text{h}^{-1}$) is similar to the average rate over 6 hours (0.88 $\text{ng cm}^{-2} \text{h}^{-1}$).

Table 4.11 Summary of leach tests investigating the effect of exposure time and surface area

Exposure time hr	Number of coupons	Coupon No.	Run No.	Total PAH		Fluoranthene			
				ng l ⁻¹	ng l ⁻¹	% Total PAH	Leaching rates		
							ng cm ⁻² h ⁻¹	ng h ⁻¹	ng cm ⁻²
6	1	28	1	79	79	100	0.85	33	5.1
			2	119	110	92	1.2	46	7.1
6	1	26	1	96	92	96	0.94	38	5.6
			2	75	75	100	0.76	31	4.6
6	2	18+20	1	130	130	100	0.78	54	4.7
			2	385	340	88	2.0	142	12
6	2	27+29	1	170	170	100	0.83	71	5.0
			2	166	160	96	0.78	67	4.7
18	1	9	1	202	200	99	0.75	28	13
			2	220	220	100	0.83	31	15
18	1	12	1	164	160	98	0.72	22	13
			2	263	230	87	1.0	32	19
18	2	34+5	1	489	460	94	0.88	64	16
			2	311	310	100	0.60	43	11
18	2	4+8	1	569	560	98	0.91	78	16
			2	599	590	98	0.96	82	17

(d) Reproducibility of results for individual test coupons

The laboratory leach tests have involved up to five exposures under similar test conditions for each of twelve test coupons used singly (i.e. excluding the results for pairs of coupons). The reproducibility of the results for each test coupon was examined in order to assess the reliability of the overall findings. Figure 4.16 shows the variability measured. For most of the coupons the variability was around the precision of the analysis, as estimated from the variability of the recovery of control samples of about 20% relative standard deviation. For the four coupons used in the first series temperature test the variability was much greater, but only if the unexplained and possibly erroneous results from run 1 of this test are included. (The reproducibility in the second series temperature tests has not been included because of the experimental design which involved an alternating sequence of high and low temperatures, a factor which is expected to contribute variation.)

X > 90% fluoranthane
 ■ < 90% fluoranthane

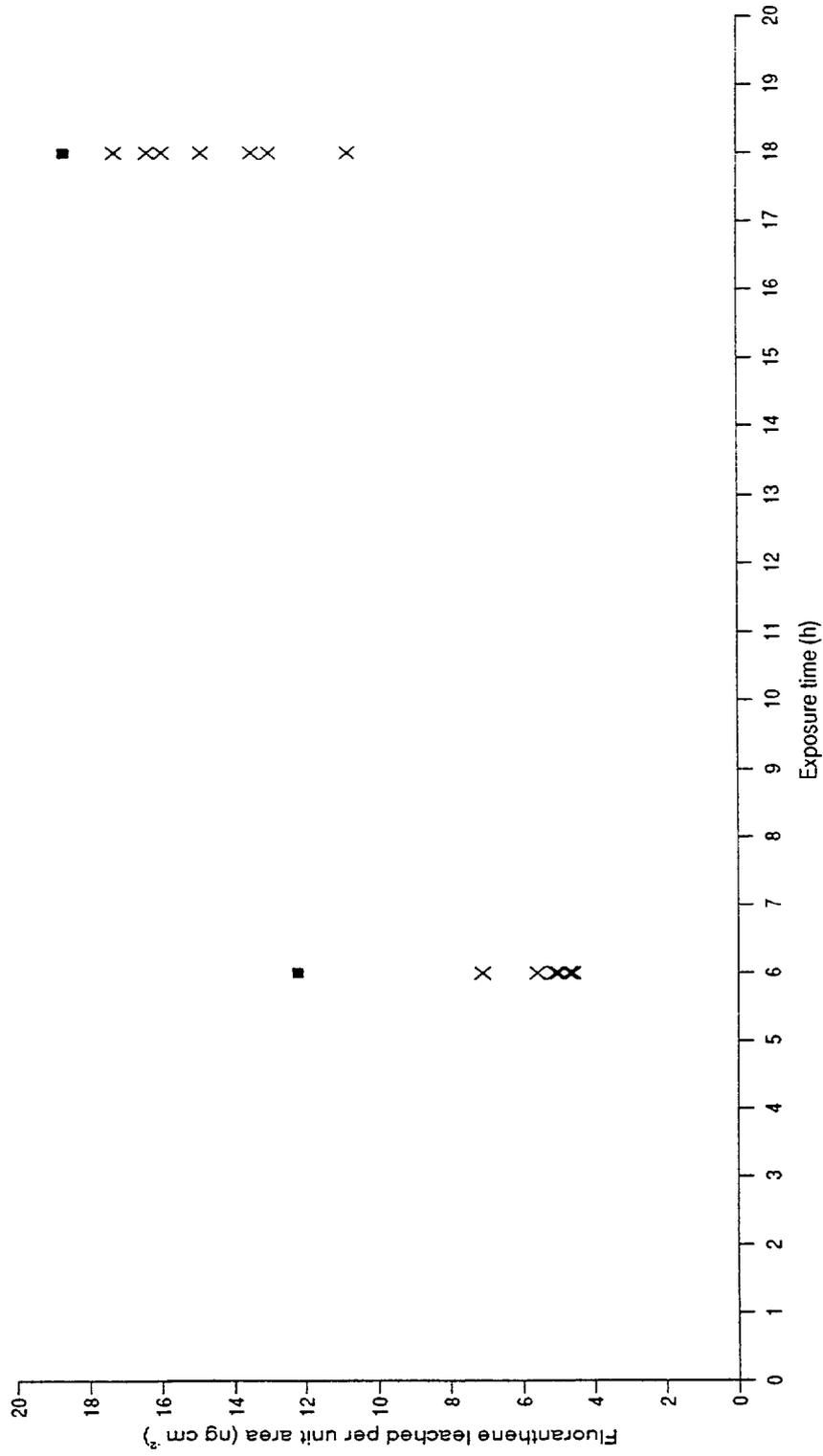


Figure 4.14 Fluoranthene leached per unit area with respect to time

X > 90% fluoranthene
 ■ < 90% fluoranthene

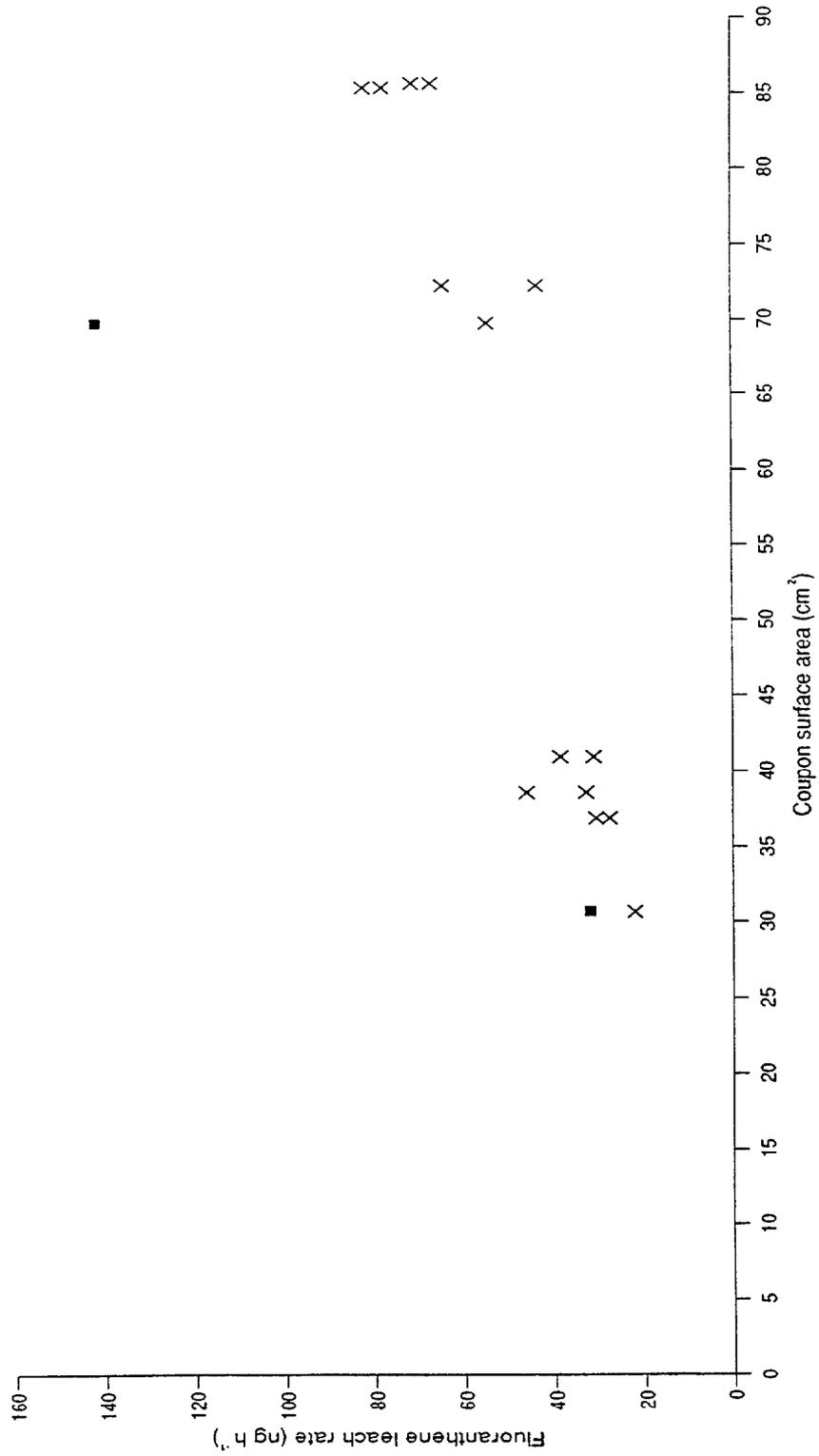
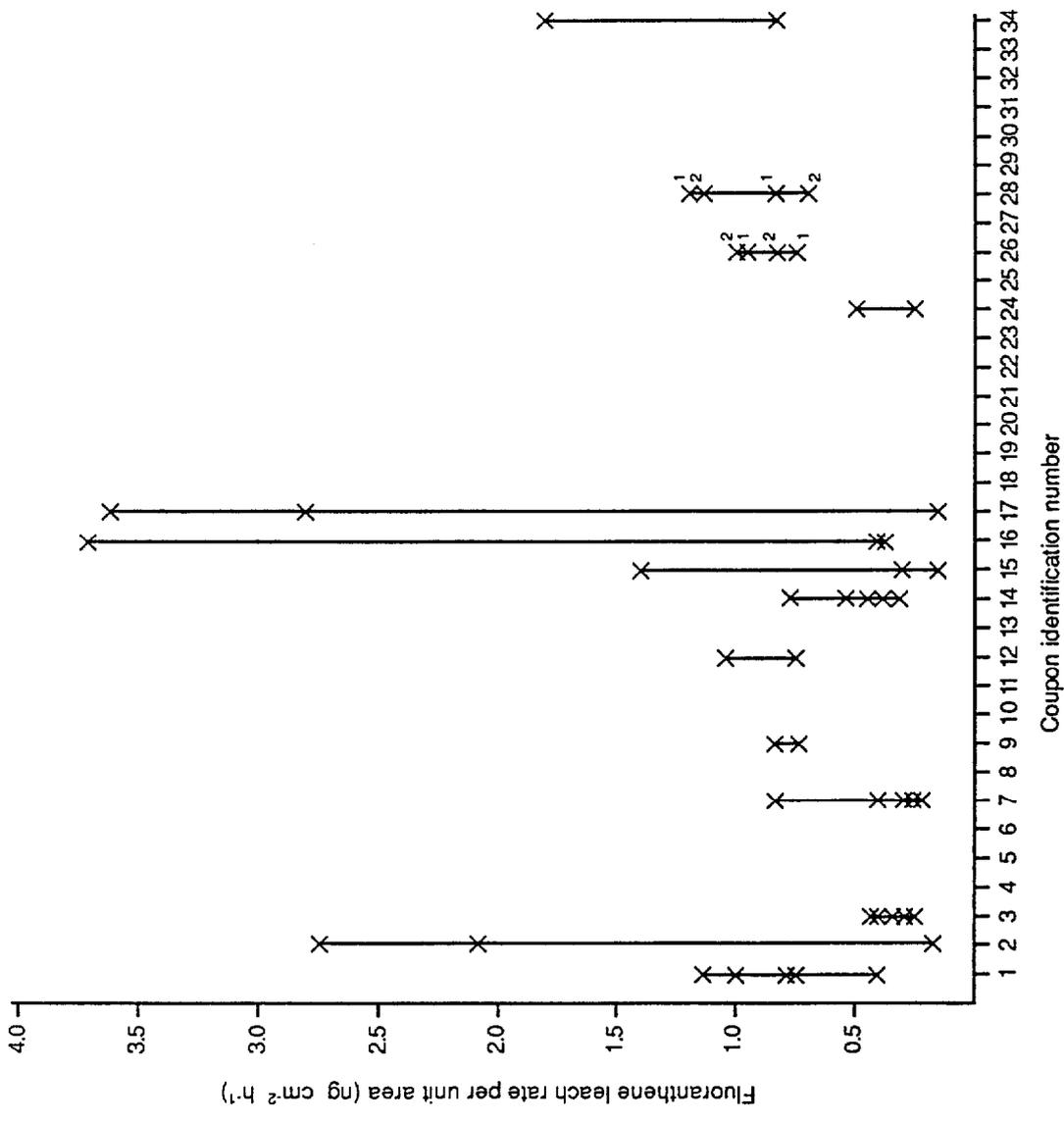


Figure 4.15 Fluoranthene leach rate with respect to coupon surface area exposed



Coupon identification number	Test factor
9	Time/surface area*
12	
26 ¹	
28 ¹	
1	pH
34	
24	
26 ²	
14	Temperature
28 ²	
2	
15	
16	
17	

* coupons exposed in pairs could not be assessed for variability

Figure 4.16 Variability in fluoroanthene leach rate per unit area (ng cm⁻² h⁻¹) measured for individual coupons during replicate test runs under similar test conditions

4.4.4 Tests on possible remedial measures

The findings of the tests investigating possible solutions to PAH leaching problems are summarised below.

(a) Woven Nylon Hose

The test was carried out with four coupons and four runs for each coupon. In the first and third runs there was no cover on the coupons and on the second and fourth runs the coupons were covered with woven nylon hose, which provided an even netting-type of cover which did not, however, prevent the water reaching the coupon.

A summary of the results of these tests is presented in Table 4.12. The results are shown graphically in Figure 4.17. The average fluoranthene leach rates with no nylon and with nylon present were 1.5 and 0.27 ng cm⁻² h⁻¹ respectively. The highest 'with-nylon' result (0.93 ng cm⁻² h⁻¹) was higher than the lowest 'without-nylon' result (0.58 ng cm⁻² h⁻¹) and close to two other 'without-nylon' results. However, inspection of the scatter of all the results does indicate a reduction in leach rate for the 'with-nylon' results compared to the 'without-nylon' results with six of the eight 'with-nylon' results in the range 0.1 to 0.18 ng cm⁻² h⁻¹.

In summary, the woven nylon hose has produced a marked decrease in the fluoranthene leaching rate, on average representing a five-fold reduction. The hose clearly acted as an effective hindrance to fluoranthene leaching during the short timescale of the test (16 hours).

(b) Dosing with silicate and polyphosphate

Silicate tests

The silicate tests were carried out in tap water dosed nominally with 5 and 10 g SiO₂ l⁻¹ using sodium silicate (Crystal 79). In order to effect improvements as the tests progressed, the design of the test at each dose rate was different. In the 5 g l⁻¹ test four coupons were tested for three runs each. The blank (i.e. zero dose) results were generated from single runs on four coupons, three of which were then used for three runs each in 10 g l⁻¹ dosed water.

Table 4.13 contains a summary of the results. The results are shown graphically in Figure 4.18. The average fluoranthene leach rates for the blanks, 5 g l⁻¹ and 10 g l⁻¹ runs were 0.82, 0.7 and 0.91 ng cm⁻² h⁻¹ respectively. The 10 g l⁻¹ average excludes one result where the coupon was damaged. Most of the samples from the 5 g l⁻¹ runs contained fluoranthene at less than 90% of the Total PAH concentration, with the results for individual coupons showing a 2.2- to 9.9-fold difference in fluoranthene leach rates between runs. This makes interpretation difficult. Comparisons of leaching rates for individual coupons in the higher dose rate tests (where leaching was the predominant mechanism - ≥90% fluoranthene i.e. coupons numbered 19 and 21.) with their behaviour during zero dose tests do show increased leaching when silicate is present.

Table 4.12 Summary of results of leach tests investigating the effect of nylon hose

Test	Coupon No.	Run No.	Total PAH ng l ⁻¹	-----Fluoranthene-----					
				ng l ⁻¹	% Total PAH	Leach rate ng cm ⁻² h ⁻¹	Mean leach rate		
No hose	2	1	123	120	98	0.58	1.5		
		3	-	285	>90	1.4			
	4	1	322	320	99	1.1			
		3	-	280	>90	0.98			
	9	1	782	730	93	3.3			
		3	-	415	>90	1.9			
	27	1	242	240	99	0.99			
		3	-	410	~95	1.7			
	Hose	2	2	40	26	65		0.13	0.27 (0.15*)
			4	-	23	>90		0.11	
4		2	322	265	82	0.93			
		4	-	42	>90	0.15			
9		2	88 [^]	21	24	0.10			
		4	-	39	>90	0.18			
27		2	47	36	77	0.15			
		4	-	107	~84	0.44			

16 hours exposure

[^] analytical interference appearing as 59 ng l⁻¹ benzo(b)fluoranthene

* mean values excluding results where fluoranthene is <90% of Total PAH

- quantitative analysis for fluoranthene only, provisional assessment only of analytical results for the other 5 PAH

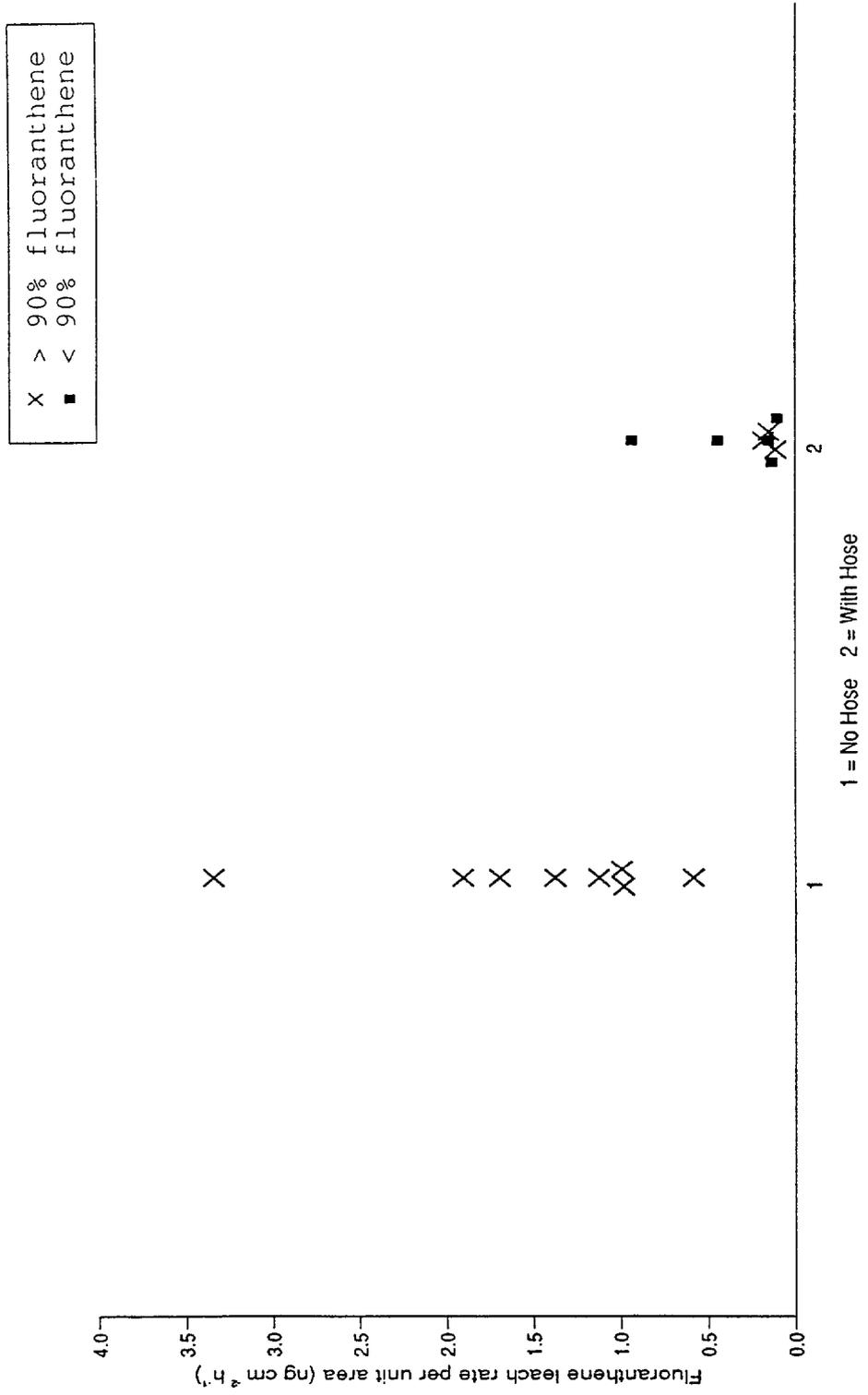


Figure 4.17 Fluoranthene leach rate with and without a hose covering

Table 4.13 Summary of results of leach tests investigating the effect of silicate dosing

Test	Coupon No.	Run No.	Total PAH ng l ⁻¹	Fluoranthene				
				ng l ⁻¹	% Total PAH	Leach rate ng cm ⁻² h ⁻¹	Mean leach rate ng cm ⁻² h ⁻¹	
No dose	33	1	307	230	75	0.93	0.82 (0.17*)	
	19	1	-	41	>90	0.19		
	21	1	-	28	>90	0.15		
	23	1	-	410	~73	2.0		
5 g l ⁻¹ SiO ₂ (a)	22	1	-	42	>90	0.24	0.70 (0.27*)	
		2	191	120	63	0.68		
		3	715	420	59	2.4		
	25	1	-	55	>90	0.24		
		2	76	73	96	0.32		
		3	135	120	89	0.53		
	15	1	1	-	54	~78		0.28
			2	80	56	70		0.29
			3	207	125	60		0.65
		32	1	-	250	~69		1.3
			2	181	110	61		0.56
			3	260	190	73		0.97
10 g l ⁻¹ SiO ₂ (b)	19	2	-	305	>90	1.4	1.3 (0.91*)	
		3	-	155	>90	0.73		
		4	-	125	>90	0.59		
		21	2	-	86	>90		0.45
	21	3	-	125	>90	0.65		
		4	-	62	>90	0.32		
		23	2	-	870 [^]	~83		4.3
		3	-	350	>90	1.7		
	4	-	280	>90	1.4			

16 hours exposure

a) Nominal dose; chemical analysis of a low dose solution recorded 1.81 g l⁻¹ soluble silicon = 3.9 g l⁻¹ SiO₂.

b) Nominal dose; chemical analysis of a high dose solution recorded 3.98 g l⁻¹ soluble silicon = 8.5 g l⁻¹ SiO₂.

[^] Sample holder repaired prior to test, coal-tar pitch coating may have been disturbed.

* Mean values excluding results where fluoranthene is <90% of Total PAH.

- Quantitative analysis for fluoranthene only, provisional assessment only of analytical results for the other 5 PAHs.

X > 90% fluoranthene
 o < 90% fluoranthene

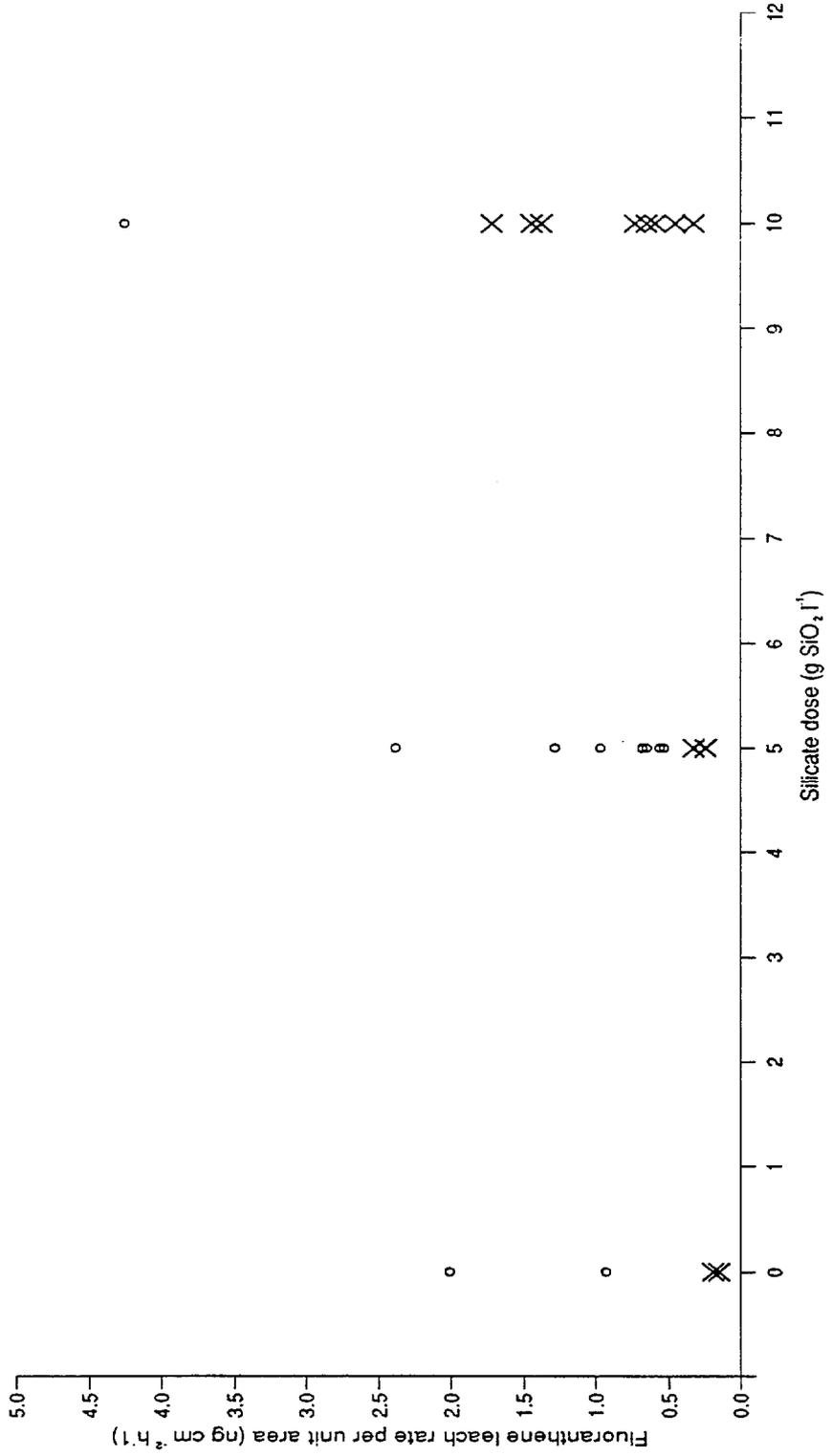


Figure 4.18 Effect of silicate dose on fluoranthene leach rate

Polyphosphate tests

The polyphosphate tests were carried out using test waters containing nominally 0.6 and 2.1 mg P l⁻¹ which were prepared by dissolving sodium hexametaphosphate (Calgon SWB) in tap water. Three coupons were used at each dose rate with one zero dose (blank) run followed by three test runs for each coupon.

Table 4.14 contains a summary of the results. The results are shown graphically in Figure 4.19. The average fluoranthene leach rates for the blanks, 0.6 and 2.1 mg l⁻¹ runs were 0.25, 0.20 and 0.60 ng cm⁻² h⁻¹ (ignoring results where fluoranthene levels are <90% of Total PAH). As an additional comparison, the blank tests on the three coupons eventually tested at 0.6 mg P l⁻¹ recorded a mean leaching rate of 0.13 ng cm⁻² h⁻¹. A similar comparison for the higher dose tests and blanks could not be made because the blanks recorded fluoranthene proportions substantially below 90% in 2 out of the 3 cases. In particular one blank had a fluoranthene concentration which was 20% of the Total PAH concentration, in the other fluoranthene was about 80% of the Total PAH concentration. The third blank gave a fluoranthene leach rate of 0.59 ng cm⁻² h⁻¹ which is to be compared with the average rate for this coupon at high dose of 0.54 ng cm⁻² h⁻¹ and with the average for the high phosphate-dosed runs of 0.6 ng cm⁻² h⁻¹ (range 0.29 to 1.05 ng cm⁻² h⁻¹). Therefore it is considered that no real differences between fluoranthene leach rates had been demonstrated.

It is possible that the short timescale of these experiments was insufficient to permit the formation of surface films as is believed to occur when chemicals of this type are dosed into water supplies. Thus the potential benefits of such dosing may not have become evident.

Table 4.14 Summary of results of leach tests investigating the effect of polyphosphate dosing

Test	Coupon No.	Run No.	-----Fluoranthene-----			
			ng l ⁻¹	% Total PAH	Leach rate ng cm ⁻² h ⁻¹	Mean leach rate ng cm ⁻² h ⁻¹
No dose	6	1	22	>90	0.11	0.25*
	10	1	33	>90	0.14	
	12	1	27	>90	0.15	
	26	1	1280	20	5.4	
	28	1	145	80	0.65	
	29	1	155	>90	0.59	
0.6 mg l ⁻¹ as P (a)	6	2	23	>90	0.12	0.20*
		3	525	- 65	2.7	
		4	465	- 65	2.4	
	10	2	47	>90	0.21	
		3	44	>90	0.19	
		4	51	>90	0.22	
	12	2	40	>90	0.22	
		3	54	>90	0.30	
		4	27	>90	0.15	
2.1 mg l ⁻¹ as P (b)	26	2	255	>90	1.1	0.60*
		3	125	>90	0.53	
		4	225	>90	0.94	
	28	2	92	>90	0.41	
		3	105	>90	0.46	
		4	82	>90	0.37	
	29	2	180	>90	0.69	
		3	77	>90	0.29	
		4	170	>90	0.65	

16 hours exposure

* Mean values excluding results where fluoranthene is <90% of Total PAH

a) Nominal dose; chemical analysis of a low dose solution recorded 0.162 mg l⁻¹ as soluble P.

b) Nominal dose; chemical analysis of a high dose solution recorded 0.361 mg l⁻¹ as soluble P.

(c) **Contact with plastic pipe materials**

Six coupons were used for testing the effect of contact with PVC and MDPE pipe materials. In the first run no plastic was present (blank runs) and in the second run a section of PVC pipe (about 150 x 13 x 4.5 mm) or MDPE pipe (about 145 x 12 x 11.5 mm) was suspended in each bottle with the coupon (test runs).

Table 4.15 contains a summary of the results for these tests. Figure 4.20 shows the results graphically.

Table 4.15 Summary of results of leach tests investigating the effect of contact with plastic pipe materials

Test	Coupon No.	Run No.	-----Fluoranthene-----			
			ng l ⁻¹	% Total PAH	Leach rate ng cm ⁻² h ⁻¹	Mean leach rate
No pipe (control MDPE)	1	1	32	>90	0.16	0.17
	7	1	9	>90	0.05	
	3	1	14	>90	0.07	
	8	1	58	>90	0.26	
	5	1	68	>90	0.31	
	17	1	38	>90	0.18	
MDPE	1	2	820	~93	4.0	0.21*
	7	2	8	>90	0.04	
	3	2	32	>90	0.16	
	8	2	39	>90	0.18	
	5	2	120	>90	0.54	
	17	2	30	>90	0.14	
No pipe (control PVC)	11	1	6	>90	0.03	0.14
	20	1	50	>90	0.23	
	14	1	61	>90	0.27	
	24	1	42	>90	0.22	
	16	1	14	>90	0.06	
	34	1	9	>90	0.05	
PVC	11	2	19	>90	0.10	0.09
	20	2	34	>90	0.15	
	14	2	36	>90	0.16	
	24	2	17	>90	0.09	
	16	2	<5	-	0.00	
	34	2	10	>90	0.05	

16 hours exposure

* Mean values excluding result for MDPE Coupon 1.

- All 6 indicator PAH below the detection limit.

For the PVC test the average fluoranthene leach rates for the six blank and six test runs were 0.14 and 0.09 ng cm⁻² h⁻¹ respectively. For the MDPE test the corresponding results were 0.17 and 0.21 ng cm⁻² h⁻¹. The MDPE test results exclude the one result where the leach rate was 20 times the average rate for the other five coupons (and nearly eight times the next highest value). Looking at the individual results for both tests shows that in some cases there was an increase in leach rate between control and test runs, in some cases a decrease and some where the rate was nominally identical. Therefore the conclusion is that neither test indicated a real change in leach rates.

In summary it is evident that short-term contact with plastic pipe materials (i.e. PVC and MDPE) does not consistently reduce fluoranthene leaching rates. It is possible that in practical situations other factors may be operating in the pipe network which cause the plastic materials to behave differently, e.g. the presence of internal surface films of a composition which provides benefits in terms of fluoranthene adsorption.

(d) Carbon dioxide stripping of groundwater

The water used for this test was Medmenham borehole water which was taken from a chalk aquifer and at the time of abstraction was supersaturated with carbon dioxide. For the high carbon dioxide tests, the carbon dioxide levels were topped up using a cycle tyre inflator. For the low carbon dioxide tests the water was purged with nitrogen. The tests were done with four coupons at each carbon dioxide level with a series of three runs for each coupon to give a total of 24 runs. The initial pHs of the three carbon dioxide-rich test waters were 7.2, 6.2 and 5.8 and for the nitrogen-purged waters 8.1, 7.7 and 7.3. During the tests these levels varied by small amounts, mostly less than 0.2 units and with a maximum change of 0.4.

The leaching results are summarised in Table 4.16 and shown graphically in Figure 4.21. If the results where fluoranthene was less than 90% of the Total PAH are excluded, the leach rates are 0.27 and 0.57 for the high and low carbon dioxide contents respectively. These differences may indicate a real effect. However the between-coupon variation was even greater (e.g. see results for coupon 30 tested in nitrogen-purged water which were all below the carbon dioxide-rich average). This test was the only one where the procedural blanks showed the presence of fluoranthene. A re-consideration of the experimental and analytical procedures did not reveal any obvious reason for this apparent contamination. (Considering the sample batches in which these two blanks were processed might suggest a possible contamination from the two test samples, coupon 18 run 1 for the high carbon dioxide blank and coupon 31 run 3 for the low carbon dioxide blank. The only other two samples in these batches were coupon 13 run 1 and coupon 30 run 1, neither of whose chromatograms showed similar peak patterns to that of coupon 18, run 1. The controls and analytical blanks in these two batches showed no abnormalities. Therefore it is considered that only the blanks exhibited contamination. Exclusion of the results from coupon 13 run 1 and coupon 30 run 1 would not significantly affect the conclusion drawn from this test.)

Thus, this series of tests produced no positive indication that one of the two carbon dioxide concentrations was of more benefit in terms of reduced fluoranthene leaching than the other.

Table 4.16 Summary of results of leach tests investigating the effect of carbon dioxide levels.

Test	Coupon No.	Run No.	-----Fluoranthene-----				
			ng l ⁻¹	% Total PAH	Leach rate ng cm ⁻² h ⁻¹	Mean leach rate ng cm ⁻² h ⁻¹	
CARBON DIOXIDE HIGH	2	1	45	>90	0.22	0.27*	
		2	49	>90	0.24		
		3	29	>90	0.14		
	4	1	150	~87	0.53		
		2	770	~65	2.7		
		3	50	>90	0.18		
	13	+1	40	~78	0.22		
		2	49	>90	0.27		
		3	66	>90	0.31		
	18	+1	280	~72	1.4		
		2	53	>90	0.28		
		3	105	>90	0.54		
	CARBON DIOXIDE LOW	9	1	185	>90		0.86
			2	160	>90		0.74
			3	165	>90		0.76
27		1	600	~66	2.5		
		2	220	>90	0.90		
		3	145	>90	0.59		
30		+1	23	>90	0.11		
		2	39	>90	0.19		
		3	25	>90	0.12		
31		1	215	>90	0.87		
		2	2300	~40	9.6		
		++3	770	~73	3.2		

16 hours exposure

* Mean values excluding results where fluoranthene is <90% of Total PAH

+ Samples run in same batch as high carbon dioxide blank.

++ Sample run in same batch as low carbon dioxide blank.

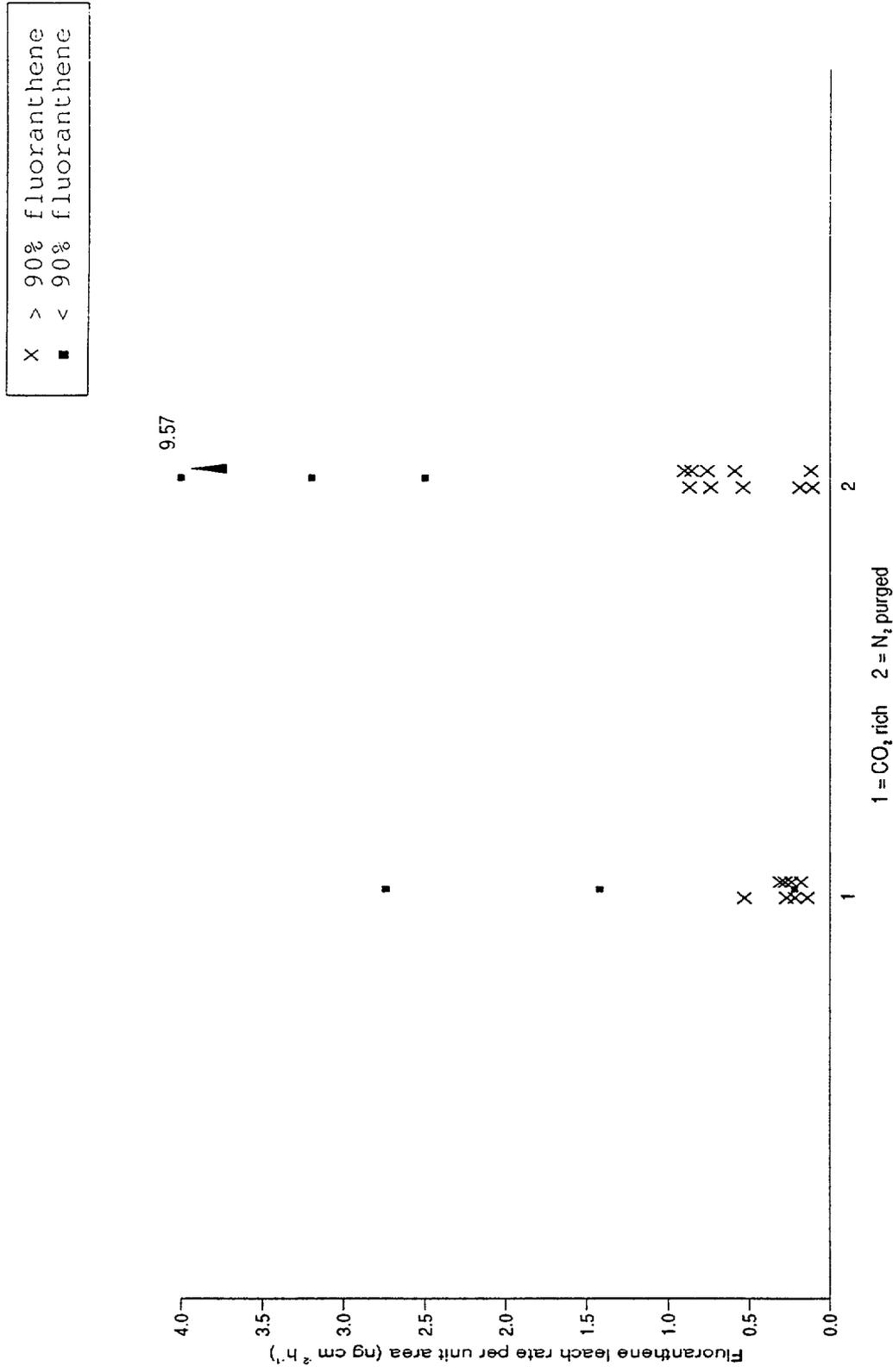


Figure 4.21 Effect of carbon dioxide level on fluoroanthene leach rate

5. ANALYSIS AND DISCUSSION

The aim of analysing data from the DoE surveys and the two water undertakers was to see whether any relationships could be found between PAH levels and other water quality and distribution system variables. The only generally consistent correlations found were positive correlations between PAH levels and water temperature and water hardness and a negative correlation between PAH levels and Total Organic Carbon. PAH levels also had a tendency to be elevated in samples taken at dead ends of distribution systems.

One problem with this type of analysis is deciding how to relate data from specific samples (e.g. PAH concentrations) to data for other variables averaged (usually from a small number of samples) over a whole supply zone and possibly over a long period of time. Is the average value of a parameter likely to be related to PAH levels, e.g. because it may affect the long-term condition of the lining material, or is the value at the time of PAH sampling more relevant? (In this work the choice was not available.)

Consideration of the history of lining procedures indicated that there are likely to be variations in the composition of the linings throughout a distribution system, even when it consists of pipes of similar age from the same manufacturer. Is the lining closest to the sample point necessarily the most influential on the PAH level in the sample? It was noted that in some cases high levels of PAH were found in samples taken from new pipes which should not have been lined with coal-tar pitch, which implies that the sources of PAH were upstream from the sample points.

The laboratory tests ('factor tests') undertaken in this work are believed to be the first attempts to correlate PAH leaching rates with single variables. These experiments showed that, as in most distribution systems, of the six indicator PAHs, it is generally fluoranthene which leaches into water to the greatest extent. It was also observed that other PAHs with similar or greater water-solubility than fluoranthene, such as naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, pyrene and chrysene were also leached. In some cases benz(a)anthracene was found. (In coal-tar pitch lined distribution systems the naphthalene, acenaphthene and fluorene may already have disappeared. Fielding and Crane (1988) found this to be the case in samples of mains deposits taken from a variety of systems. However, phenanthrene/anthracene and larger PAHs were still present in these samples.)

Positive correlations were established between amounts of PAH leached into water and the temperature of the water, the length of exposure and the ratio of surface area of coal-tar pitch to volume of water. These correlations were apparent even after allowing for differences between individual coal-tar pitch samples and from repeat runs on the same samples. The choice of two temperatures, 5 and 25 °C, in this work was made to provide a simple answer on the existence of a correlation. The surface-to-volume ratio results are consistent with the observation that PAH levels are generally higher at dead-end sites in a distribution system. Such sites are often associated with smaller diameter mains (and hence offer a higher surface area:volume ratio) and longer retention times.

A change of pH from a slightly alkaline 7.9 to a slightly acid 6.0 appeared to have no effect on the rate of PAH leaching. (In order to maintain the stability of the pH

throughout this experiment the water was buffered so that there was also a difference in the ionic strength and ion content of the two aqueous media.)

Potential remedial measures were investigated in laboratory tests similar to the factor tests. Only the use of a woven nylon hose, providing partial cover of the lining material, appeared to have the desired effect of reducing the rate of fluoranthene leaching. With the design of the test in this work an average fivefold reduction in fluoranthene leach rate was achieved. It is hypothesised that the reduction is achieved, not by reducing the leach rate, but by sorption of the leached fluoranthene into or on the nylon. It was envisaged that this technique could be applied in practice by using flexible nylon-based lining inserted into critical areas of distribution systems if no other less disruptive measure was effective. Alternatively, if there was not likely to be an adverse effect on water pressure due to a build-up of deposits on the filter, nylon mesh filters could be inserted into a system. The test probably did not saturate the absorptive capacity of the nylon. However, in practice this is likely to occur. It may be worth investigating other materials which may have a greater absorptive capacity and could be inserted into critical areas of distribution systems in similar ways.

With the other measures investigated, no obvious reductions in fluoranthene leach rates were apparent during these tests. The dosing of phosphate and silicate and the presence of plastic pipe materials were investigated on the basis that they appeared, from various previous studies in distribution systems, to have the desired effects in real-life situations, albeit without control of other possible factors.

The reason for the failure of phosphate and silicate dosing may have been the short duration of the current tests because it was perceived that any reduction of fluoranthene leaching would be achieved by the formation of a deposit on the lining material acting as a barrier to leaching. However, the existence of such coatings on coal-tar pitch linings in distribution systems where phosphate or silicate are dosed has not been demonstrated in practice. If such linings do form then it is expected that the formation would take time and might require ageing of the lining to ensure adhesion of a coating.

Samples of PVC and MDPE pipe failed to absorb fluoranthene leached from the lining material. Again this failure may be due to the short duration of the tests. Previous investigations of a number of distribution systems suggests that in practice such pipe materials absorb PAHs, possibly by developing adsorptive internal coatings or ageing their surfaces thereby increasing their adsorptivity.

Different levels of carbon dioxide did not appear to have any effect on fluoranthene leach rates. This test was undertaken because many of the waters exhibiting high levels of fluoranthene in distribution systems are extracted from chalk aquifers and such waters have a tendency to be supersaturated with carbon dioxide. If the level of carbon dioxide does have an effect on PAH levels it may be that the effect is linked with other properties of the water such as concentrations of metal ions and anions. In these experiments only the excess carbon dioxide was removed although this also means that there were changes in the bicarbonate concentrations.

6. CONCLUSIONS

From the analysis of data from distribution systems it is concluded that information on system geometry, water hardness, temperature and Total Organic Carbon may be used to identify areas where PAH levels due to the presence of fluoranthene are likely to be high. However, this and other water quality data have not yielded any definitive cause-and-effect relationships which could lead to practical direct action (other than elimination of dead-ends) to reduce PAH concentrations in drinking water. Nor are further analyses of this type considered likely to yield such information because of the intercorrelations between the various water quality parameters and the generally greater day-to-day variations in PAH levels than the variations in other monitored parameters.

The correlation between dead ends and higher levels of PAHs appears to be genuine and may be related to increased contact times. Therefore it is considered worthwhile to investigate practical measures to avoid dead ends where possible. Such measures could include modifying valving arrangements and including loop configurations in systems.

The laboratory tests on factors have demonstrated positive correlations between the fluoranthene leach rates and temperature, exposure time and the ratio of the surface area of lining to volume of water. These results were as expected.

The change from slightly alkaline to slightly acid water had no apparent effect on the leach rate for fluoranthene even though, in theory, an increase in acidity could increase the stability of PAHs in aqueous solution.

Covering coal-tar pitch lining material with woven nylon hose led to a reduction in the amount of fluoranthene leaching into water possibly because of the ability of nylon to absorb fluoranthene rather than a reduction in the leach rate because of physical obstruction of the surface of the lining. It is considered that techniques based on this idea, possibly with alternative absorbent materials, could provide relatively (compared to mains replacement or full relining) cheap and rapid means of reducing PAH levels in problem areas.

The failure of phosphate and silicate dosing in these laboratory tests to reduce fluoranthene leach rates could be attributed to the tests not being long enough to allow the build-up of a protective coating. Similarly the failure of the presence of PVC or MDPE pipe sections to reduce fluoranthene leach rates in these tests may be because of the inability of new, clean plastic surfaces to be effective PAH adsorbents.

Removing carbon dioxide from a carbon dioxide-rich chalk borehole water had no apparent effect on the fluoranthene leach rate.

Work on running this set of laboratory tests has led to an increased appreciation of how to control the design of such tests according to the perceived mechanism of the factor or potential remedial measure. The work also demonstrated that, besides the six PAHs specified in the drinking water regulations, a variety of other lower molecular weight PAHs (e.g. naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, pyrene and chrysene) also leach from coal-tar pitch linings. The levels of these substances may match

or even exceed the concentration of fluoranthene. It is expected that naphthalene, acenaphthene and fluorene will leach fairly quickly from the coal-tar pitch linings of real distribution systems.

7. RECOMMENDATIONS

A number of recommendations can be made from the research carried out. The Drinking Water Inspectorate should consider the urgency and the need for the following:

1. A policy of reducing the retention time of water in distribution systems by reducing the numbers of dead ends should be considered as a means of reducing exceedances of the PAH PCV and reducing the concentration of PAHs in tap waters.
2. Investigations of factors thought to have an effect on the leaching rate of fluoranthene should, where possible, be carried out in laboratory-based tests designed to provide variation of only one factor per test. The procedures developed in the current project could form the basis of such tests.
3. Some factors that could be investigated in further laboratory tests include:
 - an extension of the effect of temperature to see whether there exists a critical temperature at which leach rates begin to increase;
 - variation of the levels of metal ions such as calcium or magnesium, anions or total ionic strength.
4. Investigation of remedial measures, including some of those investigated in this project, may require tests of longer duration than was possible in the present work, especially if the measure is expected to work by building up a barrier to leaching on the lining material.
5. Practical ways of using the effect of nylon or other materials on leach rates could be investigated. The mechanism of removal should be investigated and field trials would be necessary to establish the practicality of a variety of ways of applying this type of technique.
6. The presence of PAHs other than those specified in the Total PAH parameter in tap waters should be investigated because there is no UK data on typical levels.

REFERENCES

Anonymous (1936) Cast iron pipe: its life and service. Stanton Ironworks Company, Nottingham.

Collins, H.H. and Smith, T.R.(1978) Bore coatings for spun iron pipes. Proceedings: Water Distribution Systems, Maintenance of Water Quality and Pipeline Integrity. Keeble College, Oxford, 25 - 27 September 1978, Paper No. 11, 17pp.

Crane, R.I., Fielding, M., Gibson, T.M. and Steel, C.P. (1981) A survey of polycyclic aromatic hydrocarbon levels in British drinking water. Technical Report TR 158, Water Research Centre, Medmenham.

Fielding, M. and Crane, R.I. (1988) Coal-tar pitch particles in drinking water. Report PRD 1778-M, Water Research Centre, Medmenham.

International Agency for Research on Cancer (IARC) (1973) Evaluation of carcinogenic risk of the chemical to man - certain polycyclic aromatic hydrocarbons and heterocyclic compounds, Vol. 3, WHO, Geneva.

Lijinsky, W., Domsy, I., Mason, G., Ramahi, H.Y. and Safavi, T. (1963) The chromatographic determination of trace amounts of polynuclear hydrocarbons in petroleum, mineral oil, and coal-tar. *Analytical Chemistry*, **35**, 952 - 956.

Verschueren, K. (Ed.) Handbook of Environmental Data on Organic Chemicals. p671, Van Nostrand Reinhold.

APPENDIX A - STANDARDS RELATING TO INTERNAL LININGS IN WATER MAINS

A1 STANDARDS RELATING TO COAL TAR BASED LININGS

No British Standard specifications existed to define the properties of coating materials until 1967 when BS 4164:1967 'Coal tar based hot-applied coating materials for protecting iron and steel' was issued.

BS 4164:1967

The types covered by this specification pertinent to the water supply industry are Type I (unmodified coal tar) and Type III (modified coal tar).

Type I

This lining was applied without a primer. A thin coating of 0.4 mm maximum was obtained. The specified requirements for the material composition are as follows:

Type I material shall consist of refined coal tar of a viscosity within the limits found by experience to give a coating of the desired quality on the ferrous article. Evaporation of oil occurs in the dipping bath as well as on the coated articles after dipping, thus changing the composition of the material. [The] refined coal tar and coal tar distillate oil [specified below] are required for the replenishment of the bath and the maintenance of the viscosity of the coating material within the required limits.

Type III

This material was manufactured by the hot digestion of powdered coal in coal tar or in suitable coal tar oils. The specified requirements for the material composition are as follows:

Type III material shall consist of modified coal tar of characteristics within the limits found by experience to give a coating of the desired quality on the ferrous article. Evaporation of oil occurs in the dipping bath as well as on the coated articles after dipping, thus changing the composition of the material. [The] modified coal tar [specified below] is required for the replenishment of the bath and the maintenance of the characteristics of the coating material.

The coating is intended for uses similar to those for Type I. The modification imparts improved physical characteristics.

A2 STANDARDS RELATING TO INTERNAL COATING OF WATER MAINS

In addition to the British Standard relating directly to coal tar based coatings, a number of standards refer to the internal coating of pipes to be used for water mains. The following passages contain relevant references to such internal lining procedures.

ISO 2531 - relating to the dimensions of pipes and fittings

The only reference to a coating in this document is as follows:

Except when otherwise specified, all pipes, fittings and accessories shall be coated inside and outside. The coating must dry rapidly with good adherence and not scale off. The inside coating must not contain any constituent soluble in water or any ingredient liable to impart taste or smell to the water after suitable washing out of the mains. For pipe lines carrying potable water, or alimentary fluids, the inside coating must not contain any toxic constituent.

Note - the requirements concerning the coating of various castings are based on similar requirements in ISO/R13 for grey iron pipes and fittings.

BS 78 Cast iron spigot and socket pipes (vertically cast) and spigot and socket fittings.

1917:

[The article] shall be heated to a suitable temperature not exceeding 250 °Fahr. and perfectly coated in the most approved manner, by being dipped, except in the case of pipes which are to be only partially coated, in a bath of approved composition maintained at a temperature of not less than 300°, nor more than 330 °F, according to Dr Angus Smith's process. When the Pipe is removed from the bath it shall be properly drained, and the coating must fume freely and set within an hour. If the coating does not so fume and set, the Pipe shall be recoated.

1938:

The pipe shall be uniformly heated by being immersed vertically in hot water being maintained at such a temperature, and the pipe being immersed so long, that the pipe dries immediately upon removal or, alternatively, the pipe shall be uniformly heated in a stove wherein the fumes of combustion do not come in contact with the pipe.

The hot pipe shall be thoroughly cleaned and then coated by being properly dipped (except in the case of pipes which are to be partially coated) in a bath containing a composition having a tar base, and maintained at a temperature between 290 °F and 330 °F, the proportions of the ingredients of the composition being regulated so as to produce a coating of the quality hereinafter specified. When the pipe is removed from the bath it shall be properly drained, and the coating must fume freely and set hard within an hour.

....

The coating shall be such that it shall not impart taste to the water and shall be smooth, glossy and tenacious, sufficiently hard so as not to flow when exposed to a temperature of 145 °F (Note for pipes for use in, or transport through, a tropical country, temperature of 170 °F shall apply) and not so brittle at a temperature of 32 °F as to chip off when scribed lightly with the point of a penknife.

Any pipe which is imperfectly coated, or the coating of which does not fume and set or conform to the quality as herein specified shall be recoated.

1965:

Coating shall not be applied to any fitting unless its surfaces are clean, dry and free from rust.

Except when otherwise agreed between the purchaser and the manufacturer, all fittings shall be coated externally and internally with the same material, the fitting being pre-heated prior to total immersion in a bath containing a uniformly heated composition having a tar or other suitable base.

...

The coating material shall set rapidly with good adherence and shall not scale off.

In all instances where the coating has a tar base, it shall be smooth and tenacious and hard enough not to flow when exposed to a temperature of 62 °C (145 °F) but not so brittle at a temperature of 0 °C (32 °F) as to chip off when scribed lightly with a penknife.

The inside coating shall not contain any constituent soluble in water or any ingredient which could impart any taste or odour whatsoever to potable water after sterilization and suitable washing out of mains, unless it is specifically stated that the pipes are not to be used for conveying potable water.

BS 1211:1958 Centrifugally cast (spun) iron pressure pipes for water, gas and sewage

Coating shall not be applied to any pipe unless its surfaces are clean, dry and free from rust.

Except when otherwise agreed between the purchaser and the manufacturer, all pipes shall be coated externally and internally with the same material, the pipe being pre-heated prior to immersion in a bath containing a uniformly heated composition having a tar or other suitable base.

In the case of pipes (wholly or partially coated) which are imperfectly coated or where the coating does not set or conform to the quality specified above, the coating shall be removed, and the pipes recoated.

The coating material shall set rapidly with good adherence and shall not scale off.

In all cases where the coating material has a tar or similar base, it shall be smooth and tenacious and hard enough not to flow when exposed to a temperature of 145 °F (Note for pipes for use in, or transport through, a tropical country, a temperature of 170°F shall apply) but not so brittle at a temperature of 32°F as to chip off when scribed lightly with a penknife.

When the pipes are to be used for conveying potable water, the inside coating shall not contain any constituent soluble in such water or any ingredient which could impart any taste or odour whatsoever to the potable water after sterilization and suitable washing out of the mains.

Related specifications

Some related specifications are :

American Water Works Association C203-73
British Gas PS/CW1
American Military Specification MIL-P-15147C

AWWA Standard C203 specifies materials to be used and the practices to be observed in works coatings and linings of steel pipes and in their installation in the field. The first issue was in 1940 and this has been regularly updated, the latest revision being in 1991.

In relation to the American experience, in 1978 The Food and Drug Administration reaffirmed its position with respect to coal tar pitch coatings in contact with drinking water.

In the January 1978 edition of JAWWA the following letter appeared (in an advertisement for plastic pipes) - written by P T Adamo, Assistant to the Director, Division of Regulatory Guidance, Bureau of Foods, dated August 5 1977, addressed to Mr J C Woods, Pres. Engards Coatings Corporation, 15541 Commerce Lane, Huntington Beach, California 92649.

"This replies to your letter of July 15 concerning coal tar pitch as a component of coatings in contact with potable water.

Coal tar pitch is a term used to describe a conglomeration of chemical substances many of which are indefinitely identified. Of particular concern would be the presence of polycyclic aromatic hydrocarbons some of which are carcinogenic. There is likely to be considerable variation in the various coal tar pitch compositions with respect to the presence of polycyclic aromatic compounds.

For this reason we have never considered coal tar pitch as a suitable component of coatings which will be used in contact with potable water or any other food.

Coal tar pitch, therefore, is considered a food additive. We are not aware of any prior sanctions which would authorize the use of coal tar pitch as a component

of a food contacting surface. Also, there is no authority or regulation in effect which would permit the use of coal tar pitch in food contact coatings.

This has been FDA's position in the past in regard to coal tar pitch and is still our position. While this position has not been formally published, we have advised inquirers of this position in informal letters of opinion over a period of many years.

State Health Departments have been advised of our position on the status of coal tar pitch only if they have inquired as to its status.

The Environmental Protection Agency is well aware of our position in regard to coal tar pitch. Specific dates of our communications with that Agency are not readily available. However in response to a specific inquiry from Mr Hutchinson of the Water Supply Branch of that Agency, we advised him by letter of our position on July 11 1977."

APPENDIX B - HISTORICAL DEVELOPMENT OF COAL TAR LININGS

B1 SOURCE OF INFORMATION

The following information has been kindly provided by Stanton plc of Nottingham, manufacturers of cast iron pipes for many years.

B2 EARLY DEVELOPMENT OF THE COATING SOLUTION

Originally Dr Angus Smith's solution was used. The patent specification for this material was taken out in 1848 and stated "coal tar reduced by distillation or otherwise to a thick pitch-like mass". This material was to be kept at 300 °F (149 °C). Pipes were to be kept clean, free from oxide, and treated with linseed oil if they were to be kept in stock prior to dipping. Before dipping, pipes were to be heated to 300 °F (149 °C), and immersed in the dipping mixture for one hour. On withdrawal, linseed oil was poured onto the hot pipes to soften the coating and dipping mixture. Various modifications of this solution have appeared from time to time, such as the inclusion of additions of lime and cement. The basic material was a soft coal-tar pitch containing probably a high percentage of creosote and naphthalene. These two substances evidently served as volatile solvents, and there is no doubt that they helped to retain linseed oil in solution of pitch; linseed oil and pitch being incompatible. Pipe dips, unless they had been in use for some time (i.e. well stewed in the dipping tank), were liable to give a phenolic taste to water when the pipes were first put into service. The taste would have been dependent on the proportion of volatiles evaporated from the surface of the pipe as the pipes were removed from the dip.

The use of chlorinated water increased the tendency to taste. To overcome this, in 1937, a dipping mixture was developed consisting of soft pitch cut back to dipping consistency with washed creosote oil. The oil was washed by treatment with weak caustic soda to remove phenols, dilute sulphuric acid to remove pyridine bases, and finally with dilute sodium carbonate to neutralise any acid left in the material. On this basis a series of dipping mixtures was devised known as Stanton Dipping Mixtures (SDM). Table B1 gives a typical specification. The naphthalene content was subsequently reduced so that no matter was deposited on standing. Naphthalene content was then below 5%; the effect of this was to prevent crystallisation in the storage tanks. The resulting mixture was coded SDM 30, Table B1.

Practical experience quickly demonstrated that the creosote oil was completely volatile at temperatures used for dipping so that after a short time its softening action would be lost. It thus had no softening action whatsoever on the pitch, and coating products from the original SDMs were exceptionally brittle, although, if properly applied, they were absolutely free from taste.

Table B1 Stanton Dipping Mixture and SDM 30 specifications

Property	SDM	SDM 30
Specific gravity at 25 °C	1.040	1.20
Viscosity	thin fluid	30 seconds
Fractionation		
0 - 230 °C	9.6%	2%
230 - 270 °C	49.4%	12%
270 - 300 °C	24.0%	8%
300 - 330 °C	11.2%	8%
over 330 °C	5.8%	-
pitch	-	70%
water	-	below 0.5%
naphthalene	14.4%	below 2%
tar acids	0.8%	below 1%
pyridine bases	0.12%	below 1%

- no information

It was not possible to guarantee dipping mixtures completely free from water. The pitch used for SDM 30 was stipulated as a medium soft coke oven pitch.

In 1940 a second series of dipping mixtures was formulated in which the washed creosote oil was replaced by a heavy anthracene oil. The anthracene oil was a material which had not previously been available and was an exceptionally thick semi-drying oil produced during the destructive distillation of pitch to coke for the manufacture of arc carbons. The new series of dipping mixtures was known as Stanton Anthracene Dipping Mixtures (SADM). These were mixtures of equal parts of medium soft coke oven pitch and heavy anthracene oil No. 1697. The specification is given in Table B2.

SADM was solid at ambient temperatures and could only be transported in tank wagons fitted with steam heating coils. Likewise it could only be stored in steam-heated tanks.

Because of these requirements and the limited number of suitable facilities, Stanton devised a mixture (SADM 7, Table B3) which consisted of SADM diluted with washed creosote oil to fluid consistency. The proportion of tar acids and bases was controlled to limit the tasting constituents of the mixture.

Table B2 Stanton Anthracene Dipping Mixture specification

Property	Value
SOFT COKE OVEN PITCH	
Viscosity	300 secs at 77 °F 10 secs at 50 °C
Specific gravity	1.22
Fractionation	
0 - 230 °C	0.5%
230 - 270 °C	1.5%
270 - 300 °C	6.0%
300 - 330 °C	7.0%
over 330 °C	85.0%
melting point of residual pitch	128 °F
penetration at 25 °C	28
tar acids	under 1%
pyridine bases	under 1%
HEAVY ANTHRACENE OIL NO. 1697	
Specific gravity at 77 °F	1.14
Fractionation	
0 - 230 °C	0.5%
230 - 270 °C	1.5%
270 - 300 °C	7.0%
300 - 330 °C	11.0%
over 330 °C	80.0%
tar acids (by volume)	1.0%
pyridine bases	0.5%

The ingredients were purchased ready-mixed from Yorkshire Tar Distillers, since the cutting back of molten pitch with oil required special apparatus. In use, the material in the dipping tank gradually hardened up and thickened until of the correct consistency for application. This initial conditioning was necessary to give a satisfactory coating and was hastened by raising the working temperature by 10 to 15 °C. Thereafter the additions to the tank consisted of fresh dipping mixture, or oil to keep the consistency approximately constant. When the mixture became too hard, it was softened by the addition of oil known as Stanton Mixed Oil (SMO), Table B3. This is a mixture of equal parts of washed creosote oil and heavy anthracene oil No.1697.

Table B3 SADM 7 and SMO specification

Property	SADM 7	SMO
Viscosity at 77 °F (25 °C)	7 secs	-
Specific gravity	1.15	1.09
Fractionation		
0 - 230 °C	-	6.0%
230 - 270 °C	6.7%	20.6%
270 - 300 °C	7.6%	9.2%
300 - 330 °C	7.6%	10.1%
over 330 °C	78.1%	54.1%
tar acids(0 - 270 °C)	0.7%	1.0%
bases (0 - 270 °C)	1.0%	1.3%

- no information

B3 DEVELOPMENT SINCE LATE 1940s

By 1949, Stantons were preparing the coating mixture on site based on anthracene oil and coal dust. This represented a development on the coatings prepared using medium soft coke oven pitch. The anthracene oil was purchased with most of the volatiles removed, the specification being that the oil should not lose more than 5% of its weight on heating to 330 °C. The oil was dried before use. The oil was introduced at a temperature of 120 °F (49 °C) into drying kettles. Once the oil was in, the temperature was increased to around 300 °F (149 °C), thus removing water. The coal dust was then added over a period of one hour. When full mixing was achieved, the burners were applied and the temperature raised to 685 °F (363 °C) and maintained for 20 hours for distillation to take place. The procedure was modified and by 1976 a 48-hour distillation at 360 °C (182 °C) was used. During this process the resinous constituents of the coal go into solution in the oil. On completion, cooling commenced. At certain periods slate dust was added and thoroughly mixed. The proportions of coal dust and oil could be changed to influence the properties.

Experimental work had indicated that various types of coal were suitable (e.g. Vitrain, Clarain, Durain and Fusain). It was found, however, that it was essential that the coal be pulverised to a particle size not larger than 210 µm. Because of problems with the heterogeneity of the coals used, further work was conducted using Cannel coal (3.3% water, 15.7% ash, 39.5% volatile, 41.5% carbon, 0.8% sulphur). Frothing occurred because of vaporisation of the water content. Thus, a drying stage was introduced comprising three hours at 220 °F (104 °C) for the coal dust (and for the anthracene oil as described above). By 1950, the remaining Cannel coal seams in England had become

uneconomical to work and a substitute was found in a powdered bituminous coal (3.6% water, 5.59% ash, 33.84% volatile, 56.97% carbon, 1.44% sulphur).

In appearance, the resulting coating was similar to that obtained with coal tar pitch but was superior in the following properties:

- water proofing qualities,
- temperature susceptibility,
- ductility.

Stanton report that chemically it was more inert than coal-tar pitch. The resulting material was also more viscous than coal-tar pitch with the result that thicker coatings could be obtained at slightly higher dipping temperatures.

B4 COATING PIPES

At the time of the developments in the 1930s and early- to mid-1940s, the method of coating pipes was as follows:

Pipes were pre-heated either by immersion in boiling water, until the water flashed off when the pipes were withdrawn, or in a stove to a temperature of approximately 180 °F (82 °C). They were then immersed in the dipping mixture for a period ranging from 10 minutes to 30 minutes depending on the size of the casting. On withdrawal from the dipping tank the pipes were allowed to drain, laid on gantries, turned over then brushed internally and externally to spread the coating and remove runs. They were then allowed to cool off and were ready for shipment. The main troubles were due to overheating, arising mainly from the banking of fires overnight and at weekends. The temperature range was ideally 300 to 320 °F (149 to 160 °C).

At this time Stanton were making routine taste tests. A pipe was rinsed with water and then filled with water for 24 hours. At the end of this period the water was tasted. It was assumed that taste was due to phenols and pyridine bases, hence endeavours to cut these down were made. It was reported that very occasionally taste was produced by naphthalene which distilled from the lower portion of the pipe coating and condensed on the upper part of the pipe as the pipe was withdrawn from the dipping tanks.

The following is a list of coating plants and the coating used by the time of the late 1940s:

Spun Plant	}	Pipes - SADM + additions of heavy anthracene oil No 1697 as required
Cochranes		
Nutbrook		
New Works	}	Fittings - SDM 7 with additions of SMO
Holwell		
Riddings		
Cochranes Foundry		

By 1964 the following was reported:

Stanton used coal-in-tar-oil dispersion (BS 4164 Type III).

Cochrane and Staveley used fixed coal-tar pitches (BS 4164 Type I).

Subsequent to the early 1960s (at least by 1964), Staveley began to use the coal dispersion as at Stanton.

The following coating method was employed:

The pipes were pre-heated to 160 °C and introduced to the dipping bath at the same temperature. A considerable degree of evaporation of tar oils occurred, both from the liquid in the bath and from the films on the coated pipes. The composition of the bath was maintained between selected viscosity limits by periodic addition of flux oil. Thus the bath composition was not constant but controlled between specific limits.

By 1976, the castings were pre-heated by passage through a pre-heat stove to raise their temperature to approximately 150 °C. The dipping tanks were also maintained at this temperature. The heated castings were immersed in the dipping material and then removed and allowed to drain. The castings were then immersed in water to rapidly solidify the coating to permit handling. Coatings of thickness between 0.08 to 0.13 mm were obtained. The coatings were reported to be more ductile than coal-tar pitches and more resistant to the effect of temperature, i.e. their adhesion at low temperature was better than that for normal pitch and they softened less readily on heating.

B5 SUMMARY OF DEVELOPMENTS

A summary of the developments in coal-tar pitch based linings is presented in Table B6.

Table B6 Summary of recorded developments made in the preparation of coal tar pitch based lining materials

Year	Name	Constituents
1848 - 1930	Dr Angus Smith's solution	Coal tar reduced by distillation
1937 - 1940	Stanton Dipping Mixtures	Soft pitch plus washed creosote oil
1940	Stanton Anthracene Dipping Mixtures (SADM)	Soft pitch plus heavy anthracene oil
1940+	SADM7	SADM (above) plus washed creosote oil
Late 1940 (by 1949)	Stanton's coal in oil dispersion	Coal dust plus anthracene oil

It is evident that significant changes in the constituents and concentrations of coal-tar pitch coatings have occurred over the approximately 150 years of use. The descriptions in the preceding sections also demonstrate that even for specific preparations, variations in composition were experienced as a result of a gradual loss of certain constituents from the dipping baths during their period in use. In addition, the coating process provided a degree of choice to the customer in terms of physical characteristics by means of bath composition control with a consequent effect on coating composition.

This all suggests that the composition of coal-tar pitch linings could, in practice, be very variable, pipe section to pipe section, even for pipes of similar age and manufacturing origin.

APPENDIX C - DATA ASSESSMENT

C1 DoE PAH SURVEYS

In 1988, after concern at the Department of the Environment (DoE) about levels of PAH in drinking water, a two-part nation-wide survey of PAH levels in drinking water was commissioned by the DoE. All water supply utilities were asked to take part in these surveys, excepting those affected by the discretionary status of small water undertakers for Survey 2 (see Table C1 below).

Survey 1 was performed by all the water undertakers and involved taking random samples at customers' taps. One sample per 5000 head of population was requested.

Survey 2 concentrated on zones and locations believed to be at greatest risk of high levels of PAH. Water undertakers were asked to consider areas which they considered most likely to exhibit high PAH values and to explain the reason for this judgement. The number of zones investigated by each water undertaker was determined by the population supplied, as shown in Table C1.

Table C1 Identification of Zones for Part 2 of DoE Survey

Population supplied by undertaker	Number of zones to be sampled
< 0.5 million	Discretionary
0.5 - 1.5 million	1
1.5 - 5.0 million	2
> 5.0 million	3

Within each of these identified zones supplied predominantly by coal-tar pitch lined mains, a discrete area, such as a metering district, was identified. A downstream sampling route consisting of ten sampling points was mapped out. The first two points monitored water quality in the trunk main feeding the system and the input to the area. Three points were located on 4" or 6" through-mains located within the system. The remaining five points were situated on dead end locations (3" or 4" mains not more than 100 m from the end of the main) supplied by these through-mains.

Two-litre water samples were taken from the kitchen tap after flushing the service pipe at maximum flow rate. For each sample, approximately two service pipe volumes were flushed. Sampling was undertaken four times on separate days spread over two weeks. Samples were analysed for the six indicator PAH using the method approved by the Standing Committee of Analysts.

The data were examined visually for evidence of correlations between PAH concentrations and water type and position of sampling point within the distribution system. In addition a two-way analysis of variance was used to examine the relationships between PAH and water quality parameters including iron, pH, turbidity and temperature.

C2 WATER UTILITY 1 - STATISTICAL ANALYSIS OF PAH COMPLIANCE SAMPLES

C2.1 Objectives

The objectives of the analysis were:

1. to investigate relationships between the PAH concentrations and the values of other water quality parameters;
2. to investigate the relationships for samples failing the PCV for PAH, between PAH concentrations and the values of other water quality parameters and the characteristics of the local distribution main. In addition, to investigate the differences between compliance and specifically PAH PCV failure data.

C2.2 The data

(a) Compliance data

Compliance data were supplied for the year 1990. For compliance purposes the sampling locations are chosen 'at random' although it is not clear whether the sampling is random in the strict statistical sense of the word. The data have been analysed assuming random samples. In addition it should be noted that the PAH samples are not necessarily taken at the same points in the distribution system as samples for other water quality parameters.

The data consisted of Total PAH concentrations measured for individual samples taken within a number of distribution zones and single mean values for each of these zones for water quality parameters: temperature, turbidity, hardness, pH and TOC. The number of samples used in the mean value calculation was not always supplied, but was believed to be in excess of thirty in most cases. A summary of these data is presented in Table C2.

For statistical analysis, the PAH data were summarised for each zone.

Table C2 Summary statistics of data - compliance data set 1, Water Utility 1

Variable	No.	Zone parameter means		
		Minimum	Mean	Maximum
PAH (ng l ⁻¹)	186	4	49	394
Temperature (°C)	186	6.0	11.9	15.4
pH	186	7.2	7.5	7.9
Turbidity (NTU)	186	0.14	0.35	0.99
Hardness (mg Ca l ⁻¹)	172	20	93	129
TOC (mg C l ⁻¹)	172	0.3	1.9	5.3

Except for PAH values, raw data were supplied as compliance zone mean values. The number of samples used to calculate these means was not available.

The total number of PAH determinations was 1169.

(b) PAH PCV failures

Data on PAH PCV failure sites corresponding to individual addresses were supplied. For each address a single PAH value was given. In addition the following water quality parameters were supplied either as values recorded for samples taken at the same property and the same time as the PAH samples (*) or as mean values for the corresponding compliance zone (+). The number of samples from which these mean values were calculated was not stated, but was believed to be at least 12 in each case.

- temperature (+)
- pH (+)
- turbidity (+)
- iron (+)
- aluminium (+)
- manganese (+)
- free chlorine (*)
- total chlorine (*)

The following information about the main supplying the property was also provided:

- diameter
- age
- dead-end (yes/no)
- material (iron/non-iron)
- lining (coal tar/other)

All of these data were only supplied for addresses where the PAH value was above the PCV level of 200 ng l⁻¹. They were not randomly sampled data. A summary of the data examined is presented in Table C3.

Table C3 Summary statistics of data - PAH PCV failures, Water Utility 1

Variable	No.	Minimum	Mean	Maximum
Total PAH (ng l ⁻¹)	68	202	521	4082
Temperature (°C)*	18	9.0	15.7	21.2
pH*	17	7.23	7.43	7.70
Iron (µg l ⁻¹)*	23	10	17.8	50
Aluminium (µg l ⁻¹)*	17	5	16.9	27
Manganese (µg l ⁻¹)*	17	5	5.3	10
Turbidity (NTU)*	17	0.10	0.32	0.9
Free chlorine (mg Cl l ⁻¹)	63	0.02	0.14	0.33
Total chlorine (mg Cl l ⁻¹)	62	0.04	0.21	0.39
Diameter (inch)	62	2	4	8
Age (years)	54	<1	25.4	60

* Raw data supplied as compliance zone mean values

C2.3 Statistical methods

(a) Compliance data

The compliance data were analysed using the following methods.

Firstly, graphs, histograms and tables were used to visually inspect the data in order to obtain a qualitative view of the data and possible relationships. Correlation matrices were also used for this purpose.

Secondly, regression models were used to assess any relationships in a more quantitative manner.

Visual Inspection

A histogram was produced for the distribution of each continuous variable and its logarithms. These were used to visually assess whether the variable should be logged before being used in regression, the criterion being that the shape of the distribution should be as near to the normal distribution as possible.

Scatter graphs were produced for mean Total PAH against each continuous water quality parameter in turn. These were used to visually assess whether there was likely to be any relationship between them.

The histograms and graphs were also used to identify outliers, and in some cases data were removed from the analysis. This was only done in the case of extreme outliers as there was no way of establishing whether they were erroneous data, the results of some identifiable cause such as a disturbance in the system or whether they were actually representative data.

Regression models

Regression models were used to attempt to show relationships between PAH concentrations and the other variables. For each of mean PAH and maximum PAH in turn, the following procedures were used.

1. Simple linear regression using a single explanatory variable. The PAH variable was regressed against each explanatory variable in turn to assess a possible relationship with this variable alone.
2. Multiple stepwise linear regression. A multiple linear regression model was used with all of the possible explanatory variables at once. At each stage in the procedure, the variable which most reduces the residual mean squares was added to the model. The procedure stopped when either all of the variables were added or when the reduction in the residual sum of squares obtained by adding a new variable was not large enough to justify its inclusion.

In all of the regression models, the PAH means were weighted by the number of samples. (The variance of a PAH mean obtained from five samples would not be the same as that obtained from 50 samples, which is a requirement of regression if weights are not used. A more realistic assumption is that the variance of individual sample concentrations are the same. Weighting by number of samples allows this assumption to be included in the regression.)

The reason for including both individual and stepwise regressions was that the explanatory variables were themselves likely to be intercorrelated. In such circumstances it is very difficult to establish causal relationships because it is not clear which variables are really responsible for the indicated relationships. Stepwise models can give an indication of the number of explanatory variables which can significantly be added to the same model.

(b) PCV failures

Some preparation of the data was required before analysis, to remove outliers and to band pipe ages.

Two methods were then used to examine the data corresponding to the PAH PCV failures. Firstly, means and medians for each of the quality parameters corresponding to the PCV failures were produced and compared with means and medians calculated from the routine compliance data for the zone providing the data. Secondly, simple linear regression models were used to examine the relationship between PAH and the other water quality parameters for the PCV failures only.

Data preparation

Some of the ages were stated as 20+, 30+, 40+, 50+ or 1-. These were replaced by 25, 35, 45, 55 and 1 respectively before analysis. Ages were also grouped into the following bands:

0 - 5
6 - 10
11 - 20
21 - 30
31 - 40
41 - 50
> 50

Comparison of failure samples with routine compliance samples

Student t tests were used to see whether the level of the water quality parameters differed significantly between the failure data and the routine compliance data. Some caution is required in the use of this method because:

1. the data came from different sampling schemes, which may well have introduced bias into the comparisons;
2. in both cases the quality parameters were given as means over an unspecified number of samples; it was therefore impossible to make accurate assumptions about the variances being used in the calculation of the t statistic. It was believed that the means were based on enough samples that the t test would give a good indication of significant differences.

Regression models

Histograms were first produced of the distributions of each continuous variable in order to ascertain whether to use the raw variable or logged values in the regression models. Log(Total PAH) was used as the dependent variable in a series of simple linear regression models using each water quality parameter in turn as the explanatory variable. Age, diameter and the factors for dead-end, material and lining were also used as explanatory variables in turn.

Since these analyses were performed only on the PCV failure data, they could not yield any information on the relation between other variables in general, but only for the high PAH values. The use of zone mean values for many of the parameters also limits the usefulness of the application of regression analysis to these PAH PCV failure data.

C3 WATER UTILITY 1 - DATA ANALYSIS FOR EFFECT OF TEMPERATURE

C3.1 Objectives

The main objective of the data analysis was to investigate the relationship between PAH concentrations and temperature. The data set also permitted a study of the relationship between PAH concentration and other water quality variables (pH, alkalinity, hardness, TOC, turbidity and conductivity) and the variables zone and time of year (indicated by month). This formed a secondary objective.

C3.2 The data

A data set comprising a series of analytical results obtained from compliance samples collected during 1989 to 1991 was provided. The variables included were PAH concentration, temperature, pH, alkalinity, hardness, TOC, turbidity and conductivity. The data set was incomplete in that not all these variables were measured for all samples, a number of missing values resulted. Table C4 gives a summary of the statistics for the data set.

Table C4 Summary statistics of data - compliance data set 2, Water Utility 1

Variable	No.	Minimum	Mean	Maximum	No. missing values
Total PAH (ng l ⁻¹)	428	1	71	1820	0
Temperature (°C)	361	4	11.5	24	67
pH	290	7.07	7.45	7.97	138
Alkalinity (mg HCO ₃ l ⁻¹)	33	55	122	149	395
Hardness (mg Ca l ⁻¹)	33	73	95	122	395
TOC (mg C l ⁻¹)	31	0.4	1.9	3.3	397
Turbidity (NTU)	289	0.10	0.34	2.60	139
Conductivity(µS cm ⁻¹)	355	408	528	701	73

C3.3 Statistical methods

The following were prepared and examined:

1. Graphs of mean PAH and median PAH and mean temperature against month of the year.
2. Histograms of PAH and log(PAH) to determine whether to take logarithms of PAH for the regression analysis.
3. Scattergraphs of PAH against the measured variables pH, alkalinity, hardness, TOC, turbidity, temperature and conductivity, in order to visually assess any correlations.
4. Tables of means and medians of PAH by month.

The histograms showed that log(PAH) was much less skewed than PAH. Log(PAH) was therefore used for subsequent analysis. The following analyses were undertaken.

1. Simple linear regression of log(PAH) against each of the above variables. Each variable was examined individually because the large number of missing values for some variables markedly reduced the number of values available for a multiple regression model.
2. ANOVA (Analysis of Variance) of log(PAH) against zone.
3. ANOVA of log(PAH) against month and year.
4. Multiple stepwise linear regression of log(PAH) against month, temperature, pH, turbidity, conductivity and zone. Alkalinity, hardness and TOC were not included in this regression because of the large number of missing values.

C4 WATER UTILITY 2 - STATISTICAL ANALYSIS OF PAH COMPLIANCE SAMPLES

C4.1 Objectives

1. To examine the relationship between PAH and temperature and other explanatory variables during the study period.
2. To examine changes in PAH concentration with time of year.

C4.2 The data

The data consisted of spot samples from the Water Utility 2 compliance monitoring programme. The data covered the period from April to October 1991.

Compliance samples were taken at properties within the distribution system which were chosen 'at random'. It is not clear whether the sampling is random in the strict statistical sense of the word. The data were analysed assuming random samples. The PAH and other samples were taken from the same property at the same time, but in different sample bottles.

A total of 76 samples were taken representing 31 zones; of these 12 had only a single sample. In view of the small number of samples per zone and because changes in PAH between zones were not of primary interest, zone was not considered as a factor in the subsequent analyses. Table C5 lists the variables monitored and gives some summary statistics.

Table C5 Summary Statistics for compliance data set, Water Utility 2

Variable	Minimum	Mean	Maximum	Missing values
Total PAH (ng l ⁻¹)	5	125	1116	0
pH	7.05	7.32	7.50	33
Total Chlorine (mg l ⁻¹)	0.15	0.29	0.44	30
Temperature (°C)	9.6	14.2	20.0	30
Total Hardness (mg Ca l ⁻¹)	101	109	124	64
Aluminium (µg l ⁻¹)	10.0	13.5	44.0	63
Iron (µg l ⁻¹)	10.0	14.5	25.0	61
Manganese (µg l ⁻¹)	1.40	1.40	1.40	62
TOC (mg l ⁻¹)	1.60	1.73	1.90	73

Several points were immediately obvious from the raw data:

1. of the 13 aluminium values, all but 3 were recorded as 10 µg l⁻¹;
2. all of the 14 manganese values were recorded as 1.4 µg l⁻¹;
3. there were only 3 TOC values.

Therefore, aluminium, manganese and TOC were excluded from the statistical analyses.

C4.3 Statistical methods

The statistical analyses consisted of two parts. Firstly various graphs and tables of summary statistics were produced in order to visually assess the data. This was followed by attempting to fit regression and analysis of variance models.

(a) Visual assessment

The visual assessment comprised three stages:

1. Graphs of PAH against date and monthly means of PAH and temperature against month were examined to see how these variables changed over time. The monthly means were also tabulated.
2. Graphs of PAH against temperature and other explanatory variables were plotted to examine for relationships.
3. Histograms of each variable and its logarithms were produced to assess whether to log the variable in subsequent regression models.

(b) Fitting models

Analysis of variance models were fitted to test for significant variations in PAH and temperature from month to month. For the other explanatory variables, a linear regression model of PAH against the variable in question was fitted to look for a significant relationship.

C5 WATER UTILITY 2 - STATISTICAL ANALYSIS OF SPECIFIC SURVEY DATA

C5.1 Objectives

The objectives of the analysis were to examine for each of two data sets:

1. Variation of PAH concentration with the measured variables: mains diameter, mains category (through, mid-point, dead end), temperature, free and total chlorine, pH, mains material, hardness and alkalinity.
2. Variation of PAH concentration with time of year.
3. Variation of PAH concentration with time of day.

C5.2 The data

The data set for each of the two study zones comprised parameter values and mains characteristics for a series of samples collected during specific studies within the zones, investigating the incidence of PAH problems, identified during routine compliance sampling. Table C6 gives a summary of the statistics for the two data sets.

Table C6 Summary statistics of data sets for the two study zones, Water Utility 2

Variable	No.	Minimum	Mean	Maximum	No. of missing values
ZONE 1					
Total PAH (ng l ⁻¹)	58	1	118	820	0
Mains diameter (inch)	45	3	4.5	12	13
Temperature (°C)	23	11.1	14.4	17.7	35
Free chlorine (mg Cl l ⁻¹)	10	0.20	0.27	0.33	48
Total chlorine (mg Cl l ⁻¹)	22	0.18	0.29	0.36	36
pH	10	7.05	7.24	7.40	48
Hardness (mg Ca l ⁻¹)	10	110	118	129	48
Alkalinity (mg HCO ₃ l ⁻¹)	10	134	149	166	48
ZONE 2					
Total PAH (ng l ⁻¹)	34	23	280	1208	0
Mains diameter (inch)	34	0.75	4	6	0
Temperature (°C)	11	12.0	14.4	15.5	23
Free chlorine (mg Cl l ⁻¹)	9	0.18	0.21	0.25	25
Total chlorine (mg Cl l ⁻¹)	11	0.20	0.26	0.30	23
pH	9	7.20	7.24	7.25	25
Hardness (mg Ca l ⁻¹)	9	104	106	106	25
Alkalinity (mg HCO ₃ l ⁻¹)	9	134	136	137	25

C5.3 Statistical methods

Owing to the small number of data for certain parameters, most of the analyses were performed on data from both study zones together. Only where specifically indicated below, were the data sets analysed separately. The age of the main was available only for a relatively small number of samples (18 of the 92 samples). These 18 samples were all from Zone 2 and in all cases the year recorded was either 1952 or 1953. The age of the main was therefore excluded from all analyses.

The following were prepared and examined:

1. Graphs of mean PAH and median PAH against month.
2. Histograms of PAH and log(PAH) to determine whether to take logarithms of PAH for the ANOVA and regression analyses.

3. Scattergraphs of PAH against each of mains diameter, time of day, temperature, free and total chlorine, pH, alkalinity and hardness in order to visually assess any correlations.
4. Tables of means and medians of PAH by month, mains category, mains material and zone.

The histograms showed that log(PAH) was much less skewed than PAH. Log(PAH) was therefore used for subsequent analysis. The following statistical analyses were undertaken.

1. Simple linear regression of log(PAH) against each of mains diameter, month, time of day, temperature, free and total chlorine, pH, alkalinity and hardness.
2. ANOVA (Analysis of Variance) of log(PAH) against each of mains category, mains material and zone.
3. Multiple stepwise linear regression of log(PAH) against mains diameter, temperature, free and total chlorine, pH, alkalinity, hardness, time of day, mains material, mains category and zone.
4. The simple linear regression and ANOVA models for log(PAH) listed in 2 and 3 immediately above were repeated for each of the two zones individually. The multiple regression was not repeated on individual zones because of the small number of data.
5. ANOVA of mains diameter and free and total chlorine was performed against zone. This was done because the earlier analyses had shown significant variation of PAH with each of these variables in the combined data set, but not for the individual zones. These analyses were performed to see whether the levels of these explanatory variables were themselves significantly different between zones.

APPENDIX D - LEACH TESTING

D1 EXPERIMENTAL PROCEDURE

D1.1 Coupon preparation

A sample of coal-tar pitch was obtained from Metrotect Ltd of Cleckheaton, West Yorkshire. This sample reflects the type of coating material which was applied to cast iron pipes prior to 1977. The coupon substrates were prepared from pieces of mild steel ground to a smooth finish with silicon carbide grit 320. The approximate dimensions were 75 mm x 12 mm x 3 mm; the dimensions and weight of each coupon were individually recorded. The coal-tar pitch was heated until molten, and the coupons were dipped into it to be coated. On removal, excess pitch was allowed to drip from the coupons, rapid cooling then followed in air with a resultant smooth, relatively thick coating (1 to 2 mm). They were then re-weighed and measured. Both before and between leaching experiments, coupons were stored suspended in beakers of hard tap water which was changed each working day. The beakers were kept in a dark cupboard. This was in order to 'age' the coupons in conditions similar to those found in distribution pipes. Previous leaching experiments have shown that coupons 'aged' in this arbitrary way produce more reproducible results than those stored in the air.

D1.2 General test procedure

Clean, silanised 2.5 litre brown glass Winchester bottles were filled with water, placed in water baths at room temperature and allowed time to reach that temperature. At the start of the experiment, an 'aged' coupon was suspended in each bottle. The bottle top was replaced and sealed with aluminium foil. One bottle with no coupon was used as a blank control. At the end of the test period the coupons were removed and the water samples were sent for analysis for PAH. A selection of the blank samples were also analysed. At the beginning and end of the experiment, pH levels were measured in the blank sample (pH was not measured in the leaching samples because of the potential for the pH probe to absorb PAH and thereby affect the result). In addition, water temperature in the bath was measured and recorded.

This basic method was altered in various ways as indicated in the following sections on each test in order to study the parameters which may affect PAH leaching.

D1.3 Factor tests

(a) Temperature

The objective of this series of experiments was to investigate the effect of temperature on the rate of PAH leaching.

Experiments were run at two temperatures which reflect the extremes likely to be experienced within a distribution system. Because of doubts over the results of the first series of tests, a second series was carried out.

Series 1

Two bottles with coupons and one control bottle were filled with deionised water and kept in a water bath at a constant 25 °C, whilst a similar pair plus control were kept at 5 °C.

These experiments were repeated twice, each time using the same coupons to give a series of three exposure periods each of 16 hours per coupon.

Series 2

Each of three coupons was exposed at 25 and 5 °C in alternating sequence for a total of four runs. This design was used to reduce the uncertainty in interpreting the results introduced by between-coupon variations in leach rates. One blank was run at 25 °C. Hard tapwater (see Table D1) was used for this test.

(b) pH

The objective of this series of experiments was to investigate the effect of pH on the rate of PAH leaching.

Buffered solutions of pH 6.0 and 7.9, levels likely to be experienced within distribution systems, were prepared by the procedures described below. Two leaching samples and one blank at each pH were set up and kept at room temperature during the experiment. These experiments were repeated twice, each time using the same coupons. In addition, two further test runs were conducted using the original two coupons and two fresh coupons at each pH. The exposure period was 16 hours per coupon.

The buffer solutions were prepared as follows:

pH 6.0

To 22.5 litre of deionised water the following were added:

50 ml 0.1M KH_2PO_4
5.6 ml 0.1M NaOH

This was bottled into silanized Winchesters. The pH of each was measured at room temperature and was found to be 6.00 ± 0.05 .

pH 7.9

To 23.2 litre of deionised water the following were added:

50 ml 0.1M KH_2PO_4
46.7 ml 0.1M NaOH

This was bottled into silanized Winchester. The pH of each was measured at room temperature and was found to be 7.90 ± 0.05 .

(c) Surface area/volume ratio and time

The objective of this series of experiments was to measure the effects of the surface area to volume ratio and exposure time on PAH leaching.

Four bottles with one coupon suspended in each were set up. In two the coupons were left in for 6 hours. In the other two, the coupons were left in for 18 hours. A further four bottles with two coupons suspended in each were set up. In two bottles, the coupons were left exposed for 6 hours. In the other two the coupons were left exposed for 18 hours. One blank sample was set up and its pH was measured after 6 and 18 hours. Deionised water was used for this test.

These experiments were repeated once.

D1.4 Potential remedial measures

(a) Woven nylon hose

The objective of this series of tests was to investigate the capacity of woven nylon hose (denier 30) to adsorb PAH leached by coal-tar pitch. This effect had been noticed previously for nylon filters used in the preparation of water samples for particulate/dissolved PAH analysis.

Four coupons were tested in the following sequence:

1. without hose;
2. with hose cover;
3. without hose;
4. with hose cover.

For Stages 2 and 4 (with hose cover) the coupons were prepared by covering the surface with woven nylon hose and securing this with thread. Fresh hose was applied for each of these two stages. The test duration was 16 hours. By its nature the woven hose does not prevent the water reaching the coupon. A blank was tested with each run. Deionised water was used for this test.

(b) Polyphosphate and silicate dosing

Dosing of phosphates and silicates is practised by the water industry in certain circumstances e.g. in order to control iron pickup or lead solubility. These chemicals are believed to act by the formation of internal layers more resistant to attack or degradation by the conveyed water. The objective of these series of leach tests was to investigate the capacity of phosphate- and silicate-containing layers to reduce PAH leaching. Two levels of dosing were used for each agent type.

(i) Polyphosphate

Solution preparation

The solutions were prepared from the chemical sodium hexametaphosphate (trade name Calgon SWB (Water Board Grade Glass)) supplied by Albright and Wilson of Oldbury, West Midlands. The manufacturer reports that the substance supplied is 29.25% by weight as phosphorus. The dose rates selected were 0.6 mg P l^{-1} (equivalent to 2 mg l^{-1} of chemical) and 2.1 mg P l^{-1} (equivalent to 7 mg l^{-1} of chemical). The water used for the preparation of the solutions was a hard supply direct from the tap reported to contain $0.084 \text{ mg P l}^{-1}$ (single compliance analysis result - see Table D1). The solutions were freshly prepared before each test run by dissolving a weighed amount of crystals in the tapwater at ambient temperature.

Test runs

For both dose rates, three coupons were tested. Firstly, the coupons were exposed to the tap water base with no chemical dosed to establish the baseline PAH leach rate. The same coupons were then subjected to three further test runs in the prepared phosphate solutions. The test duration was 16 hours. Blanks were run for both low and high dose rate waters.

Table D1 Tap water base - extract from Schedule 4 report Water Supply (Water Quality) Regulations 1989 (30(4)).

Parameter	Concentration or value			No. of samples Total	>PCV	% of samples >PCV
	Min.	Mean	Max			
Turbidity (FTU)	<0.1	0.2	0.5	12	0	0
pH	7.0	7.4	7.8	8	0	0
Sulphate as SO ₄ (mg l ⁻¹)	59	59	59	1	0	0
Magnesium as Mg (mg l ⁻¹)	10.0	10.0	10.0	1	0	0
Sodium as Na (mg l ⁻¹)	32.0	32.0	32.0	1	0	0
Potassium as K (mg l ⁻¹)	3.0	3.0	3.0	1	0	0
Nitrate as NO ₃ (mg l ⁻¹)	9.3	15.7	33.2	12	0	0
Nitrite as NO ₂ (mg l ⁻¹)	<0.003	0.008	0.044	15	0	0
TOC as C (mg l ⁻¹)	1.30	1.30	1.30	1	0	0
Aluminium as Al (µg l ⁻¹)	<10	17	33	16	0	0
Iron as Fe (µg l ⁻¹)	<10	36	209	41	1	2.4
Manganese as Mn (µg l ⁻¹)	<5	<5	<5	6	0	0
Phosphorus as P (µg l ⁻¹)	84	84	84	1	0	0
PAH (ng l ⁻¹)	<30	<30	<30	1	0	0
Conductivity at 20°C (µS cm ⁻¹)	577	611	647	28	0	0
Calcium as Ca (mg l ⁻¹)	93	93	93	1	0	0
Total hardness as Ca (mg l ⁻¹)	109	109	109	1	0	0
Alkalinity as HCO ₃ (mg l ⁻¹)	298	298	298	1	0	0

(ii) Silicate

Solution preparation

The solutions were prepared from the chemical sodium silicate (trade name Crystal 79) supplied by Crosfield of Warrington, Cheshire. The manufacturer reports that the substance supplied is on average 29.3% by weight as SiO₂ with an average specific gravity of 1.3 g l⁻¹. (Thus 1 ml of the liquid compound contains 0.41 g SiO₂.) The dose rates selected were 5 and 10 g l⁻¹ SiO₂ (one litre of test solution containing 12.2 and 24.4 ml of compound respectively). The water used for the preparation of the solutions was a hard supply direct from the tap (see Table D1). The solutions were freshly prepared before each test run by mixing measured volumes of compound and tap water appropriate to the dose rate required.

Test runs

The procedure differed slightly between the two dose rates as follows:

- 5 g l⁻¹. Four coupons were tested in silicate-dosed solutions a total of three times. For comparison a separate coupon was tested in the tap water base for one test run. The test duration was 16 hours.
- 10 g l⁻¹. Three coupons were exposed firstly to the hard tap water base with no chemical added to establish the baseline PAH leach rate. The same coupons were then subjected to three further test runs in the prepared silicate solutions. The test duration was 16 hours.
- Blanks were run for both high and low dose waters.

(c) Contact with PVC and MDPE pipe sections

An interesting observation recorded previously during downstream series sampling for PAH in Water Utility 1 was the apparent partial disappearance of PAH from the conveyed water supplied through dead-end sections of the system comprising MDPE extensions to otherwise coal-tar pitch lined cast iron networks. The objective of this series of tests was to examine this observation further and to identify whether MDPE and PVC are effective adsorbers of PAH.

For each of the two pipe materials, six coupons were tested. These were tested in the following sequence:

1. No pipe section present;
2. Pipe section present.

Testing for all stages was conducted in hard tapwater (see Table D1). For Stage 2, pipe sections of approximate dimensions 145 mm x 12 mm x 11.5 mm for MDPE and 150 mm x 13 mm x 4.5 mm for PVC were suspended in the test water, one section to each coupon. The test duration was 16 hours. Two blanks were run, one for each of the plastic pipe materials. These blanks were not exposed to coal-tar pitch coated coupons but each contained a section of the pipe material for which it acted as control.

(d) Carbon dioxide stripping

Substantial evidence suggests that groundwaters are more liable to leach PAH from coal-tar pitch linings than are supplies derived from surface waters. Not all groundwaters are, however, susceptible. Although the characteristics of groundwater which have the greatest effect on PAH leaching have not yet been conclusively identified, it is those waters derived from chalk aquifers, with a concomitant tendency to be saturated or supersaturated with carbon dioxide, that appear to be associated with generally higher

levels of fluoranthene. The objective of this series of tests was to investigate the relationship between leaching rate and carbon dioxide concentration.

Tests were conducted using a groundwater rich in carbon dioxide. The carbon dioxide content for the tests was arranged as follows:

- high - as received and boosted using injected carbon dioxide (from a cycle tyre inflating cylinder);
- low - carbon dioxide stripped using a nitrogen purge.

The water was drawn from a borehole (see Table D2). Some of the water was bottled and tightly capped as soon as possible after collection. Other samples were purged with nitrogen and then bottled and tightly capped. The experiment followed water preparation as quickly as possible to avoid change in carbon dioxide levels.

For each carbon dioxide state, four coupons were tested for a total of three test runs. The same batch of water was used for the three test runs, the carbon dioxide content of the high level water was boosted by carbon dioxide injection (from a cycle tyre inflator) immediately before the start of the test. The test duration was 16 hours. One blank sample was set up for each carbon dioxide state.

Table D2 Results of selected inorganic analysis of borehole water used for the CO₂ stripping leach tests

Parameter	Concentration mg l ⁻¹
Sodium	9.1
Magnesium	1.8
Potassium	1.0
Calcium	110.8
Chromium	<0.01
Manganese	<0.002
Iron	<0.004
Nickel	<0.01
Copper	<0.004
Zinc	<0.004
Cadmium	<0.004
Lead	<0.05
Sulphate (SO ₄)	9.8
Silica (SiO ₂)	22.3
Hardness (as Ca)	114

D2 ANALYTICAL METHOD

Water samples (1000 ml) were extracted with dichloromethane (total of 100 ml). After drying the solvent extracts with anhydrous sodium sulphate, acetonitrile (0.5 ml) was added and the dried extracts concentrated to 0.5 ml. The extracts were quantitatively transferred to autosampler vials and made up to 1 ml with acetonitrile.

AQC blank and control solutions were prepared alongside each batch of four real samples. Medmenham borehole water was used for both solutions. The control solution was spiked with the individual PAHs at levels between 15 and 30 ng l⁻¹.

Prior to analysis an internal standard (triphenylene) was added to each extract at 1 µg ml⁻¹. The function of this standard was to correct for any irreproducibility in autosampler injection volume.

Analysis was by HPLC using fluorescence detection. The instrument used was a Varian 9010 solvent delivery system, Varian 9095 autosampler and Perkin-Elmer LS40 fluorescence detector. A Supelcosil LC-PAH column (15 cm x 4.6 mm i.d.) with 5 µm packing was used. The mobile phase was acetonitrile/water at a flow rate of 1 ml min⁻¹ using the gradient below, with a steady change in composition from 3 to 20 minutes:

HPLC elution gradient

Time (min)	% Acetonitrile	% Water
0	48	52
3	48	52
20	99	1
50	99	1
51	48	52

The detector was programmed to change the excitation and emission wavelengths to optimise the detection of the range of PAHs under investigation.

Time (sec)	λ _{ex} (nm)	λ _{em} (nm)	Attenuation
0	260	380	16
100	280	340	8
840	260	380	16
910	305	430	4
1140	248	402	64
1260	260	380	16
1430	290	430	32
2300	300	500	8

In addition to detecting the six PAHs comprising the 'Total PAH' parameter, this programme allows detection of most of the sixteen PAHs comprising the US EPA indicators list (see Figure D1). The sudden changes in the position of the baseline correspond to changes in the detector wavelengths.

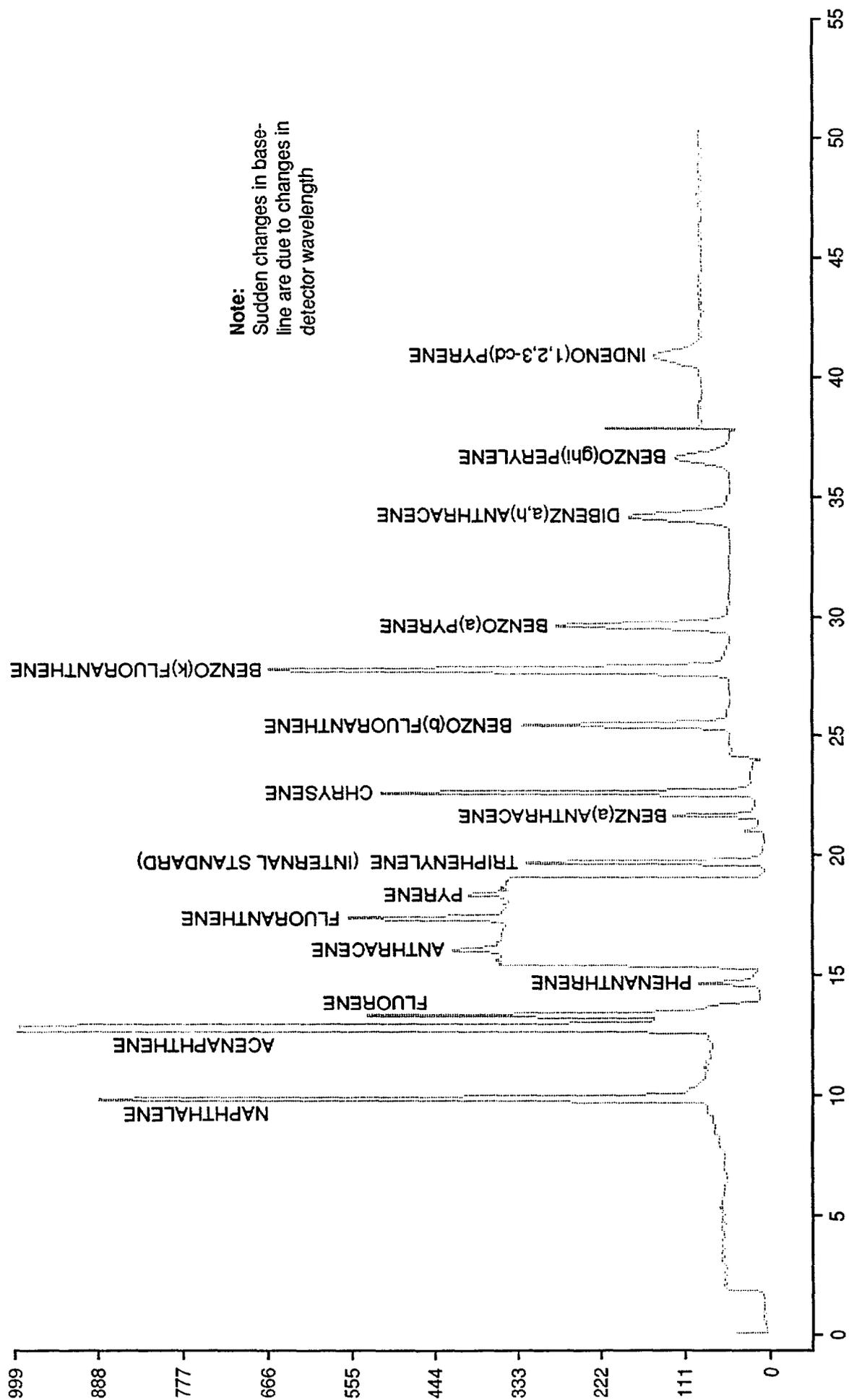


Figure D.1 Chromatogram of PAH standards

Approximate limits of detection are given below:

PAH	Approximate LOD
Fluoranthene	5 ng l ⁻¹
Benzo(b)fluoranthene	2 ng l ⁻¹
Benzo(k)fluoranthene	1 ng l ⁻¹
Benzo(a)pyrene	1 ng l ⁻¹
Benzo(ghi)perylene	4 ng l ⁻¹
Indeno(1,2,3-cd)pyrene	5 ng l ⁻¹

Quantification was by the method of internal standards except where an interfering peak co-eluted with triphenylene or where a large dilution factor was necessary to bring the peak height into the known linear range of the detector. In both of these situations external standardisation was used.

The data handling system was calibrated using a range of six concentrations for each PAH. This calibration was used to provide full quantitative results for all the fluoranthene results and for the other five PAHs during the early part of the work. During the later part of the work the results for the other five PAHs were calculated on the basis of a single point calibration.

Data from the AQC control solutions was used to calculate a mean percentage recovery for each of the six PAHs:

PAH	% Recovery (mean)	% rsd
Fluoranthene	69	20
Benzo(b)fluoranthene	75	18
Benzo(k)fluoranthene	75	17
Benzo(a)pyrene	71	16
Benzo(ghi)perylene	74	19
Indeno(1,2,3-cd)pyrene	74	19

Both the between-batch and within-batch reproducibility of the method was found to be relatively low (rsd = 16 to 20%) and so the mean recovery figures were used to correct all of the sample results. It is thought that the precision of the method could be improved if a suitable 'recovery' internal standard could be found which could be spiked into the samples and AQC solutions at the beginning of the sample preparation. Such a compound must behave similarly to PAHs during the extraction and chromatography, should be eluted from the LC column in a region distinct from other PAHs and common interference and matrix peaks, and should fluoresce - yet should not be found in typical sample matrices. Various compounds have been suggested but so far none have been found to be appropriate (The Determination of Polynuclear Aromatic Hydrocarbons in Waters (additional methods), 1992, Standing Committee of Analysts).

A representative chromatogram of a test sample is shown in Figure D2. This chromatogram also illustrates the presence in the leachate of a number of PAHs eluting before fluoranthene.

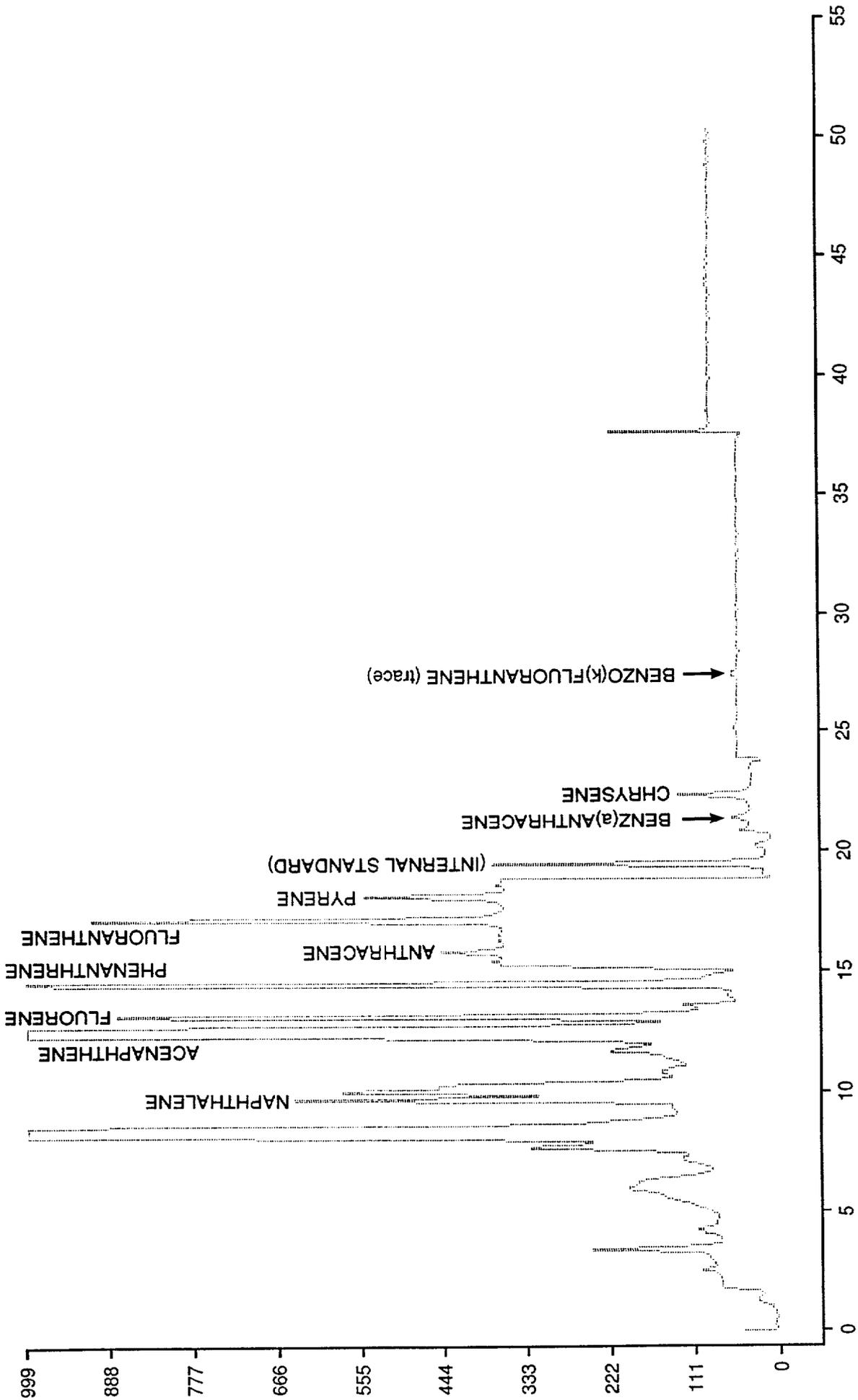


Figure D.2 Chromatogram of a test sample (Temperature Test 2; Coupon 14 Run 2)

The majority of the analytical work was performed during the period February to July 1993. During this time the analytical laboratory participated in two Aquacheck distributions for PAH analysis (Group 7c) for which the same analytical methodology and approach to result calculation and correction for recovery was adopted. For the first distribution three results were flagged (those for benzo(k)fluoranthene, benzo(a)pyrene and indeno(1,2,3-cd)pyrene), however the results for all of these compounds were closer to the spiked reference value than the mean of all labs. No results were flagged in the second distribution.

The Aquacheck results therefore support the analytical methodology and approach to result calculation which has been adopted for this work.

APPENDIX E - RESULTS OF LEACH TESTS

Key to PAH abbreviations in the table headings:

F	=	Fluoranthene
B(b)F	=	Benzo(b)fluoranthene
B(k)F	=	Benzo(k)fluoranthene
B(a)P	=	Benzo(a)pyrene
B(ghi)Pe	=	Benzo(ghi)perylene
InP	=	Indeno(1,2,3-cd)pyrene

Table E1a Results of series 1 leach tests investigating the effect of temperature

Temp. °C	Coupon number	Coupon area cm ²	Run No.	pH(a)		F	PAH, ng l ⁻¹			InP	Total	Fluoranthene leach rate ng cm ⁻² h ⁻¹
				Start	Finish		B(b)F	B(k)F	B(a)P			
25	2	35.0	1	7.3	8.4	40	<2	<1	<1	<4	<5	40
			2	8.8	9.3	620	2	<1	2	<4	<5	624
			3	8.0	10.0	470	14	7	14	7	15	527
25	17	35.0	1	7.3	8.4	35	<2	<1	<1	<4	<5	35
			2	8.8	9.3	810	3	2	3	<4	<5	818
			3	8.0	10.0	630	2	1	1	<4	<5	634
25	Blank	N/A	1	7.3	8.4	6	<2	<1	<1	<4	<5	6
5	15	32.9	1	9.5	8.0	290	4	2	4	<4	<5	300
			2	8.0	8.0	66	6	3	6	7	5	93
			3	7.7	8.1	27	<2	<1	<1	<4	<5	27
5	16	39.2	1	9.5	8.0	930	3	2	3	<4	<5	938
			2	8.0	8.0	96	5	2	4	<4	<5	107
			3	7.7	8.1	94	2	1	2	<4	<5	99
5	Blank	N/A	1	9.5	8.0	2	<2	<1	<1	<4	<5	2

NOTES: a) pH values were measured in blank samples

b) The volume of each sample was 2.5 l

c) Each run was 16 h

N/A Not applicable

Table E1b Results of series 2 leach tests investigating the effect of temperature

Temp. °C	Coupon number	Coupon area cm ²	Run No.	F	PAH, ng l ⁻¹				Total	Fluoranthene leach rate ng cm ⁻² h ⁻¹
					B(b)F	B(k)F	B(a)P	B(ghi)Pe		
5	3	34.6	1	9	(-)	(-)	(-)	(-)	(-)	0.04
	9	36.9	1	14	(-)	(-)	(-)	(-)	(-)	0.07
	14	38.6	1	86	(t)	(t)	(-)	(-)	(-)	0.38
	3	34.6	3	<5	(-)	(-)	(-)	(-)	(-)	0.00
	9	34.9	3	28	(-)	(-)	(-)	(-)	(-)	0.14
	14	38.6	3	21	(-)	(-)	(-)	(-)	(-)	0.09
25	3	34.6	2	30	(-)	(-)	(-)	(-)	(-)	0.15
	9	36.9	2	163	(-)	(-)	(-)	(-)	(-)	0.76
	14	38.6	2	296	(-)	(-)	(-)	(-)	(-)	1.3
	Blank	N/A	2	7	(-)	(-)	(-)	(-)	(-)	N/A
	3	34.6	4	74	(-)	(-)	(-)	(-)	(-)	0.37
	9	34.9	4	180	(-)	(-)	(-)	(-)	(-)	0.89
	14	38.6	4	276	(-)	(-)	(-)	(-)	(-)	1.2

NOTES: a) pH values were measured in blank samples

	Run 1	Run 2	Run 3	Run 4
Start	8.4	8.3	8.4	8.4
Finish	8.4	8.4	8.4	8.4

b) The volume of each sample was 2.75 l

c) Each run was 16 h

d) (-) = Provisional assessment of analytical results for PAHs other than fluoranthene: t = trace, - = not detected
N/A Not applicable

Table E2 Results of leach tests investigating the effect of pH

Nominal pH	Coupon number	Coupon area cm ²	Run No.	F	B(b)F	B(k)F	PAH, ng l ⁻¹ B(a)P	B(ghi)Pe	InP	Total	Fluoranthene leach rate ng cm ⁻² h ⁻¹
6.0	1	34.1	1	170	2	1	2	<4	<5	175	0.78
			2	84	<2	<1	<1	<4	<5	84	0.38
			3	220	<2	<1	<1	<4	<5	220	1.0
			4	241	<2	<1	<1	<4	<5	241	1.2
			5	154	<2	<1	<1	<4	<5	154	0.76
6.0	3	34.6	1	73	<2	<1	<1	<4	<5	73	0.33
			2	59	<2	<1	<1	<4	<5	59	0.27
			3	81	<2	<1	<1	<4	<5	81	0.37
			4	103	<2	<1	<1	<4	<5	103	0.50
			5	104	<2	1	2	<4	<5	107	0.51
6.0	34	35.0	4	181	<2	<1	<1	<4	<5	181	0.87
			5	388	4	1	10	45	6	454	1.9
			4	82	<2	<1	<1	<4	<5	82	0.42
			5	52	<2	<1	<1	<4	<5	52	0.27
			1	<5	<2	<1	<1	<4	<5	<18	N/A
6.0	Blank	N/A	4	<5	<2	<1	<1	<4	<5	<18	N/A
			5	30	<2	<1	<1	<4	<5	30	N/A
			1	81	<2	<1	<1	<4	<5	81	0.33
			2	130	3	2	3	<4	<5	138	0.53
			3	110	<2	<1	<1	<4	<5	110	0.45
7.9	14	38.6	4	174	3	2	2	<4	<5	181	0.76
			5	137	<2	2	3	<4	<5	142	0.60

Table E2 continued

Nominal pH	Coupon number	Coupon area cm ²	Run No.	F	B(b)F	B(k)F	PAH, ng l ⁻¹		InP	Total	Fluoranthene leach rate ng cm ⁻² h ⁻¹
							B(a)P	B(ghi)Pe			
7.9	7	30.3	1	54	<2	<1	<1	<4	5	59	0.28
			2	47	<2	1	2	<4	<5	50	0.24
			3	59	4	2	3	<4	<5	68	0.30
			4	79	<2	<1	<1	<4	<5	79	0.44
			5	152	<2	<1	<1	<4	<5	152	0.85
7.9	26	41.0	4	233	<2	<1	<4	<5	233	0.96	
			5	209	<2	<1	<1	<4	<5	209	0.86
7.9	28	38.6	4	236	10	<1	<4	<4	<5	246	1.0
			5	153	<2	<1	<1	<4	<5	153	0.67
7.9	Blank	N/A	1	<5	<2	<1	<1	<4	<5	<18	N/A
			4	<5	<2	<1	<1	<4	<5	<18	N/A
			5	<5	<2	<1	<1	<4	<5	<18	N/A

NOTES: a) pH values were measured in blank samples. In all cases the measured values matched the nominal values both at the start and the end of each run

b) Each run was 16 h

c) For runs 1,2 and 3 the sample volume was 2.5 l; for runs 4 and 5 the sample volume was 2.7 l

d) The temperatures at the start and finish of each run were:

Run	1	2	3	4	5
Start	16	16	17	20	19
Finish	16	17	18	20	19

Table E3 Results of leach tests investigating exposure time and area exposed

Exposure time hr	Coupon number	Coupon area cm ²	Run No.	Temp./pH		F	B(b)F	B(k)F	PAH, ng l ⁻¹		InP	Total	Fluoranthene leach rate ng cm ⁻² h ⁻¹
				Start	Finish				B(a)F	B(ghi)Pe			
18	9	36.9	1	16/8.6	16/8.4	200	<2	<1	2	<4	<5	202	0.75
				16/8.5	16/8.5	220	<2	<1	<1	<4	<5	220	0.83
18	12	30.7	1	16/8.6	16/8.4	160	<2	1	3	<4	<5	164	0.72
				16/8.5	16/8.5	230	9	4	9	6	5	263	1.0
18	34 + 5	72.3	1	16/8.6	16/8.4	460	8	4	8	9	<5	489	0.88
				17/8.7	18/8.9	310	<2	<1	1	<4	<5	311	0.60
18	4 + 8	85.4	1	16/8.6	16/8.4	560	<2	7	2	<4	<5	569	0.91
				17/8.7	18/8.9	590	4	2	3	3	<5	599	0.96
6	28	38.6	1	16/8.6	16/8.4	79	<2	<1	<1	<4	<5	79	0.85
				17/8.7	18/8.9	110	4	2	3	<4	<5	119	1.2
6	26	41.0	1	16/8.6	16/8.4	92	2	<1	2	<4	<5	96	0.94
				17/8.7	18/8.9	75	<2	<1	<1	<4	<5	75	0.76
6	18 + 20	69.8	1	16/8.6	16/8.4	130	<2	<1	<1	<4	<5	130	0.78
				17/8.7	18/8.9	340	6	2	8	24	5	385	2.0
6	27 + 29	85.6	1	16/8.6	16/8.4	170	<2	<1	<1	<4	<5	170	0.83
				17/8.7	18/8.9	160	3	1	2	<4	<5	166	0.78
18	Blank	N/A	1	16/8.6	18/8.4	<5	<2	<1	<1	<4	<5	<18	N/A

NOTES:

- a) pH values were measured in blank samples
- b) The sample volume for each run was 2.5 l

Table E4 Results of leach tests investigating the effect of nylon hose

Coupon number	Coupon area cm ²	Hose	Run No.	Temp. pH Start	Temp. pH Finish	F	B(b)F	B(k)F	PAH, ng l ⁻¹ B(a)P	B(ghi)Pe	InP	Total	Fluoranthene leach rate ng cm ⁻² h ⁻¹
2	35.0	No Hose	1	20/9.0	20/8.2	120	<2	1	2	<4	<5	123	0.58
		Hose	2	19/9.0	19/8.1	26	6	3	5	<4	<5	40	0.13
		No Hose	3	20/9.5	20/9.1	285	(1)	(1)	(0)	(-)	(-)	(-)	1.4
		Hose	4	20/9.0	20/9.0	23	(1)	(1)	(0)	(-)	(-)	(-)	0.11
4	48.1	No Hose	1	20/9.0	20/8.2	320	<1	1	1	<4	<5	322	1.1
		Hose	2	19/9.0	19/8.1	265	26	2	7	17	5	322	0.93
		No Hose	3	20/9.5	20/9.1	280	(1)	(1)	(0)	(-)	(-)	(-)	0.98
		Hose	4	20/9.0	20/9.0	42	(1)	(1)	(0)	(-)	(-)	(-)	0.15
9	37.0	No Hose	1	20/9.0	20/8.2	730	6	1	9	36	<5	782	3.3
		Hose	2	19/9.0	19/8.1	21	59*	3	5	<4	<5	88	0.10
		No Hose	3	20/9.5	20/9.1	415	(1)	(1)	(0)	(0)	(-)	(-)	1.9
		Hose	4	20/9.0	20/9.0	39	(1)	(1)	(0)	(-)	(-)	(-)	0.18
27	41.0	No Hose	1	20/9.0	20/8.2	240	<1	1	1	<4	<5	242	0.99
		Hose	2	19/9.0	19/8.1	36	5	2	4	<4	<5	47	0.15
		No Hose	3	20/9.5	20/9.1	410	(10)	(5)	(7)	(-)	(0)	(430)	1.7
		Hose	4	20/9.0	20/9.0	107	(10)	(5)	(7)	(0)	(0)	(129)	0.44
Blank	N/A		1	20/9.0	20/8.2	<5	<2	<1	<1	<4	<5	<18	N/A
			2	19/9.0	19/8.1	<5	<2	<1	<1	<4	<5	<18	N/A
			3	20/9.5	20/9.1	<5	(-)	(-)	(-)	(-)	(-)	(-)	N/A
			4	20/9.0	20/9.0	<5	(-)	(-)	(-)	(-)	(-)	(-)	N/A

NOTES:

- a) pH values were measured in blank samples
- b) The sample volume for each run was 2.75 l
- c) Each run was 16 h
- d) (-) = Provisional assessment of analytical results for PAHs other than fluoranthene; t = trace, - = not detected
- * This value for benzo(b)fluoranthene is most likely to be the result of an interfering peak
- N/A Not applicable

Table E5 Results of leach tests investigating the effect of silicate dosing

Test series	Dose SiO ₂ g l ⁻¹	Coupon number	Coupon area cm ²	Run No.	Temp./pH		F	PAH, ng l ⁻¹			InP	Total	Fluoranthene leach rate ng cm ⁻² h ⁻¹	
					Start	Finish		B(b)F	B(k)F	B(a)P B(ghi)Pe				
LOW DOSE	5	22	30.3	1	18/10.8	18/10.9	42	(0)	(0)	(-)	(-)	0.24		
	5			2	18/-	19/-	120	20	10	14	12	191	0.68	
	5			3	19/-	19/-	420	83	40	72	47	53	715	2.4
LOW DOSE	5	25	38.7	1	18/10.8	18/10.9	55	(0)	(0)	(-)	(-)	0.24		
	5			2	18/-	19/-	73	2	1	<1	<4	<5	76	0.32
	5			3	19/-	19/-	120	6	3	6	<4	<5	135	0.53
LOW DOSE	5	15	32.9	1	18/10.8	18/10.9	54	(7)	(4)	(-)	(-)	(69)	0.28	
	5			2	18/-	19/-	56	8	4	5	<4	<5	88	0.29
	5			3	19/-	19/-	125	27	10	19	14	12	207	0.65
LOW DOSE	5	32	33.7	1	18/10.8	18/10.9	250	(50)	(20)	(-)	(-)	(360)	1.3	
	5			2	18/-	19/-	110	21	10	17	11	12	181	0.56
	5			3	19/-	19/-	190	19	10	15	13	13	260	0.97
LOW DOSE	5	Blank	N/A	1	18/10.8	18/10.9	<5	<2	<1	<1	<4	<5	N/A	
	0	33	42.7	1	19/-	19/-	230	22	11	19	11	14	307	0.93
HIGH DOSE	0	19	36.4	1	19/7.2	19/-	41	(0)	(0)	(-)	(-)	(-)	0.19	
	10			2	20/11.1	20/11.1	305	(0)	(0)	(-)	(-)	(-)	1.4	
	10			3	20/11.0	20/10.9	155	(-)	(-)	(-)	(-)	(-)	0.73	
	10			4	19/10.9	20/10.9	125	(0)	(0)	(-)	(-)	(-)	0.59	
HIGH DOSE	0	21	32.9	1	19/7.2	19/-	28	(0)	(0)	(-)	(-)	(-)	0.15	
	10			2	20/11.1	20/11.1	86	(0)	(0)	(-)	(-)	(0)	0.45	
	10			3	20/11.0	20/10.9	125	(0)	(0)	(-)	(-)	(-)	0.65	
	10			4	19/10.9	20/10.9	62	(-)	(-)	(-)	(-)	(-)	0.32	

Table E5 continued

Test series	Dose SiO ₂ g l ⁻¹	Coupon number	Coupon area cm ²	Run No.	Temp/pH		F	PAH, ng l ⁻¹		InP	Total	Fluoranthene leach rate ng cm ⁻² h ⁻¹		
					Start	Finish		B(b)F	B(k)F				B(a)P	B(ghi)Pe
HIGH DOSE	0	23	35.1	1	19/7.2	19/-	410	(30)	(15)	(60)	(20)	(30)	(565)	2.0
	10			2	20/11.1	20/11.1	870	(50)	(25)	(50)	(20)	(30)	(1045)	4.3
	10			3	20/11.0	20/10.9	350	(t)	(t)	(t)	(-)	(-)	(-)	1.7
	10			4	19/10.9	20/10.9	280	(-)	(-)	(-)	(-)	(-)	(-)	1.4
HIGH DOSE	10	Blank	N/A	4	19/10.9	19/10.9	<5	(-)	(-)	(-)	(-)	(-)	(-)	N/A

NOTES: a) pH values were measured in blank samples

b) The sample volume for each run was 2.75 l

c) Each run was 16 h

d) (-) = Provisional assessment of analytical results for PAHs other than fluoranthene; t = trace, - = not detected

Table E6 Results of leach tests investigating the effect of phosphate dosing

Test series	Phosphate dose mg P l ⁻¹	Coupon number	Coupon area cm ²	Run No.	Temp./pH		F	PAH, ng l ⁻¹			InP	Total	Fluoranthene leach rate ng cm ⁻² h ⁻¹
					Start	Finish		B(b)F	B(k)F	B(a)P			
LOW DOSE	0	6	33.1	1	18/7.1	18/7.0	22	(-)	(-)	(-)	(-)	(-)	0.11
	0.6			2	19/7.3	19/7.4	23	(0)	(0)	(0)	(0)	(0)	0.12
	0.6			3	19/7.3	19/7.7	525	(80)	(40)	(60)	(40)	(785)	2.7
	0.6			4	19/7.9	19/7.4	465	(80)	(40)	(60)	(40)	(725)	2.4
LOW DOSE	0	10	39.0	1	18/7.1	18/7.0	33	(0)	(0)	(0)	(0)	(0)	0.14
	0.6			2	19/7.3	19/7.4	47	(0)	(0)	(0)	(-)	(-)	0.21
	0.6			3	19/7.3	19/7.7	44	(-)	(-)	(-)	(-)	(-)	0.19
	0.6			4	19/7.9	19/7.4	51	(-)	(-)	(-)	(-)	(-)	0.22
LOW DOSE	0	12	30.7	1	18/7.1	18/7.0	27	(0)	(0)	(0)	(0)	(0)	0.15
	0.6			2	19/7.3	19/7.4	40	(0)	(0)	(0)	(-)	(-)	0.22
	0.6			3	19/7.3	19/7.7	54	(-)	(-)	(-)	(-)	(-)	0.30
	0.6			4	19/7.9	19/7.4	27	(-)	(-)	(-)	(-)	(-)	0.15
LOW DOSE	0.6	Blank	N/A	2	19/7.3	19/7.4	10	(-)	(-)	(-)	(-)	(-)	N/A
	0.6			3	19/7.3	19/7.7	<5	(-)	(-)	(-)	(-)	(-)	N/A
HIGH DOSE	0	26	41.0	1	20/7.2	20/7.4	1280	(300)	(150)	(260)	(150)	(2340)	5.4
	2.1			2	20/7.7	20/7.9	255	(0)	(0)	(0)	(-)	(-)	1.1
	2.1			3	20/7.7	19/7.5	125	(-)	(-)	(-)	(-)	(-)	0.53
	2.1			4	19/7.4	19/7.4	225	(0)	(0)	(-)	(-)	(-)	0.94
HIGH DOSE	0	28	38.6	1	20/7.2	20/7.4	145	(10)	(5)	(8)	(-)	(176)	0.65
	2.1			2	20/7.7	20/7.9	92	(0)	(0)	(-)	(-)	(-)	0.41
	2.1			3	20/7.7	19/7.5	105	(-)	(-)	(-)	(-)	(-)	0.46
	2.1			4	19/7.4	19/7.4	82	(-)	(-)	(-)	(-)	(-)	0.37

Table E6 continued

Test series	Phosphate dose mg P l ⁻¹	Coupon number	Coupon area cm ²	Run No.	Temp./pH Start Finish	F	B(b)F	PAH, ng l ⁻¹ B(k)F	B(a)P	B(ghi)Pe	InP	Total	Fluoranthene leach rate ng cm ⁻² h ⁻¹
HIGH DOSE	0	29	44.7	1	20/7.2	20/7.4	155	(-)	(-)	(-)	(-)	(-)	0.59
	2.1			2	20/7.7	20/7.9	180	(t)	(t)	(-)	(-)	(-)	0.69
	2.1			3	20/7.7	19/7.5	77	(-)	(-)	(-)	(-)	(-)	0.29
	2.1			4	19/7.4	19/7.4	170	(t)	(t)	(-)	(-)	(-)	0.65
HIGH DOSE	2.1	Blank	N/A	3	20/7.7	19/7.5	<5	(-)	(-)	(-)	(-)	(-)	N/A

NOTES:

- a) pH values were measured in blank samples
- b) The sample volume for each run was between 2.7 and 2.8 l
- c) Each run was 16 h
- d) (-) = Provisional assessment of analytical results for PAHs other than fluoranthene; t = trace, - = not detected

Table E7 Results of leach tests investigating the effect of contact with plastic pipe materials

Test series	Coupon number	Coupon area cm ²	Run No.	Pipe present	Sample volume, l	F	PAH, ng l ⁻¹ (d)			InP	Total	Fluoranthene leach rate ng cm ⁻² h ⁻¹	
							B(b)F	B(k)F	B(a)P				
MDPE	1	34.1	1	NO	2.7	32	(-)	(-)	(-)	(-)	(880)	0.16	
	7	30.3	2	YES	2.7	820	(0)	(0)	(0)	(60)	(-)	4.1	
	3	34.6	1	NO	2.7	9	(-)	(-)	(-)	(-)	(-)	0.05	
	8	37.3	2	YES	2.7	8	(-)	(-)	(-)	(-)	(-)	0.04	
	5	37.3	1	NO	2.65	14	(-)	(-)	(-)	(-)	(-)	0.07	
	17	35.0	2	YES	2.7	32	(0)	(0)	(0)	(0)	(0)	0.16	
	Blank	N/A	2	YES	2.7	58	(-)	(-)	(-)	(-)	(-)	0.26	
						2.7	39	(-)	(-)	(-)	(-)	0.18	
						2.7	68	(0)	(0)	(0)	(0)	(0)	0.31
						2.7	120	(0)	(0)	(0)	(0)	(0)	0.54
						2.7	38	(0)	(0)	(0)	(0)	(0)	0.18
						2.7	30	(0)	(0)	(0)	(0)	(0)	0.14
					2.75	6	(-)	(-)	(-)	(-)	(-)	N/A	
PVC	11	33.1	1	NO	2.7	6	(-)	(-)	(-)	(-)	(-)	0.03	
	20	37.3	2	YES	2.7	19	(0)	(0)	(0)	(0)	(0)	0.10	
	14	38.6	1	NO	2.7	50	(0)	(0)	(0)	(0)	(0)	0.23	
	24	32.7	2	YES	2.65	34	(0)	(0)	(0)	(0)	(0)	0.15	
	16	39.2	1	NO	2.7	61	(0)	(0)	(0)	(0)	(0)	0.27	
	34	35.0	2	YES	2.7	36	(-)	(-)	(-)	(-)	(-)	0.16	
	Blank	N/A	2	YES	2.75	42	(0)	(0)	(0)	(0)	(0)	0.22	
						2.75	17	(0)	(0)	(0)	(0)	(0)	0.09
						2.7	14	(-)	(-)	(-)	(-)	(-)	0.06
						2.8	<5	(-)	(-)	(-)	(-)	(-)	<0.02
						2.8	9	(-)	(-)	(-)	(-)	(-)	0.05
						2.8	10	(0)	(0)	(0)	(0)	(0)	0.05
					2.7	<5	(-)	(-)	(-)	(-)	(-)	N/A	

Table E7 continued

NOTES:

- a) pH values were measured in blank samples; all samples were between 7.6 and 7.8
- b) The temperatures of the water baths recorded at the beginning and end of all these tests were in the range 20 to 21 °C
- c) Each run was 16 h
- d) () = Provisional assessment of analytical results for PAHs other than fluoranthene; t = trace, - = not detected

Table E8 Results of leach tests investigating the effect of carbon dioxide content

Test series	Coupon number	Coupon area cm ²	Run No.	Sample volume, l	F	B(b)F	PAH, ng l ⁻¹ (d)		InP	Total	Fluoranthene leach rate ng cm ⁻² h ⁻¹		
							B(k)F	B(a)P					
HIGH CARBON DIOXIDE	2	35.0	1	2.69	45	(1)	(1)	(-)	(-)	(-)	0.22		
			2	2.75	49	(-)	(1)	(-)	(-)	(-)	(-)	0.24	
			3	2.69	29	(1)	(1)	(-)	(-)	(-)	(-)	0.14	
	4	48.1	1	2.70	150	(10)	(5)	(7)	(-)	(172)	(-)	0.53	
			2	2.73	770	(110)	(50)	(100)	(70)	(75)	(1175)	(-)	2.7
			3	2.70	50	(1)	(1)	(1)	(-)	(-)	(-)	(-)	0.18
	13	30.7	1	2.65	40	(*)	(12)	(1)	(1)	(1)	(52)	0.22	
			2	2.70	49	(1)	(1)	(1)	(-)	(-)	(-)	0.27	
			3	2.68	66	(1)	(1)	(1)	(-)	(-)	(-)	0.31	
	18	32.5	1	2.64	280	(30)	(15)	(30)	(15)	(20)	(390)	1.4	
			2	2.71	53	(-)	(1)	(-)	(-)	(-)	(-)	0.28	
			3	2.68	105	(1)	(1)	(1)	(-)	(-)	(-)	0.54	
	Blank		N/A	3	2.48	28	(-)	(-)	(-)	(-)	N/A		
LOW CARBON DIOXIDE	9	36.9	1	2.73	185	(1)	(1)	(-)	(-)	(-)	0.86		
			2	2.73	160	(-)	(1)	(-)	(-)	(-)	(-)	0.74	
			3	2.72	165	(1)	(1)	(1)	(-)	(-)	(-)	0.76	
	27	41.0	1	2.73	600	(80)	(40)	(80)	(55)	(50)	(905)	2.5	
			2	2.69	220	(-)	(1)	(-)	(-)	(-)	(-)	0.90	
			3	2.67	145	(1)	(1)	(1)	(-)	(-)	(-)	0.59	
	30	34.6	1	2.65	23	(-)	(-)	(-)	(-)	(-)	(-)	0.11	
			2	2.68	39	(1)	(1)	(1)	(-)	(-)	(-)	0.19	
			3	2.70	25	(-)	(1)	(1)	(-)	(-)	(-)	0.12	
	31	40.5	1	2.63	215	(7)	(3)	(6)	(1)	(1)	(231)	0.87	
			2	2.70	2300	(940)	(460)	(880)	(570)	(690)	(5840)	9.6	
			3	2.70	770	(80)	(40)	(60)	(40)	(60)	(1050)	3.2	
	Blank		N/A	3	2.75	87	(9)	(5)	(-)	(110)	N/A		

Table E8 continued

NOTES:

a) pH values were measured in blank samples:

HIGH CARBON DIOXIDE:			COUPONS 2 & 4			COUPONS 13 & 18			
Run	1	2	3	1	2	3	1	2	3
Start	7.2	6.1	5.8	7.2	6.2	5.9	7.2	6.2	5.9
Finish	7.2	6.0	5.9	7.3	6.3	6.0	7.3	6.3	6.0

LOW CARBON DIOXIDE:			COUPONS 9 & 27			COUPONS 30 & 31			
Run	1	2	3	1	2	3	1	2	3
Start	8.1	7.7	7.3	8.2	7.6	7.5	8.2	7.6	7.5
Finish	7.9	7.5	7.4	7.8	7.6	7.5	7.8	7.6	7.5

b) The temperatures of the water baths recorded at the beginning and end of all the runs tests varied by up to 0.5 °C.

All the tests were carried out in the temperature range 20.5 to 23 °C

c) Each run was 16 h

d) () = Provisional assessment of analytical results for PAHs other than fluoranthene; t = trace, - = not detected
 (*) = interfering peak