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EFFECT OF DISTRIBUTION ON ORGANIC CONTAMINANTS IN POTABLE WATER (EHT 9155)

Final report to the Department of the Environment

DoE 2215-M/1

MARCH 1990

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Report No: DoE 2215-M/1

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Authors: B Crathorne, C P James and M Norris

Contract Manager: M Fielding (A)

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Any enquiries relating to this report should be referred to the Contract Manager at the following address:

Water Research Centre (1989) plc, Henley Road, Medmenham, PO Box 16,
Marlow, Buckinghamshire SL7 2HD. Telephone: Henley (0491) 571531

SUMMARY

I OBJECTIVES

The objectives of the contract were:

i) to determine the effect of water supply distribution systems on organic contaminants present in finished water.

ii) to determine the effects on the organic content of distributed water of materials of construction and pipe and reservoir lining materials.

iii) to investigate the contamination of drinking water arising from mains renovation techniques.

II REASONS

Most studies to date on the nature of organic contamination of water supplies have focussed on raw and finished water samples. Little information is available on the fate of organic contaminants during distribution or on the introduction of new contaminants before water reaches the consumer's tap, eg by leaching from pipe materials or following application of mains renovation processes. The exposure of consumers to organic contaminants introduced during distribution either from materials of construction or by processes such as renovation needs to be assessed since such substances go directly to the consumer.

III CONCLUSIONS

Epoxy resin relining of cast iron water mains

Four hour cure process

The laboratory and field trials on the original process involving 4 hour cure prior to return to service showed that relatively high levels of organic contaminants leached into water during the first 24 hours after relining. A full report on the laboratory and field investigations was submitted to the DoE Committee on Chemicals and Materials of Construction for use in Public Water Supply and Swimming Pools (CCM), who were considering applications for approval of epoxy resin formulations for in-situ relining of water mains. The Committee concluded that the high levels of organic contaminants leached from the resins were unacceptable on health grounds.

Sixteen hour cure process

Extending the curing period substantially reduced the degree of leaching of organic contaminants from the resin into the water. Results from leaching tests were submitted to the CCM who concluded that a resin system could be used by the Water Industry, on a limited basis, in order that the process could be further developed.

Consideration of new toxicity data and additional leachate data has enabled full approval to be given for an epoxy resin formulation for the in-situ relining of water mains. One requirement was that the epoxy resin must be applied in accordance with various stipulations.

Organic compounds introduced into drinking water by plastic pipes

Leaching of organic contaminants from PE pipe

Laboratory studies showed that a variety of organic chemicals leach from blue MDPE pipe to give low concentrations in drinking water. These were generally substances used in the manufacture of the pipe such as antioxidants, UV stabilisers and their degradation products. The same substances were detected at very low levels in several field studies particularly from recently installed blue MDPE mains. In particular, Irganox 1010 and 1076 were found to leach from MDPE pipe and their degradation product, 2,6-di-tert-butyl-p-benzoquinone, was found to be a common contaminant in water distributed by MDPE pipe. This degree and type of leaching is not believed to be significant in relation to possible risks to health but some alkylated-p-benzoquinones have a strong tendency to cause tastes and further investigations would be prudent. Phthalimide was also found to leach from blue MDPE and this proved to be due to its presence as an impurity related to the blue pigment copper phthalocyanine. Results showed that while phthalimide could leach from new MDPE pipe its presence in water distributed through MDPE systems was very sporadic. Evidence for the formation of chlorophthalimide was obtained, but accurate quantitative analysis of this compound proved difficult due to its instability. There is little toxicological data for phthalimide and none for chlorophthalimide.

Leaching of organic contaminants from u-PVC pipe

Studies showed that a range of organic chemicals leached from new u-PVC pipe into water. However, the levels were very low and do not appear to pose any risks to health based on available toxicity data.

Leaching of organic contaminants from GRP pipe

A wide range of contaminants were found to leach into drinking water from GRP pipe including a range of phthalates and styrene. The leaching rates were appreciable although depletion with time would be expected.

Permeation of PE pipes by organic chemicals

Permeation by natural gas odorants

A contact time of at least 40 days was required for natural gas odorants to permeate blue MDPE and produce a discernible taste/odour in a water sample. Once breakthrough had occurred it appeared that at least two days were required for a sufficient amount of odorants to permeate the pipe and cause a slight off-taste. For a strong taste to be transmitted to the water a 7 day exposure to the pipe was required.

With the use of PE gas pipes, which are much less likely to leak than iron gas pipes, the likelihood of PE water pipes being exposed to natural gas for long periods seems remote.

Permeation of PE by potential soil contaminants

The laboratory experiments demonstrated that blue MDPE was readily permeated by non-polar chemicals such as toluene, slowly permeated by phenol, a more polar substance, but not permeated by more complex polar molecules such as the pesticides paraquat, malathion and atrazine. In additional experiments significant penetration of MDPE occurred with m-cresol, nitrobenzene, chlorobenzoic acid and cyclohexane. Although attempts were made, accurate prediction of the rate of permeation by chemicals from physical/chemical data could not be made. PE pipe is clearly vulnerable to permeation by certain chemicals which could lead to significant contamination of supplies, at least on a local basis.

Permeation of PE pipe laid in contaminated ground

No significant permeation of a MDPE service pipe (and a u-PVC fire main) installed in a contaminated land site was encountered. In view of the known susceptibility of MDPE to permeation by certain organic compounds, the experimental results appear surprising. However, the site was contaminated mainly with compounds thought not to readily permeate MDPE or u-PVC. In addition, it is possible that compounds bound onto soil particles may not be 'available' for permeation. The results from this investigation indicate that the effect of soil particles on permeation behaviour may be significant. Since the soil contaminants were specific to this particular site it was not possible to draw broad conclusions covering other sites, with different contaminants.

The effect of the distribution system on organic compounds in drinking water

The work carried out to determine the changes, during distribution, in the nature of organic contaminants present in finished water and also to identify any contaminants arising from the distribution system itself showed that few changes took place. However only one treatment works/distribution system was studied and it is possible that other systems may give different results.

A wide range of organic contaminants was always present in the finished water and virtually all of these were found in distributed samples, even at the extremities. Contaminants such as phthalates, atrazine, simazine and organic phosphates showed no marked changed in levels during distribution. THM levels increased through the distribution system, due to further chlorination reaction or breakdown of chlorinated THM precursors but TOC and AOX did not show any significant changes.

A small number of organic contaminants were found only in distribution samples. However, the source of these is difficult to explain in terms of our knowledge of distribution materials and other potential sources. The information gathered suggests that monitoring for the Water Supply (Water Quality) Regulations 1989 could be undertaken for some substances at supply points (treatment works, service reservoirs etc) rather than consumers taps. For example, this should be the case for atrazine and simazine.

Effect of mains renovation techniques on water quality

All the techniques studied led to levels of PAH in drinking water exceeding for a substantial period of time maximum values specified in the Water Supply (Water Quality) Regulations 1989. These techniques remove corrosion products from the inside of the mains which may uncover fresh coal-tar pitch surfaces from which leaching can take place. Subsequent work carried out by WRc Engineering, indicated that relining with epoxy resin reduced the PAH to acceptable levels. Clearly, use of the cleaning/renovation techniques described in the report without relining the pipe cannot be recommended at the present time.

Leaching of organic compounds into water from reservoir/tank linings

Only a limited amount of experimental work was possible on the leaching of organic contaminants from tank or reservoir linings. However the one product examined (an epoxy-resin based coating) did demonstrate that a relatively high concentration of one of the ingredients used in the formulation could leach into water in the short term, although this level did rapidly reduce with time. Although it is difficult to use the results from the epoxy resin coating studied to predict the behaviour of other coatings, it does appear likely that some ingredients in any product will leach into water, particularly in the first few hours after application and following the first contact with water.

General conclusions

The work has shown that the distribution system is a potential source of organic contamination of drinking water. This is important bearing in mind that distributed water goes directly to the consumer. Thus it is vital to ensure that distribution materials and processes do not lead to significant organic contamination of supplies. Currently this is covered mainly by the Committee on Chemicals and Materials of Construction for use in Public Water Supply and Swimming Pools (CCM) and to some extent the Water Byelaws Advisory Scheme.

Organic substances can enter supplies in several ways, ie leaching from plastic materials, application of renovation processes and permeation of certain plastic pipes. Some introduction of organic chemicals from such sources is inevitable at some level, particularly in the early stages - ie with a newly laid pipe or after a recent renovation. This is not significant in itself. However, it is important to fully evaluate materials and processes prior to use with respect to any potential to introduce, or cause, significant levels of organic contamination. Such evaluation inevitably requires complex trace organic analysis for known substances (formulation components) and unsuspected components (formulation impurities, byproducts etc) - the latter needing techniques such as gas chromatography - mass spectrometry (GC-MS). An assessment of the possible effect of chlorine (or any other disinfectant in supply) is essential in many cases. This is because new chemicals could be formed.

An outcome of this work has been that the CCM has largely incorporated several of the methods or approaches developed into their approval scheme for materials and chemicals for use in contact with potable water.

At the present time the testing of materials is being considered by several EEC Committees with a view to establishing standard methods for EEC countries. In many ways the UK systems for evaluating materials is more stringent than the schemes operated in other countries. Such schemes rarely include any evaluation of unsuspected chemicals. Consequently the strength of the UK approach needs to be included in any future EC protocol.

IV RECOMMENDATIONS

General

It is recommended that materials, chemicals and processes connected with the distribution system are rigorously evaluated before use for any potential to cause significant levels of organic contamination. This assessment requires complex trace organic analysis, not only for the known formulation constituents but also for unsuspected impurities and byproducts using techniques based on mass spectrometry. In addition, the effect of chlorine (or any other disinfectant in supply) needs to be evaluated. Such evaluations need to be carried out where appropriate under realistic conditions. It should be noted that during the duration of this project these recommendations have been largely incorporated into the approval scheme operated by CCM. The Water Bill has added mandatory power to the UK approval scheme and the CCM is under revision. It is recommended that the vigorous approach of CCM is maintained and that the new revised scheme is made more 'visible' to industry.

The more stringent UK approach should be incorporated in any new scheme developed by the EEC Committees. Possibly the data in this report could help in assuring this.

Specific

1. Recommendations associated with the work on in situ applied epoxy resin have been made to CCM during the progress of the work and have been acted upon. With the emergence of an approved relining system the only recommendation now is that the associated stipulations aimed at assuring the quality of the applied lining are strictly followed.

2. With respect to leaching from plastic pipes;

   - more toxicological data on phthalimide and 2,6-di-tert-butyl-p-benzoquinone (impurities in blue MDPE pipe) would be of value in assessing their significance. Further investigation of the taste potential of the latter would be prudent.

   - more investigation of the leaching of organic substances from GRP pipe is needed.

3. PE pipe is vulnerable to permeation by certain organic chemicals when they contaminate soil. However, it is difficult to accurately predict the degree of permeation and subsequent contamination of drinking water; further work in the area is needed.

4. The application of the aggressive pipe renovation techniques described in the text led to significant contamination by PAH. Consequently, is it recommended that further investigations are carried out on water quality effects arising from these and other renovation techniques. The renovation techniques studied in this work should not be used without subsequent relining of the mains.

5. Further work is needed on the leaching of organic contaminants from reservoir/tanks linings. While new products are covered by the CCM scheme (and probably its successor), older products may need some re-evaluation.

V RESUME OF CONTENTS

The report covers studies aimed at assessing the potential for organic chemical contamination of water supplies in the distribution system and includes, pipe renovation techniques, especially *in situ* epoxy resin relining, leaching from plastic materials and their permeation by chemicals from contaminated soil. In addition a detailed investigation was carried out on the effect of distribution on the range of organic chemicals in finished water.

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PREFACE

The work covered by this report was funded by the Department of the Environment. It began 1 August 1983 and was extended on 1 August 1987 and subsequently on 31 April 1989. It finished on 31 September 1989.

SECTION 1 - INTRODUCTION

Most studies to date on the nature of organic contamination of water supplies have focussed on raw and finished water samples. For example, most of the routine analytical work carried out by water authorities and much of the research work on organic contaminants in water supplies has involved monitoring water samples at the intake to a treatment works and water samples leaving the treatment works. Little information is available on the fate of organic contaminants during distribution or on the introduction of new contaminants before water reaches the consumers tap, eg by leaching from pipe materials or following application of mains renovation processes. The exposure of consumers to organic contaminants introduced during distribution needs to be assessed since such substances will go directly to the consumer. In addition, the EC Directive on the Quality of Water for Human Consumption (the Drinking Water Directive 80/778/EEC) applies to water at the consumer's tap. It is therefore important to obtain information on the behaviour of organic contaminants during distribution. This might help to decide whether, for some parameters, compliance with the Directive could be monitored at the water treatment works.

1.1 PIPE RENOVATION TECHNIQUES

Potable water is supplied to the consumer via a complex network of reservoirs and underground pipework. The development of these water distribution systems has followed population growth and industrial expansion. In the UK, over 99% of the population has access to a mains supply and this is achieved by approximately 340 000 km of trunk and distribution mains and a similar length of the smaller service pipes(1).

Problems from corrosion of old cast-iron mains have led to the development of renovation techniques as a cheaper alternative to renewal. Such techniques involve the removal of corrosion products, cleaning the pipe and, in some cases, relining to improve water quality and flow.

Until recently cement mortar and bitumen were the only relining materials used and each material has limitations. Bitumen is not very durable(3) and cement mortar can cause unacceptably high pH values in some soft waters. It was apparent that an alternative lining material was needed to satisfy all the requirements of the Water Industry. Preliminary investigations suggested that epoxy resins were the most suitable materials as they offered sufficient durability, had no effect on the pH of soft waters, and the smooth finish achieved gave a high carrying capacity to the main.

Insufficient information existed, however, on the effect on water quality of organic contaminants that may leach from sections of pipe relined in situ with epoxy resin. This report includes work carried out to monitor organic contaminants leaching into water from in situ applied epoxy resin linings and which subsequently led to a fully-approved process now in routine use in the water industry(4,5).

Concern has been expressed about the possible adverse effects on water quality following the application of aggressive renovation or cleaning techniques without subsequent relining of the pipe. For example, observations have shown that removing tuberculations can cause discoloration of water in the short term. It is also possible that in the case of coal-tar pitch lined mains, removal of the corroded surface, will expose a fresh surface of coal-tar pipe to the water and may lead to an increase in the levels of polycyclic aromatic hydrocarbons (PAH) and inorganic contaminants such as iron. However, little systematic monitoring has been carried out to monitor this observation and an investigation of effects on water quality following the application of aggressive cleaning techniques has been carried out as part of this contract. It should be noted that about 85% of the water mains in the UK are constructed of cast iron and, until about 1977, the majority of these were coated internally with coal-tar pitch. Coal-tar pitch can contain up to 50% PAH and thus there is potential for leaching these substances into the water supply. A survey of PAH levels in British waters(2) showed that very low levels of PAH can often be detected in water that has passed through pipes lined with coal-tar pitch.

1.2 THE USE OF PLASTIC WATER PIPES

In the UK there is an increasing use of plastics for pipeline materials and they now represent about 50% by length of current usage, about 80% of which is in nominal diameters of 150 mm or less. The materials used are predominately unplasticised polyvinyl chloride (u-PVC) and medium density polyethylene (MDPE) while a much smaller amount of glass reinforced plastic (GRP) is used(6). Pipes made of plastic offer many technical advantages over traditional materials; they do not corrode, are lightweight and less expensive.

Polyethylene (PE) was first produced on a commercial scale late in the 1930's and has been refined and improved by polymer engineering over the intervening years. There are many forms or categories of the material but in the manufacture of pipes the categories are generally described by reference to their molecular density, ie low, medium and high. Both the low and high density materials have been used in the Water Industry since the 1950's with varying degrees of success. More recently there has been a considerable expansion in the use of MDPE and a wide range of pipe sizes are now available and are becoming widely used.

u-PVC has been used for the installation of new mains although very little has been laid as service pipe. This is mainly because of its lack of flexibility compared to polyethylene(6).

The use of GRP pipe for potable water supply is increasing, although it is generally restricted to large diameter trunk mains. GRP is a composite material which consists primarily of glass fibres embedded in a polymerised resin matrix. Unsaturated polyester resins are most commonly used for the manufacture of GRP pipe for potable applications in the UK.

The leaching into water of organic and inorganic compounds from materials which are used in contact with water has been studied in detail in only very few instances(7,8,9). In recent years, materials approved for use in contact with potable water by the DoE Committee on

Chemicals and Materials of Construction for use in Public Water Supply and Swimming Pools (CCM) would have been assessed for their potential to leach ingredients used in their manufacture into water. Testing procedures now specified by the CCM were developed as part of the work described in this report.

The work carried out as part of this contract on the leaching into water of ingredients used in manufacturing plastic pipe was stimulated by work carried out by WRc in 1983, which revealed that since the mid 1970's a number of taste and odour complaints had been received by the water industry that were linked with PE pipes. Subsequent work at WRc showed that the cause was an antioxidant used in the production of MDPE pipes(10). This work led to the use of an alternative antioxidant. Since insufficient was known in general about the leaching into water of organic compounds present in the formulations of MDPE, u-PVC and GRP pipes, a series of laboratory and field trials were undertaken to gather basic information on this subject. During the course of this work general material testing methods were devised.

The ability of a wide range of organic compounds to permeate plastic pipes has been known for a number of years(11). For example, several cases of failure of u-PVC pipe have been reported following the spillage of petrol or other petroleum products near to the pipe(12). Evidence emerged in the late 1970's that contamination of drinking water can occur from permeation of plastic pipes in polluted soil in situations other than gross contamination. For example, it has been shown that low molecular weight, relatively non-polar compounds such as benzene, toluene, trichloroethylene, chlorobenzene etc will readily permeate PE. However, the number of compounds tested was small and no data were available on the possible penetration of PE by more complex, polar organic compounds, such as commonly used pesticides, which may occur as soil contaminants. This contract has investigated the phenomenon of permeation of plastic pipes by organic chemicals in three ways. Laboratory experiments were carried out to determine whether natural gas odorants would permeate MDPE pipe and cause taste and odour problems in the conveyed water. Further laboratory work was commissioned at

Pipeline Consultants Ltd where a technique using radio labelled standards was used to measure the rate of permeation of a variety of organic chemicals through MDPE pipe. Finally, investigations were carried out at a contaminated land site at which MDPE and u-PVC had been laid. The permeation through the plastic pipes of organic contaminants in the soil was monitored over an 18 month period.

1.3 THE FATE OF ORGANIC MICROPOLLUTANTS IN THE DISTRIBUTION SYSTEM

Most of the published analytical work on drinking water refers to the analysis of finished water samples, ie water from a treatment works immediately before distribution. Gas chromatography-mass spectometry (GCMS) has provided much of the data on the range of compounds present in such samples. However, there is little information available about the behaviour of organic compounds during distribution. For example, organics present in the water could degrade and volatile compounds may evaporate. The potential for contamination within the distribution system from plastic pipes, renovation processes and permeation from contaminated grounds have been studied as part of this contract. Little is known, however, about other sources of organic micropollutants in distribution systems which would be supplied directly to consumers. Investigations on the behaviour of organic contaminants during distribution have therefore been undertaken. This involved a detailed study of the range of contaminants present in water samples taken from various points of one distribution system.

1.4 THE USE OF RESERVOIR/TANK LININGS

A range of linings are used by water undertakers as protective coatings for reservoirs and water tanks. Several products have been approved under the Water Byelaws Advisory Service (WBAS) and are listed in the Water Fittings and Materials Directory. However, the WBAS scheme is designed to monitor only for general effects on water quality and carries out testing for taste and odour, the leaching of metals, the ability to support microbial growth and cytotoxicity. The use of products, which may contain a variety of organic chemicals, for lining reservoirs and tanks for use in contact with potable water may lead to the leaching of low levels of such chemicals into the water. The presence of these chemicals may not be detected by the WBAS tests. More information was therefore needed on the potential for leaching contaminants into the water from such products. Such information may be useful in assessing whether current practice in the water industry with this type of product needs to be reviewed.

SECTION 2 - EPOXY RESIN RELINING OF CAST IRON WATER MAINS

2.1 INTRODUCTION

The total length of the UK water mains is currently estimated to be 340 000 km, the majority of which is in the small diameter range as illustrated below:

Diameter (mm)	%
50 - 150	81.9
151 - 300	11.3
301 - 600	5.3
601 and above	1.5

The percentage of total lengths of each material currently in use in UK water distribution systems is as follows:

Material	%
Cast Iron	85
Steel, Asbestos Cement, Concrete	10
uPVC	5

From this information it can be seen that about 70% of the distribution system comprises small diameter cast iron mains. These mains were traditionally protected internally and externally by a thin (0.1 mm) coal-tar pitch, or less frequently, bituminous, coating.

About half of the waters conveyed by cast iron mains can be considered to be aggressive to the pipe material. Under these conditions the coal-tar pitch/bitumen lining breaks down, leading to a range of problems. These include:

a) consumer complaints of discoloured water and poor supply;
b) an increased risk of water mains bursts;
c) an increase in the growth of micro-organisms.

As corrosion proceeds, the iron is converted into various forms of iron oxide which can either be released into the water and cause discolouration or remain attached to the pipe wall leading to blockages and subsequent poor pressure at the consumers tap. The loss of iron from the pipe wall reduces the strength of the pipe which can lead to failure and subsequent bursts. The internal surface of the corroded pipe is as ideal support for microbial growth. The growth of these micro organisms can lead to the loss of chlorine residuals and the depletion of the dissolved oxygen level, often leading to unpalatable water.

There is therefore a potential for about 50-100 000 km of water mains to require attention during the next 30 years. The most effective options for overcoming the problems associated with cast iron mains are to replace the corroded pipe with a new one or to renovate the old pipe. The renovation process involves the mechanical scraping of corrosion debris out of the main and then applying a lining on to the inside of the main. The most common material used for lining is cement mortar, but this technique has some disadvantages:

a) In some situations, particularly in areas supplying soft water, there can be problems of high pH after lining

b) The rough 'orange peel' finish produces a high hydraulic roughness factor reducing flow capacity in comparison with a new pipe.

Alternative materials which can overcome these problems are bitumen and epoxy resin. Because of lack of durability the use of bitumen is not now widely practised. A more recent development has been the use of epoxy resin which is durable. The development of the in situ applied epoxy resin relining process in use in the water industry today has taken place through various stages.

The development began in 1977 with laboratory and field trials on equipment and process design. This led to the production of a solvent-free epoxy resin, applied with a system which enabled relining of a pipe and return to service in the same day. This process employed a four hour period for curing the resin following application to the pipe, followed by flushing to waste for 1 hour before return to service. The manufacturers of the in situ applied epoxy-resin linings sought the approval of the DoE Committee on Chemicals and Materials of Construction for use in Public Water Supply and Swimming Pools (CCM) for the use of their products in contact with potable water. Following a request from the CCM for information on compounds used in formulating the resins leaching into water from the applied lining, an extensive series of laboratory and field trials were undertaken on two resin systems.

The results from these investigations showed that relatively high concentrations of some ingredients could be leached into the water under certain circumstances during the first few hours after the relined pipe was returned to service. In particular, dead-end mains in which the water in the pipe could be stagnant and in contact with the epoxy resin lining for up to 10 hours (ie overnight) were shown to be a potential problem. The high concentrations detected under these circumstances were considered by the CCM to be unacceptable and this led to the development of an alternative process. This process was based on an extended time for the resin to cure, ie a minimum period of 16 hours before flushing to waste for 1 hour and then return to service.

The change to an extended air-cure period was accompanied by minor refinements by the manufacturers in the epoxy resin formulations used for in situ applications. A further, extensive series of laboratory and field trials were therefore undertaken to monitor the leaching of organic contaminants from the reformulated epoxy resin linings applied using the extended air-cure process. The results showed that much lower levels of organic contaminants leached into the water compared to the 4 hour cure system. The results were sufficiently encouraging for the modified process to be granted interim approval by the CCM for limited use in the water industry so that further data could be gathered, modifications to the process investigated and a detailed quality assurance scheme developed to ensure that linings were always applied correctly. At the same time, toxicological studies on the organic compounds found to leach from the epoxy resins were commissioned. The toxicological data generated would enable an opinion to be provided by medical advisors to the CCM on any potential effects on health of consumers from the ingestion of water containing low concentrations of these compounds.

During the two year period in which the toxicological data were generated, additional information was obtained on the leaching into water of specific organic contaminants from a series of field trials. These were designed to gather data on the influence of factors such as water temperature, general water quality and age of the lining.

The final reports on toxicology, leachate information and the quality assurance schemes have recently been considered, with the result that the only submission to CCM to be maintained, Geopox GX 014 epoxy resin, has been fully approved by the CCM for use in contact with water (supplement to the 15th statement).

2.2 BACKGROUND TO THE WORK AND EXPERIMENTAL DESIGN

2.2.1 Background to the work

In 1981 WRc, and initially STWA, undertook a limited programme of work to try to identify organic compounds leaching from epoxy resin applied to water mains(13). The study was carried out on water collected from two sites at which sections of water main were being lined with epoxy resin. Initially two samples were studied from each site, (a) taken immediately on resumption of public supply and (b) taken from the same point 14 days later. In addition, further samples were taken 6 months after the relining had been carried out.

The results showed that many compounds present in the resin and hardener formulations were leached into the water passing through the relined pipe. Most of the compounds detected in the sample taken immediately on resumption of supply were also present in the sample taken 14 days after relining and several compounds were still detectable in the sample taken six months after relining.

Table 1 lists the compounds identified in this study (major components only). Due to the nature of the work carried out it was not possible to give reasonably accurate estimates of the levels of most of the compounds detected. An assessment of any risk to health due to the presence of these compounds in drinking water could not be made without more information on the amount of each compound present in the water.

2.2.2 Limits of detection

Before reasonably accurate quantitative data could be provided, a detection limit had to be set for each substance(s) of interest so that analytical methods could be developed. Therefore, toxicological assessments were undertaken, substances for which exposure data, was required and limits of detection suggested (Table 2).

Table 1 - Compounds identified in water after passing through water mains lined with epoxy resin

Benzyl alcohol
Bisphenol A diglycidyl ether
Bisphenol F diglycidyl ether
Dimethyldiheptadecylammonium bromide
Dimethyldioctadecylammonium bromide
Tetradecyltrimethylammonium bromide
Isophorone diamine
2,2,4-Trimethylhexamethylenediamine
Salicyclic acid
p-Toluenesulphonic acid

Table 2 - Compounds of interest and limits of detection

Substance(s)	Limits of detection in $\mu g\ l^{-1}$ (individual substances)	
	Required	Achieved
Quaternary ammonium compounds	3	5
Bisphenol diglycidyl ethers	1	1
Diamines	1	1
p-Toluenesulphonic acid	1	5

These evaluations and limits of detection were derived by WRc in close consultation with DHSS.

All those compounds identified in the original qualitative work (Table 1), with the exception of benzyl alcohol, isophorone diamine and salicylic acid which were removed from the epoxy resin formulations before this work was undertaken, were included in the work carried out and reported here.

2.2.3 Field versus laboratory assessment of leaching

The assessment of the concentration of specific organic compounds in water flowing through an epoxy-resin-lined system could have been tackled in two ways. One way would have been to measure concentrations at a consumer's tap situated down flow of a freshly relined water main. This would, however, only have provided data for the system under examination at the point from which the sample was taken and would not have been applicable to other systems with different characteristics. A second approach, would have been to measure, under controlled conditions in the laboratory, the leaching rate of specific organic compounds using small test cells. This data, along with typical flow data, could then be used to estimate the likely concentration at a consumer's tap. This second approach formed the basis of the initial work. The approach enabled the estimation of the concentration of leached organics at consumer's taps over a range of circumstances such as:

i) systems with varying water demand;
ii) lengths of sequentially lined pipe;
iii) dead ends, ie situations in which demand may be low and water supplied through a series of relined lengths;
iv) feed mains, ie where demand will be high and the sequential effect low.

Laboratory leaching tests were therefore used extensively to predict the likely range of concentrations of organic contaminants present in water exposed to epoxy resin linings. Subsequently, however, more time-consuming and expensive field trials were conducted. These were needed in order to confirm predictions made from laboratory experiments and also to provide data on leachate concentrations which would occur during the routine use of this process in the water industry.

The field trials conducted were designed to represent likely worst cases, ie a 100 mm diameter main running to a dead-end and supplying a small number of consumers. This situation could give rise to high concentrations of organics in the water due to the long residence times (eg about 10 hours) of water in the main during overnight periods. These conditions would not apply to most water pipes relined with epoxy resin since these are through mains with higher flows of water resulting in lower residence times and, consequently, reduced concentrations of organics.

2.3 EXPERIMENTAL

2.3.1 Analytical methodology

Suitable analytical methods were developed for the following compounds: bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, 2,2,4-trimethylhexamethylenediamine, p-toluenesulphonic acid and various quaternary ammonium compounds(14,15,16,17,18).

(a) Sampling

Samples (2.5 l) were taken directly from the test site by completely filling glass bottles equipped with ground glass stoppers. For the laboratory experiments this involved emptying the contents of the test cell into the glass bottle. For field experiments a suitable tap was installed at the end of the relined section of pipe. All tap samples were taken after running water to waste for at least 3 minutes. When it was not possible to concentrate samples immediately, they were stored in the dark and kept as cool as possible. Limited experiments on the stability of samples during storage were carried out and the results showed that no deterioration could be observed following storage for up to 24 hours.

(b) Extraction/concentration techniques

The method of extraction and concentration used for each determinand is summarised in Table 3.

Table 3 - Extraction/concentration techniques

Determinand	Sample volume	Extraction technique	Concentration technique
Bisphenol A and bisphenol F diglycidyl ethers	500 ml	Absorption into C_{18} bonded silica. Desorption by elution with methanol-dichloromethane.	Under a stream of nitrogen.
2,2,4-Trimethylhexamethylenediamine	100 ml	Acidification (pH2) followed by vacuum evaporation to dryness. Derivatisation using 2N NaOH/benzoyl chloride followed by extraction into diethyl ether.	Under a stream of nitrogen.
p-Toluenesulphonic acid	100 ml	Vacuum evaporation to dryness. Methanol extraction of the solid residue.	Rotary evaporation with adjustment to final volume under a stream of nitrogen.
Quaternary ammonium compounds	500 ml	Acidification (pH2) followed by solvent extraction with dichloromethane.	Rotary evaporation with adjustment to final volume under a stream of nitrogen.

(c) Separation/quantification techniques

Separation and quantification techniques are outlined in Table 4.

High performance liquid chromatography (HPLC) was used as the separation technique for all determinands except the quaternary ammonium compounds. These compounds are not amenable to conventional

Table 4 - Separation/quantification techniques

Determinand	Technique
Bisphenol A diglycidyl ether	Separation using reversed phase high performance liquid chromatography (HPLC). Quantification based on separation of standards under identical conditions and comparison of response to an ultra violet detector (uv) at 275 nm.
Bisphenol F diglycidyl ether	Separation using reversed phase HPLC. Quantification based on separation of standards under identical conditions and comparison of response to a uv detector at 275 nm.
2,2,4-Trimethylhexamethylenediamine	Separation and quantification as above with uv detection at 240 nm
p-Toluenesulphonic acid	Separation using ion pair HPLC. Quantification as above with uv detection at 254 nm.
Quaternary ammonium compounds	No separation technique was used. Fast atom bombardment mass spectrometry was used to monitor compounds of interest. Specificity was obtained by accurately focusing the instrument on the molecular ion. Quantification was based on relative response compared to an internal standard added to the water sample before extraction.

HPLC detection techniques and were therefore monitored using fast atom bombardment (FAB) mass spectrometry.

Quantification using HPLC was achieved by analysis of known amounts of the compound to be monitored under specific elution conditions. Analysis of the water extract under identical conditions to those of the known compound indicated the presence of that compound in the original sample. Quantification was then achieved by a comparison of the response (based on ultra violet absorption) of the standard and sample.

The nature of FAB mass spectrometry is such that only very approximate quantitative data can be readily obtained from complex water extracts. This is a result of the altered instrumental characteristics of compounds when analysed as part of a mixture compared to that of the pure compound. Quantification in this instance was achieved by addition of an internal standard (in this case, a compound similar to that being monitored) to the water sample before extraction. Quantification was based on the relative response of the internal standard and the compound of interest.

(d) Analytical errors

The method developed for each determinand was tested by analysis of water samples to which had been added a known amount of the compound of interest. The recovery of each compound was determined by analysis of samples over a range of concentrations, ie from the detection limit up to the maximum concentration expected. For these experiments, recoveries were determined over the range of interest. The results are listed in Table 5.

Table 5 - Results of recovery experiments

Determinand	Recovery
Bisphenol A and bisphenol F diglycidyl ether	80-95%
2,2,4-Trimethylhexamethylenediamine	60-80%
p-Toluenesulphonic acid	40-75%
Quaternary ammonium compounds	Accurate recovery figures cannot be given (see Section 2.3c), but were probably in the region of 40%.

An average recovery of 60% was assumed for the results of the p-toluenesulphonic acid determinations and 70% for the results of the 2,2,4-trimethylhexamethylenediamine determinations. All figures for these determinands were adjusted accordingly. Quantitative recoveries were assumed for bisphenol diglycidyl ethers. In order to account for variations in recovery, differences in experimental conditions etc, it was estimated that all figures were subject to a maximum error of ±30%. Actual errors were likely to be smaller than this but it was not possible to carry out sufficient work on recoveries to calculate a more accurate figure for each determinand.

2.3.2 Laboratory leaching tests

The test rig consisted of a Pyrex glass chromatography tank capable of holding the four glass test plates and 2.5 l of test water. This is shown in Figure 1. The material under test was coated on one side of each of the glass plates and immersed in the test water. The surface area to volume ratio of the exposed plates and the water were the same as that of a 100 mm diameter pipe. To ensure adequate adhesion of the epoxy resin, ground glass plates were used throughout the trials.

Before use all the glass surfaces in contact with the test water and epoxy resin coatings were cleaned with a proprietary inert cleaning agent using a standard procedure. To avoid organic contamination or extraneous microbiological activity, the test vessels were covered and held in the dark in an environment free from organic vapours. The test containers were agitated at regular intervals.

Resin and hardener, previously stored at the temperature at which the plates were to be cured, were measured into a beaker in a known ratio by weight using a laboratory balance. The two components were rapidly mixed for 2 minutes using a spatula, and then quickly poured onto the centre of the plate to be coated. This plate was surrounded by glass of 1 mm greater thickness thus forming a well. The mixed resin was then spread using a metal former to ensure 1 mm thickness and any excess material removed.

Table 6 - Laboratory leaching experiments

Resin System	Date	Air cure time (hr)	Cure temp (° C)	Period of flushing (hr)	Samples taken for analysis (hr)
Sikagard DW2	29.11.83	4	10	1	0.5, 1, 2, 4, 7, 22
	25.01.84	4	10	1	0.5, 1, 2, 4, 7, 22, 44, 98, 140, 332, 502, 694, 842, 1004
	05.11.84	16	10	1	1, 4, 7, 22
	20.11.84	24	10	1	1, 4, 7, 22
	05.12.84	16	5	1	1, 4, 7, 22
modified	28.01.85	16	10	1	1, 4, 7, 22
Geopox GX-012	07.12.83	4	10	1	0.5, 1, 2, 4, 7, 22, 46, 97, 142, 190, 332, 380, 692, 1004
Modification 1	11.01.84	4	10	1	0.5, 1, 2, 4, 7, 22, 44, 165, 476
Modification 2	22.11.84	16	10	1	1, 4, 7, 22
Modification 3	29.01.85	16	10	1	1, 4, 7, 22
Modification 4	06.02.85	16	10	1	1, 4, 7, 22
Modification 4	04.03.85	16	10	1	1, 4, 7, 22

The plates were then air cured in an incubator for a given period of time at about 95% relative humidity to similate curing in the field. After approximately 2 hours the resin was sufficiently hard to allow the side plates forming the well to be removed. At the same time any residual resin was removed and the plate returned to the incubator.

One extra plate was coated on each occasion and retained for physical examination to ensure that the materials were representative of field applied linings in terms of thickness, pin-holes and mix efficiency.

After 4 hours the plates were removed and immersed in a glass vessel containing 2.5 l of water chlorinated at 25 mg $l^{-1}Cl_2$. After a 15 minute contact time the plates were removed and immediately flushed.

The test plates were placed in a specially constructed flushing rig (see Figure 2) and flushed at 0.5 m sec^{-1} velocity for 1 hour at a water temperature between 7-10 °C. Flushing rates were controlled and recorded using a Quadrina Q flow turbine meter and Spectroscan data loggers. On the completion of the flushing the plates were immediately placed in the test container and kept in a temperature controlled environmental cabinet at 10 °C ± 2 °C. This is representative of the water temperature in water mains for a large proportion of the year.

A large number of laboratory leaching experiments were carried out during the course of the work on epoxy resin relining and these are summarised in Table 6. The sampling frequency adopted depended largely on the type of experiment being undertaken. When sampling, the total volume of the test cell was removed and the vessel refilled with water previously held at 10 °C. In addition to replenishing after sampling the water in the test cells was changed every 2 to 3 days.

2.3.3 Field trials

Field trials were conducted on both abandoned and live mains with the co-operation of the appropriate water authority or water company. A summary of all the field trials undertaken is provided in Table 7. All trials were carried out on dead-end sections of mains in order to simulate a likely worst case situation for consumers regarding exposure to components leached from the lining into the water.

The Geopox linings were applied by Mercol Descaling Co Ltd using standard cleaning and lining equipment. The resin and hardener components were heated to 13 °C and 16 °C respectively and were mixed using a Mercol static mixer. The material was centrifugally spray applied at a lining rate of 1.9 m min^{-1}.

The Sikagard linings were applied by Stamford Construction Ltd also using standard cleaning and lining equipment. The resin and hardener components were heated to approximately 30 °C and were mixed using a Graco static mixer. The material was centrifugally spray applied at a lining rate of 1.8 m min^{-1}.

Once the linings were complete the main was capped off to prevent contamination and allowed to cure for a given period of time (see Table 7). Once the cure period was completed the mains were reconnected using short lengths of pipe disinfected with a solution of sodium hypochlorite before fitting. At the downstream end a quantity of calcium hypochlorite powder sufficient to give a nominal 25 mg l^{-1} concentration of free chlorine in the main was introduced into the short length of pipe before connecting up to the main. The main was slowly filled until a free chlorine residual could be measured at the outlet stand pipe. At this point the main was shut off and allowed to stand for 15 minutes. On all occasions the maximum free chlorine residual measured was 15 mg l^{-1}. The relined section of main was then flushed to waste for 1 hour at a velocity of 0.5 m sec^{-1} after which it was returned to service.

At the end of the water sampling programme, pipe samples were taken from the centre of each relined section for assessment of lining quality in the laboratory. These assessments included lining thickness, the number of pin-holes and mix efficiency and were carried out at the WRc Swindon laboratory.

Table 7 - Summary short term field trials undertaken

Resin System	Date of relining	Air cure time (hr)	Cure temp (°C)	Period of flushing (hr)	Samples taken for analysis	Comments
Sikagard DW2 (i) dead end mains	01.05.84	4	12.5	1	0,0.5,1,2,12,16, 36,42hr.	Normal flow conditions.
(ii)	02.05.84	4	12.8	1	0,1,13,16,19,22hr.	Extra flow for first 24 hours.
Abandoned main	16.05.85	17.5	10.1	1	1,4,7,18,29,43,67, hr, 22 days, 3 and 5 months.	Simulated flow conditions.
Live main (A)	16.09.85	17	16.8	1	1,30,44,68 hr.	Extra flow for first 24 hours.
(B)	23.09.85	19	16.5	1	1,29,43,45,67,166 hr. 1.5* and 48hr*.	Extra flow for first 24 hours.
(C)	14.10.85	16	16.5	1	1,29,42,66 hr.	Extra flow for first 24 hours.

Table 7 - continued

Resin System	Date of relining	Air cure time (hr)	Cure temp (°C)	Period of flushing (hr)	Samples taken for analysis	Comments
Geopox GX-012 (i) dead end main	10.04.84	4	7	1	0,0.5,1,2,12,16, 36,42hr.	Normal flow conditions.
" " (ii)	11.04.84	4	7	1	1.5,6,12,18hr.	Extra flow for first 24 hours.
Abandoned main (A)	18.03.85	20	4	1	1,4,7,18,28,42,69 hr, 30 days, 2 and 4 months.	Simulated flow conditions.
Live main 100:42 (B)	14.04.86	16	4.5	1	1,32,44,68hr.	Extra flow for first 24 hours.
100:40 (C)	21.04.86	16	4	1	1,30,45,68hr	Extra flow for first 24 hours.
100:41 (D)	28.04.86	16	4	1	1,29,41,67hr	Extra flow for first 24 hours.

* Results from length B were higher than expected and it was suspected that a malfunction had occurred during application. Extra samples were analysed and as a precaution the lenghth of main was overlined with epoxy resin. Two additional samples were analysed from the overlined length

Flushing rate, simulated flow on abandoned mains and consumer demand were measured using a combination flow meter arrangement comprising a single 80 mm Kent Helix 3000 and two 15 mm PSMT meters. The rig was arranged with valves such that any combination of meter could be used to suit the demand required. Flow data was recorded using Spectroscan data loggers and an on-site read out was available for a visual display if required. At the inlet end of each relined section of main, a meter was installed to monitor water flow. Samples were collected via a stand-pipe sample tap arrangement at the end of each relined section of main. The sample regime was designed to give information over the period when the main was first returned to service and subsequently at periods of low flow. The sample times for each site are given in Table 7.

Field trials on abandoned mains were carried out on lengths of main on which a simulated flow pattern, typical of a dead-end main supplying a small number (about ten) of consumers, was induced. Several samples were generally taken during the first 72 hrs after the pipe was 'put back into supply' in order to monitor the relatively high leachate concentrations expected during this time. If necessary sampling was continued at less frequent intervals for up to five months after relining, to determine long-term leachate concentrations. After the initial 72 hr period, three replicate samples (taken at about 5 min intervals) were analysed in order to check on the consistency of results; results were satisfactory.

2.4 RESULTS AND DISCUSSION

2.4.1 Four-hour cure process

(a) Laboratory experiments

Typical results from the laboratory leaching experiments on the four hour cure process are provided in Table 8. Also included are the leaching rate for each compound calculated from the concentration measured and the time each sample was in contact with the resin.

Table 8 - Results from typical laboratory leaching experiment 4 hour cure process

		TMHD*		PTSA*		Bis A + Bis F*	
Sample (hr)	Time in cell (hrs)	Conc μg l^{-1}	Leaching rate μg l^{-1} hr^{-1}	Conc μg l^{-1}	Leaching rate μg l^{-1} hr^{-1}	Conc μg l^{-1}	Leaching rate μg l^{-1} hr^{-1}
0.5	0.5	122	244	605	1210	227	454
1	0.5	120	240	410	820	257	514
2	1	196	196	770	770	357	357
4	2	315	157	1093	547	928	469
7	3	745	248	1405	468	877	292
22	15	130	86.7	3422	228	1554	104
44	22	458	20.8	726	33	872	40
165	48	8	0.17	17	0.35	39	0.81
476	48	3	0.06	13	0.27	ND	0.0

* see 2.4.2 (b)

The derivation of a leaching rate for each sample was used throughout the investigations on epoxy resin relining since it was found to be a useful way of comparing results from different experiments, and, in particular, between results from laboratory experiments and field trials.

For example, the leachate concentration measured in each water sample is dependent on the residence time of the water in the test cell or in the main, ie how long the sample is in contact with the epoxy-resin lining. Thus, with high flows of water as in the case of water mains, residence time is low and, consequently, leachate concentration would be expected to be low. With low flows of water in the main, residence time is comparatively high leading to increased leachate concentrations. The pipe inner surface area to water ratio is important but in this work it was more or less constant since a 3-4" main was used or simulated.

Calculation of a leaching rate ensures that the results become independent of residence time and can be directly compared. The results showed that all compounds displayed the same general leaching characteristics. Thus concentrations were high initially, and then dropped rapidly over the first 24 hours to reach a low concentration near to the detection limit. In most instances, low concentrations were still being observed when sampling was stopped, ie 6 weeks after leaching had started. In these samples the water had been in contact with the resin for 48 hours. For example, the initial levels measured for trimethylhexamethylenediamine were 1600 $\mu g\ l^{-1}$ for the 0.5 hour sample and 548 $\mu g\ l^{-1}$ for the 1 hour sample giving a leaching rate of over 1 $mg\ l^{-1}\ hr^{-1}$ during the first hour. However after 24 hours the leaching rate dropped to about 25 $\mu g\ l^{-1}\ hr^{-1}$, although the overall pattern of leaching was consistent.

(b) Field trials

Typical results from the field trials undertaken on the four hour cure process are provided in Table 9. The results showed that the leaching pattern was broadly as predicted from laboratory experiments with high initial leaching rates which declined rapidly over the first 24 hours after the main was returned to supply. For example, levels of a few mg l^{-1} were found immediately after return to service but concentrations fell by at least an order of magnitude after 1-2 days.

(c) Overall findings on the laboratory and field trials carried out on the four hour cure process

The results from the laboratory and field trials showed that relatively high levels of organic contaminants were leached into water during the first 24 hours after relining. A full report on the laboratory and field investigations was submitted to the CCM, who were considering an application for approval of in situ applied epoxy resin linings. The Committee considered the high levels of organic contaminants leached from the resin to be unacceptable on health grounds. However, the process was considered to be sufficiently promising to encourage the development of an alternative relining procedure to try to reduce the initial high level of leaching.

2.4.2 16 hour cure process

Extending the curing period of the epoxy resin lining was considered to be the simplest way of reducing the levels of organic contaminants leaching from the resin into the water. Extending the curing time should ensure that a greater proportion of the unreacted monomers, cross linking agents etc, would be incorporated into the cured resin and therefore unavailable for leaching into water.

Table 9 - Concentration, residence time and estimated leaching rate data from a typical field trial experiment - 4 hour cure system

		TMHD*		PTSA*		Bis A + Bis F*	
Sample(hr)	Residence time (hr)	Conc μg l^{-1}	Leaching rate μg l^{-1} hr^{-1}	Conc μg l^{-1}	Leaching rate μg l^{-1} hr^{-1}	Conc μg l^{-1}	Leaching rate μg l^{-1} hr^{-1}
0	0.07	156	2340	42	630	178	2670
0.5	0.55	406	735	142	258	162	295
1	0.97	603	585	285	294	222	229
2	1.55	680	440	452	292	294	190
12	9.14	5300	580	3250	355	547	60
16	9.82	6090	620	2750	280	556	57
36	10.8	54	5	17	1.6	21	1.9
42	2.59	181	70	32	12	14	5.4

* see 2.4.2 (b)

Extending the period of air-cure from the minimum of 4 hrs to a period of at least 16 hrs (ie overnight) was suggested. This was considered acceptable operationally since a period of cure of this order is normal for cement mortar relining. When this proposal was first made no information on the effect of extended air curing on organic leachate levels was available. However, extrapolation of the results from the 4 hr cure process suggested that extended curing for 16-24 hrs would give at least an order of magnitude reduction in leachate levels. In addition, if a low flow of water was induced above normal consumer demand on dead-end mains for the first 24 hrs following return to service, the levels might be reduced by a further order of magnitude. These estimates were sufficiently encouraging for laboratory trials to be conducted.

(a) Laboratory experiments

Results from investigations on the duration of air-cure showed that a significant reduction in the level of organic leachate could be obtained by increasing cure time from 4 hrs to 16 hrs. However, no significant additional improvement was observed when the cure time was increased to 24 hrs. These results are compared with results from laboratory tests on the 4 hr cured resin in Figure 3. It should be emphasised that the results are from static laboratory tests, and no account of the effect of water flow could be made.

Results from varying the cure temperature showed that in the few experiments carried out, no significant difference was obtained in the level of organic compounds leached from the resin when curing took place at 5 °C compared to 10 °C. A full list of the laboratory tests carried out on the 16 hour cure process is provided in Table 6.

Laboratory investigations were also carried out on the leaching of organic contaminants from the resin following changes to the resin formulations (see Table 6). The results indicated that a useful reduction in the level of organic contaminants leaching from the resins could be obtained.

The conclusions drawn from the laboratory work were that an extended air-cure (a minimum of 16 hrs) could considerably reduce the level of organic compounds leaching into water compared to the 4 hour cure process. Little improvement was observed by increasing the cure-time from 16 hrs to 24 hrs. Data from the laboratory work indicated that peak leachate concentrations using these processes would be in the region of 10-100 $\mu g\ l^{-1}$.

(b) Field trials

The results from the laboratory leaching experiments on the extended air cure process were encouraging. To confirm these results, two series of field trials were carried out. In the first, two abandoned lengths of main were relined and tested using an induced water-flow. Abandoned mains were used in order to eliminate the risk of exposing consumers to high levels of organic leachates. In addition, the flow rate/residence time of water in the pipe could be controlled to ensure that a likely 'worst-case' was being monitored.

The second series of field trials were carried out to assess the likely variability in organic leachate levels arising from routine application of the relining process. Following satisfactry results from the field trials on abandoned mains 'live' mains were used for these trials, and organic leachate concentrations were monitored from six lengths of main relined with epoxy resin. Again, dead-end mains supplying a small number of consumers were selected so that a likely 'worst-case' was monitored.

The relining process studied in all field trials entailed a minimum 16 hr air-cure (ie overnight) followed by chlorination and flushing to waste for 1 hr. The relined pipe was then returned to supply. To ensure that water was not stagnant in the main during the 24 hr period immediately following return to service, a low flow (about 13 $l\ min^{-1}$ additional to consumer demand) was induced. With this additional flow the retention time of the water in the main was always less than 1 hr.

The concentrations of bisphenol A diglycidyl ether (Bis A), bisphenol F diglycidyl ether (BisF), 2,2,4-trimethylhexamethylenediamine (TMHD) and p-toluenesulphonic acid (PTSA) were determined in all samples. In addition, analyses by gas chromatography-mass spectrometry (GCMS) was carried out on dichloromethane extracts of selected water samples to detect the presence of any other contaminants.

i) Field trials on abandoned mains

These trials were carried out on lengths of main on which a simulated flow pattern, typical of a dead-end main supplying a small number of consumers (about 10), was induced. Seven samples were taken during the first 72 hrs after the pipe was 'put back into supply' in order to monitor the relatively high leachate concentrations expected during this time. Sampling was continued at less frequent intervals for up to five months after relining, to determine long-term leachate concentrations. After the initial 72 hr period, three replicate samples (taken at about 5 min intervals) were analysed in order to be able to check on the consistency of results; in general results were satisfactory.

During the period of extra, induced flow (ie 24 hours), the residence time (ie how long the water is in contact with the resin) is approximately constant at about 1 hour. After this, residence time depends on consumer demand and may be very long during overnight periods but shorter during the day time. In the field trials on the abandoned mains the flow was adjusted to give a residence time of approximately 10 hours overnight and 4 hours during the day.

Typical results obtained for the concentration of TMHD, Bis A plus Bis F and PTSA are given in Table 10 along with residence times and leaching rates. The results from these field trials were broadly in line with those predicted from the laboratory

Table 10 - Typical results from short-term field trials on abandoned main (Site A)

		TMHD		PTSA		BIS A + BIS F	
Sample (hr)	Residence time (hr)	Conc μg l^{-1}	Leaching rate μg l^{-1} hr^{-1}	Conc μg l^{-1}	Leaching rate μg l^{-1} hr^{-1}	Conc μg l^{-1}	Leaching rate μg l^{-1} hr^{-1}
1	1	16	16	32	32	6	6
4	1	13	13	21	21	3	3
7	0.8	16	20	18	23	3	4
17.75	0.7	6	9	10	14	<1	-
27.5	3.5	7	2	16	5	<1	-
41.75	10.2	30	3	39	4	<1	-
69	10.2	20	2	16	2	<1	-
30 days							
1	10.2	3	0.3	<5	-	<1	-
2	10.2	4	0.4	<5	-	<1	-
3	10.2	4	0.4	<5	-	<1	-
2 months							
1	10.5	1	0.1	<5	-	<1	-
2	10.5	3	0.2	<5	-	<1	-
3	10.5	4	0.3	<5	-	<1	-
4 months							
1	10.0	<1	-	<10	-	<1	-
2	10.0	<1	-	<10	-	<1	-
3	10.0	<1	-	<10	-	<1	-

work. For example, the peak concentration measured for TMHD was 30 µg l^{-1} in the sample taken 41.75 hours after the main was 'put back into supply'. It should be noted that this sample was taken after a period of overnight stagnation. The leaching rates shown in Table 10 provide an indication of the rate at which organic compounds are leached from the resin, and are calculated by dividing the measured concentration by the residence time in the main. The rate starts at 16 µg l^{-1} hr^{-1} but drops rapidly during the first 24 hours and after 69 hours in supply the TMHD leaching rate had dropped to 2 µg l^{-1} h^{-1}.

Results after 30 days showed that TMHD was generally being leached from the resin at a low level during this time. Thus 4 µg l^{-1} of TMHD was measured after a residence time of 10 hours. PTSA and the bisphenol diglycidyl ethers, however, were below the detection limit in these samples (ie <5 µg l^{-1} and <1 µg l^{-1} respectively).

Results after 64 days showed that low levels (ie about 3 µg l^{-1}) of TMHD were still present, but as in the previous sample (30 days) both PTSA and bisphenol diglycidyl ethers were below the detection limit. However, after 4 months none of the determinands were found and sampling was discontinued. Results from the field trials were therefore broadly in line with those predicted from the laboratory work. The leaching rate fell rapidly during the first 24-48 hours to reach a low level which was maintained for 2-3 months with none of the organics being detectable after 4 months in service.

ii) Short-term field trials on live mains

These trials were carried out to assess the variability in organic leachate levels arising from routine use of the epoxy resin relining process. Six trials were conducted on separate dead-end mains supplying a small number of consumers. Results from earlier laboratory and field trials indicated that any significant variation in organic leachate levels should occur during the first few days after relining. Sampling for field trials on live mains was therefore designed to assess the variability in leachate concentration encountered during this period.

Four samples and one blank were analysed in each field trial. These were taken at the following times after the relined pipe was put back into public supply.

Sample	Comments
1 hour	Taken to determine initial leachate concentrations (NB this sample was taken during the period of imposed flow above normal demand).
Approx 29 hour	Taken after the period of imposed extra flow and before the first overnight stagnation period.
Approx 43 hour	Taken during the first overnight stagnation period after relining.
Approx 68 hour	Taken during the second overnight stagnation period after relining.

The results from three of the field trials (sites B, C and D) are given in Table 11 and Figures 4, 5 and 6.

Peak concentrations measured were 123 $\mu g\ l^{-1}$ for TMHD, 137 $\mu g\ l^{-1}$ for PTSA and 20 $\mu g\ l^{-1}$ for Bis A plus Bis F and typical reductions in leaching rate were observed with time. The results from these 3 trials indicated that leachate concentrations were consistent and generally in agreement with those predicted from laboratory work and compared favourably with the work on abandoned mains.

Table 11 - Typical results from short term field trials on live mains - Sites B, C and D

			TMHD		PTSA		BIS A + BIS F	
Site	Sample	Residence time (hr)	Conc µg l^{-1}	Leaching rate µg l^{-1} hr^{-1}	Conc µg l^{-1}	Leaching rate µg l^{-1} hr^{-1}	Conc µg l^{-1}	Leaching rat µg l^{-1} hr^{-1}
B	1	0.4	33	83	70	175	11	28
	31.5	0.6	7	12	5	9	3	5
	42	3.0	41	14	57	19	7	2
	68	3.1	17	6	21	7	3	1
C	1	0.6	39	65	76	122	10	16
	30	9.5	71	7	69	7	13	1
	44.5	11.6	123	11	137	12	18	2
	68	32.0	77	2	101	3	11	0.3
D	1	0.5	30	60	39	74	6	11
	28.5	6.1	27	4	29	5	7	1
	41	10.6	34	3	22	2	20	2
	67	5.8	4	0.7	8	1	6	1

(c) Overall findings on the laboratory and field work undertaken to investigate the 16 hour cure epoxy resin relining process

A full report on the results from the laboratory and field work undertaken was submitted to the CCM. At this stage one of the epoxy resin formulations was withdrawn by the manufacturers. On the basis of the results obtained, the Committee agreed that the other resin system could be used by the Water Industry on a limited basis, in order that the process could be further developed. In particular, developments in control and inspection equipment were needed so that procedures could be implemented to assure the quality of applied linings. In addition, further leachate data were requested to provide information on factors such as relining in areas of different water quality, the effect of different water temperatures and long-term leaching rates.

While these data were being gathered, the manufacturers of the resin and hardener components and the resin formulator agreed to commission detailed toxicological studies on the resin and hardener ingredients. This information should then enable a decision to be made on the acceptability of the epoxy resin relining process for relining water mains.

2.5 SUMMARY OF ADDITIONAL DATA GATHERED ON THE EPOXY RESIN RELINING PROCESS AND FINAL CONCLUSIONS

A series of studies (not a part of this contract) were carried out by WRc Swindon in conjunction with epoxy resin relining contractors designed to gather further data on the specific organic compounds leaching from the epoxy resin linings.

These studies were based upon typical worst case situations, ie small diameter dead-end mains with few consumers and therefore high residence times. At the request of the CCM, care was taken to cover the range of water temperatures typically found in water supplies in the UK. Experiments were therefore conducted in four different water authorities at water temperatures ranging from 4 °C to 15 °C. In addition, all the contractors currently applying the resin system were monitored to ensure that different lining equipment and methods did not significantly influence the leaching potential of the applied lining.

Completion of these trials has shown that all the contractors monitored were capable of applying satisfactory linings and have equipment capable of delivering the resin and hardener at the correct ratio within the specified tolerances. In addition the levels of organic leachates observed confirmed the levels predicted by laboratory studies and preliminary field trials.

The data do not show any difference in leaching potential when lining in different water supplies or water temperatures. The results have confirmed the optimal cure time (16 hrs) that can practically be accommodated while minimising the potential for leaching organic components from the resin. In addition, the variation in concentration of organic contaminants leaching into water from the resin has been established in a series of field trials. Following the satisfactory outcome of toxicological studies and a consideration of all the leachate data obtained. The CCM decided to approve the resin system, on condition that the water utilities and contractors apply the linings in accordance with the in situ operational guidelines manual incorporating a code of practice prepared by the Water Research Centre (source document for the Water mains rehabilitation manual - 2nd edition)(19). As a further condition of this approval the resin is manufactured under the control of a BS5750 Quality System approved by an accredited third party certification body such as the Water Industry Certification Scheme or the BSI. The contractors are also being encouraged to work within a framework of a quality management system to BS5750 based on the requirements of the Operational Guidelines Manual with assessment and surveillance by an accredited certification body.

At present the greater share of the relining market in the UK is taken by non-structural corrosion protection techniques and there is no reason to assume that their share of the market will decline. The main advantage of epoxy resin relining is its current relative low cost compared with both structural lining and replacement, and greatly reduced social disruption compared with pipe replacement.

Epoxy resin lining has certain technical benefits over cement mortar. First, since it is a thin smooth lining with excellent hydraulic characteristics it offers distinct advantages in hydraulic carrying capacity in small diameter mains. Second, it will be of particular benefit to water utilities supplying soft waters. In these areas the traditional use of cement mortar can lead to unacceptably high pH values in the water for a considerable period of time after relining with potential deterioration of the current lining. Since epoxy resin has no effect on the pH of the transmitted water and is not itself affected, it provides an attractive alternative option.

SECTION 3 - ORGANIC COMPOUNDS INTRODUCED INTO WATER FROM PLASTIC PIPES

3.1 INTRODUCTION

In the UK there is an increasing use of plastics for pipeline materials and they now represent about 50% by length of current usage, about 80% of which is in nominal diameters of 150 mm or less. The materials used are predominantly u-PVC and MDPE while a much smaller amount of GRP is used. Considerable use has been made of u-PVC for the installation of new mains, while PE has traditionally been used for smaller diameter service pipes, owing to its greater flexibility in comparison with u-PVC(6). In recent years, however, the development of MDPE pipe of a wide range of diameters has led to a considerable expansion in the use of this material by the water industry.

Pipes made of plastic offer many technical advantages over traditional metallic material; they do not corrode, are lightweight and less expensive.

However, the use of plastic pipes has led to some water quality problems[20,21]. A series of investigations has therefore been carried out on potential water quality problems arising from the use of plastic pipes.

3.2 LEACHING OF ORGANIC COMPOUNDS FROM PE PIPE

3.2.1 Introduction

Although PE pipe has been in use for a number of years, it has been realised recently that certain organic compounds may leach from the pipe material. Low molecular weight organic compounds have recently been shown to leach from PE pipe into water[7]. Over the last ten years sporadic complaints from consumers about an objectionable taste and odour, described as lead pencil or graphite-like, have been received and investigated by Water Authorities. Work carried out at WRc showed that the cause was the antioxidant Santanox (6,6'-di-t-butyl-4,4'-thiodi-m-cresol) and/or its breakdown product (2-t-butyl-5-methyl-(1,4)-benzoquinone), used in the production of PE pipes. Santanox is no longer used in PE pipe for use in contact with potable water. One of the Irganox range of antioxidants is commonly used as a replacement.

Since it was established that an antioxidant could leach from PE pipe and cause significant problems, work was carried out to establish the leaching potential of other organic compounds used in PE formulations. These include antioxidants, UV stabilisers and pigments. The compounds studied in this work are listed in Table 12.

In order to determine the concentration of organic compounds leaching from PE pipe, suitable isolation, separation and identification techniques were developed for compounds known to be present in PE pipe material and some of their degradation products.

Table 12 - Compounds in PE pipe

Compound	Function
Santanox	Antioxidant
2-t-butyl-5-methyl-(1,4)-benzoquinone	Degradation product
Irganox 1010	Antioxidant
Irganox 1076	Antioxidant
2,6-di-t-butyl-p-benzoquinone	Degradation product
Copper phthalocyanine	Blue pigment
Cyasorb UV 531	UV stabiliser
Phthalimide	Degradation product

3.2.2 The leaching of antioxidants, their degradation products and UV stabilisers from PE pipe

a) Extraction techniques

Techniques were developed for the extraction of water samples and pipe material for each of the compounds listed in Table 12. Although the methods employed were not fully evaluated, a reasonable recovery of the compounds from both water and PE were obtained using solvent extraction with dichloromethane or diethyl ether. A summary of recovery experiments is given in Table 13.

The recovery of Santanox from tap water gave variable recovery efficiencies which indicates that some decomposition may have occurred. This was confirmed by analysis of a 10 $\mu g\ l^{-1}$ spike of Santanox in tap water which resulted in zero recovery of Santanox but 5.1 $\mu g\ l^{-1}$ of its degradation product was detected. The mechanism of the decomposition is not fully understood, but it seems to be enhanced by the presence of residual chlorine in the tap water sample since the breakdown product was not observed in extracts of distilled water spiked with Santanox.

Table 13 - Results from recovery experiments

Compounds	Sample	Spike level ($\mu g\ l^{-1}$)	Recovery (%)
Santanox	Tap water	10	ND
Santanox	Tap water (pH 2)	10	ND
Santanox	Distilled water	50	88
Santanox	Distilled water	10	58
Santanox	Distilled water (pH 2)	10	59
Santanox	Distilled water	1	58
2-t-butyl-5-methyl-(1,4)-benzoquinone	Distilled water	1	33
Irganox 1076	Distilled water	1	57
Irganox 1076	Distilled water	10	70
Irganox 1010	Distilled water	1	49
Irganox 1010	Distilled water	10	80
2,6-di-t-butyl-p-benzoquinone	Distilled water	1	70
2,6-di-t-butyl-p-benzoquinone	Distilled water	10	67

ND = not detected

b) Separation/Identification techniques

High performance liquid chromatography (HPLC) techniques were developed for monitoring the compounds listed in Table 12. A summary of the elution conditions etc is provided in Table 14. The identification of these components in both water and pipe extracts was based initially on retention time under these specific elution conditions. Wherever possible identification was confirmed by a comparison of UV spectra and using off-line mass spectrometric techniques.

c) Laboratory leaching experiments

To gain information on which compounds were likely to leach from the pipe material into water, samples of PE (approx 1 g) were extracted with dichloromethane (20 ml). Three types of PE were extracted (as

Table 14 - Summary of HPLC elution conditions

Compound	Eluent*	UV Detection	Detection limit (ng on column)
Santanox	Methanol-water (85:15)	254 nm	10
2-t-butyl-5-methyl-(1,4)-benzoquinone	Methanol-water (85;15)	280 nm	1
Irganox 1010	Methanol-water (97:3)	230 nm	5
Irganox 1076	Methanol-dichloromethane (85:15)	230 nm	15
2,6-di-t-butyl-p-benzoquinone	Methanol-water (80:20)	254 nm	3
Cyasorb UV 531	Methanol-water (97:3)	280 nm	1

* For all compounds a Spherisorb ODS column was used (5 µm, 25 cm x 4.6 mm)

shavings) and the extracts analysed by HPLC. Samples examined were (a) blue PE (from a batch made using Santanox as antioxidant) (b) black PE (also from a formulation using Santanox) and (c) medium density blue PE containing no Santanox.

The results, summarised in Table 15, showed that both Santanox, Irganox 1076 and Irganox 1010 were extracted from PE. In addition low levels of the degradation product of Santanox were observed. A chromatogram from the separation of the extract from medium density blue PE is shown in Figure 7.

Table 15 - Results from analysis of polyethylene pipe

Compound	Concentration* (µg g^{-1})
a) Blue polyethylene	
Santanox	101
2-t-butyl-5-methyl-(1,4)-benzoquinone	1
Irganox 1076	1
b) Black polyethylene	
Santanox	71
2-t-butyl-5-methyl-(1,4)-benzoquinone	4
Irganox 1076	6
c) Blue medium density polyethylene	
Irganox 1076	3.5
Irganox 1010	1.5

* Since the efficiency of recovery from polyethylene pipe was not determined, these values are tentative.

It can be seen from this chromatogram that several compounds were extracted from the pipe in addition to those listed in the formulation. The identity of these compounds was investigated using GCMS and other mass spectrometric techniques. The presence of

Santanox and its degradation product in the extracts from black PE was confirmed and an additional compound 2,6-di-t-butyl-p-benzoquinone identified in the extract from blue polyethylene. This compound is of a similar structure to the substituted quinone known to be formed from the degradation of Santanox, and it is probably derived from degradation of the antioxidants Irganox 1010 and Irganox 1076. Since the Santanox quinone has a very strong potential to cause taste and to possibly cause sensitisation in people, the identified quinone was tested but found to have a taste threshold (greater than 100 µg/l) that should not lead to problems in water supplies. However, further investigation would be prudent.

d) Field trials

In the previous section, work was described which illustrated that organic compounds added to PE during manufacture could be extracted from PE pipe. The object of the field trials was to determine whether these compounds (or certain degradation products of these compounds) leached into water supplies under conditions directly applicable to the consumer.

A list of the compounds monitored is shown below. In addition some samples were analysed by GCMS to try to identify any other organic compounds which leached from the pipe.

Sites were selected such that possible 'worst-case' situations were investigated. Thus it was judged that the sites chosen represented situations in which the maximum amount of leached substances would be present. The following conditions were applied:

- distribution of water should be predominantly in blue MDPE pipe.

- a dead-end main should be sampled which supplied a small number of consumers.

	Compound	Function
Irganox 1010	Pentaerythrityl-tetrakis [3-(3,5-di-t-butyl-4-hydroxyphenyl)] proprionate	Antioxidant
Irganox 1076	Octadecyl (3,5-di-t-butyl-4-hydroxy) hydrocinnamate	Antioxidant
-	2,6-di-t-butyl-p-benzoquinone	Antioxidant degradation product
Cyasorb UV 531	2-hydroxy-4-n-octoxy-p-benzophenone	UV stabiliser

Samples should be taken after a period in which the water in the pipe was virtually stagnant (ie overnight). This would ensure that the water had a long contact time with the pipe and possibly lead to enhanced levels of leached substances.

Suitable sites for study were located. Two field trials were initially carried out with three sites sampled in each trial. In the first trial, samples were taken from pipes which had been in use for about six months; duplicate samples were taken at each site to provide some information on the variability of the analytical results. In the second trial, sites were selected where the pipes had been installed for only 1-2 days. Duplicate samples were again taken at each site, but in these experiments one sample was immediately spiked, at a level of 1 $\mu g\ l^{-1}$, with each of the compounds to be monitored to provide information on the recovery of the compounds of interest from water samples.

Subsequently a third field trial was subsequently undertaken. Sites from the second field trial, where newly installed pipes had been sampled, were resampled six months later to determine whether leachate levels had decreased. A summary of the field trials undertaken is provided in Table 16.

Table 16 - Summary of field trials undertaken

Date of the trial	Site sampled	Approximate time the pipe was in use prior to sampling (days)	Samples taken (1)
First trial			
14.6.85	1	180	2 x 2.5
	2	180	2 x 2.5
	3	180	2 x 2.5
Second trial			
6.9.85	4	2	2 x 2.5*
	5	2	2 x 2.5*
	6	2	2 x 2.5*
Third trial			
18.3.86	5	180	2 x 2.5*
	6	180	2 x 2.5*

* One sample was immediately spiked at a level of 1 µg l^{-1} with each of the compounds being monitored

Samples (2.5 litres) were taken from a stand-pipe fitted with a tap and then stored in the dark. One litre of water from each sample was extracted with dichloromethane (2 x 100 ml) as soon as possible (in all cases this was less than four hours after sampling). Dichloromethane extracts were stored in the dark at 4 °C.

Table 17 give the results from the first field trial, ie samples taken from pipes which had been in use for about six months. Table 18 shows results from the samples taken from new pipes and the percentage recovery from the spiked samples.

The results showed that low levels of all the compounds monitored were present in certain samples, but there was a considerable variation between different sites. For example, at site 5, only the antioxidant degradation product, 2,6-di-t-butyl-p-benzoquinone was detected, whereas at site 4 low levels of all compounds were

Table 17 - Results from the first field trials

Site	Sample	Irganox 1010	Irganox 1076	2,6-di-t-butyl-p-benzoquinone	Cyasorb UV 531
1	a	<300*	220	440	<85*
	b	<300*	160	420	<85*
2	a	<300*	240	80	85*
	b	<300*	260	78	<85*
3	a	<300*	380	140	<85*
	b	<300*	390	100	<85*

All figures are ng l^{-1}

* ie less than the detection limit
a and b are duplicate samples from the same site

Table 18 - Results from the second field trials

Site	Sample	Irganox 1010	Irganox 1076	2,6-di-t-butyl-p-benzoquinone	Cyasorb UV^{x} 531
4	Unspiked	460	280	610	12
	Spiked*	48	35	89	50
5	Unspiked	<300	<275+	820	<5
	Spiked*	31	47	70	65
6	Unspiked	<300	<490+	1690	6
	Spiked*	50	57	73	54

* Results from the spiked samples are quoted as % recovery from a 1 μg l^{-1} spike. All other figures are ng l^{-1}.

\+ Higher detection limits are quoted for these samples due to a closely eluting peak.

x An improved detection limit was obtained compared to the first experiments due to increased sensitivity of detection.

detected. The only marked difference in the samples taken from newly installed pipe compared to those which had been in use for about 6 months, appeared to be in the concentration of 2,6-di-t-butyl-p-benzoquinone. It was found that consistently higher levels of this compound were present in samples taken from newly installed pipes. For example, a peak concentration of 1690 ng l^{-1} was found in the sample from site 6 (new pipe) compared to a peak concentration of 440 ng l^{-1} from site 1 (pipe 6 months in use). The only compound found in all of the sites monitored was 2,6-di-t-butyl-p-benzoquinone. Thus it would appear that this compound is a contaminant which is likely to be found in MDPE distribution systems in general.

The results obtained from the spiked samples agreed reasonably well with recoveries obtained in laboratory spiking experiments.

An HPLC chromatogram from a separation of the extract from site 4 is shown in Figure 8. The peak for 2,6-di-t-butyl-p-benzoquinone can be clearly observed. A small peak eluting at the retention time of Irganox 1010 and Cyasorb UV 531 (these compounds co-elute under the conditions used to obtain this separation) was also present. Several other peaks can be seen in the chromatogram and, chromatograms from the separation of extracts from the other sites also showed unknown peaks. Further work on these extracts, involving analysis by GCMS, was therefore carried out to confirm the identity of the compounds monitored and to try to identify the unknown compounds.

The two anti-oxidants Irganox 1076 and Irganox 1010 were not able to be analysed by GCMS but the degradation product of these compounds, (2,6-di-t-butyl-p-benzoquinone) and the UV stabiliser, (2-hydroxy-4-n-octoxy-p-benzophenone) could be monitored. The main compounds identified by GCMS are listed in Table 19. 2,6-di-t-butyl- p-benzoquinone and 2-hydroxy-4-n-octoxy-p-benzophenone were detected in samples from 3 sites and 2 sites respectively and this confirmed the results from HPLC analysis. Low concentrations (probably <1 μg l^{-1}) of 2,6-di-t-butyl-4-methylphenol and 2,6-di-t-butyl-4-ethylphenol were detected in all three sites. However, these identifications were only tentative since no authentic standards were available for these compounds. Both compounds are used as antioxidants in the plastics industry, although there are no reports of their use in the manufacture of MDPE. They may be present in the polymer as impurities, possibly from the Irganox antioxidants. The butylphthalates detected are commonly found in drinking water extracts.

Table 19 - Compounds identified by GCMS

Compound	No of sites where compound was detected	Possible origin
2,6-di-t-butyl-p-benzoquinone	3	Degradation product from Irganox antioxidants
2-hydroxy-4-n-octoxy-p-benzophenone	2	UV stabiliser
2,6-di-t-butyl-4-ethyl phenol	3	Unknown, possible impurity of antioxidant
2,6-di-t-butyl-4-methyl phenol	3	Unknown, possible impurity of antioxidant
di-iso-butylphthalate	2	Common water contaminant
di-n-butylphthalate	3	" "
Unknown (probable molecular weight, 168)	1	?
Unknown (probable molecular weight, 147)	1	?

In the second field trial samples were taken from 3 sites where pipes had been installed within the previous 2 days. Two of these sites were re-sampled 6 months after installation to assess whether leachate levels had decreased during this period. Unfortunately one of the three sites was unable to be used on the second occasion due to damage to the stand-pipe fitting. As in previous field work two samples were taken from each site with one sample being immediately spiked (at 1 µg l^{-1}) with the compounds to be monitored.

The results are given in Table 20 and the concentrations found in the previous sample from the same site are included for comparison. None of the four determinands were detected in the two samples taken, indicating that the amounts leached from MDPE pipe had decreased with time. Thus, although a concentration of 2,6-di-t-butyl-p-benzoquinone of 1690 ng l^{-1} was found in one sample taken in the original field trial, this compound was not detected (ie at >40 ng l^{-1}) when the site was sampled six months later. Results from analysis of the spiked samples gave acceptable recoveries but were generally lower than was normally obtained. There were indicators that Irganox antioxidants and the substituted benzoquinone degradation product could be further degraded in water by a high chlorine residual. It is possible therefore, that the lower recoveries of spiked compounds from these series of experiments was due to this factor. However, the actual chlorine level was not measured in this instance.

Table 20 - Organic compounds leached from MDPE pipe (ng l^{-1})

Site	Irganox 1010		Irganox 1076		2,6-di-t-butyl-p benzoquinone		2-hydroxy-4-n-octoxy-p-benozphenone	
	Sept 85	Mar 86	Sept 85	Mar 86	Sept 85	Mar 86	Sept 85	Mar 86
5	<300	<160*	<490	<190*	820	<40	<5	<10+
6	<300	<160*	<490	<190*	1690	<40	6	<10+

* A lower detection limit was obtained for the second series of experiments due to improved detector sensitivity

\+ A higher detection limit is quoted for these samples due to decreased chromatographic efficiency

3.2.3 Leaching of copper phthalocyanine into water from MDPE pipe

All MDPE pipe to be used for carrying water underground should now be coloured blue. A commonly used blue pigment is copper phthalocyanine, which is a complex high molecular weight compound in which copper is chelated to nitrogen. Due to the widespread use of this pigment it was decided to investigate whether copper phthalocyanine would leach into water distributed by blue MDPE pipe.

Copper phthalocyanine is virtually insoluble in water and in most organic solvents and attempts to develop a chromatographic method for monitoring this compound were not successful. However, some information on the potential concentration of copper phthalocyanine that could leach into water from MDPE pipe was obtained by monitoring water samples for copper using atomic adsorption spectrometry (AAS).

Experiments were carried out using two types of water (distilled and tap) which were stored in lengths of MDPE pipe for periods of 2 days and 7 days. After this time, samples were transferred to prepared bottles (250 ml polypropylene bottle to which was added 5 ml of 5M nitric acid) and then analysed for copper by AAS. Blanks consisted of the same type of water stored in a prepared bottle for an equivalent time.

Details of sampling and the results obtained are provided in Table 21. The results showed no significant difference in the copper concentration determined in distilled water stored in MDPE for two days compared to the blank water sample. Storage of distilled water in MDPE for seven days did produce a slight increase in concentration of copper above that observed in the blank; a concentration of about 10 µg l^{-1} was measured compared to <7 µg l^{-1} in the blank. The concentration of copper leached from the pipe was therefore about 3 µg l^{-1} which would be equivalent to a concentration of copper phthalocyanine of about 28 µg l^{-1}. Results from tap water samples showed no significant difference between the copper concentration in water stored in MDPE and in the blanks for both 2 day and 7 day storage periods. However, since a much higher background level of copper is present in tap water compared to distilled water, any small increase in copper concentration due to storage in MDPE would not be apparent in tap water samples. Thus there was an indication that low levels of copper phthalocyanine can be leached into water after storage in MDPE for seven days. However, the sensitivity and selectivity of the method (especially with tap water samples) appeared to be barely sufficient to give an accurate indication of the rate of leaching of copper (and potentially copper phthocyanine).

Table 21 - Sampling details and results from the analysis of copper phthalocyanine in water

Water sample	Duration of storage	Storage condition	Concentration (µg l^{-1} as copper)
Distilled	2	Polypropylene bottle+	<7, <7
Distilled	2	MDPE pipe	<7, 8
Distilled	7	Polypropylene bottle+	<7, <7
Distilled	7	MDPE pipe	10, 11
Tap water	2	Polypropylene bottle+	67, 73
Tap water	2	MDPE pipe	63, 62
Tap water	7	Polypropylene bottle+	64, 65
Tap water	7	MDPE pipe	61, 67

* The two results refer to duplicate analysis carried out on the same sample

\+ Samples stored in polypropylene bottles are used in blanks

3.2.4 Chlorination products of copper phthalocyanine

GCMS analysis of extracts of water taken from MDPE distribution systems, for example during the field work described in Section 3.2.2 (d), had shown that low concentrations of phthalimide were often present. Initially this was not linked to leaching from MDPE. However, it has been reported that copper phthalocyanine decomposes in the presence of dilute acidic permanganate to yield phthalimide. The possibility that this compound was formed by decomposition of copper phthalocyanine in the presence of aqueous chlorine was therefore investigated.

Experiments were carried out to determine if either aqueous chlorination or aqueous hydrolysis of copper phthalocyanine produced phthalimide, or whether phthalimide was present as an impurity in copper phthalocyanine.

Copper phthalocyanine (20 µg l^{-1}) was added to water (2 litres, deionised and eluted through activated carbon). Sodium hypochlorite (10 mg l^{-1} Cl_2) was then added and the flask stirred in the dark for 4 hours at room temperature. The water sample (1 litre) was adjusted to pH 2, extracted with dichloromethane (2 x 100 ml) and concentrated using rotary evaporation and finally under a stream of nitrogen. A duplicate sample, with no addition of sodium hypochlorite, was processed at the same time to determine whether aqueous hydrolysis of copper phthalocyanine could produce phthalimide. To determine whether phthalimide was an impurity in copper phthalocyanine, copper phthalocyanine (20 µg) was added to dichloromethane (200 ml) and then the solution concentrated as for aqueous sample extracts.

Dichloromethane extracts were analysed by reversed-phase HPLC to determine the amount of phthalimide. Results, given in Table 22, show that phthalimide could be formed by the action of aqueous chlorine on copper phthalocyanine. Thus, from 20 µg l^{-1} of the blue dye, 1.3 µg l^{-1} of phthalimide was produced. In the batch of copper phthalocyanine examined, phthalimide was not present as an impurity. It was not formed by aqueous hydrolysis of the copper phthalocyanine. As suggested later some of the phthalimide generated may have reacted with chlorine to produce chlorophthalimide.

Phthalimide found in water samples taken from MDPE distribution systems is therefore probably formed from the blue pigment added to the pipe.

3.2.5 The leaching of phthalimide into water from blue MDPE pipe

In Section 3.2.4 experiments were described which showed that copper phthalocyanine (the blue pigment added to MDPE pipe) could react with aqueous chlorine to produce phthalimide. Thus, from a concentration of

Table 22 - Results from the determination of phthalimide

Sample	Concentration (μg l^{-1})
Water spiked with copper phthalocyanine plus chlorine	1.3*
Water spiked with copper phthalocyanine	<0.1
Dichloromethane spiked with copper phthalocyanine	<0.1

* Identity confirmed by GCMS

20 μg l^{-1} of the blue pigment in water, about 1 μg l^{-1} of phthalimide was produced. A series of experiments was therefore undertaken to investigate the leaching of phthalimide from MDPE pipe into water.

a) Extraction of phthalimide from water

To obtain information on typical concentrations of phthalimide in drinking water distributed by MDPE pipe, a series of water samples taken from an MDPE distribution system would need to be analysed. So that a large number of samples could be taken in one visit to a suitable area, a quick extraction method for phthalimide in water was required. The method developed involved elution of the water sample (100 ml) through a Sep-pak cartridge followed by elution of the Sep-pak with methanol (2 ml). The methanol extract is then concentrated for analysis by HPLC (or GC). Recovery experiments gave the results summarised below:

Water sample (ml)	Concentration of phthalimide ($\mu g\ l^{-1}$)	Recovery (%)
Distilled-deionised (100)	10	81,85
" (100)	1	57,70,68,65*
" (250)	1	26,33
Tap water (100)	1	41,25

* Mean recovery at 1 $\mu g\ l^{-1}$ was 65% (standard deviation 5.7)

The low recovery using a 250 ml sample volume indicated that phthalimide was breaking through the Sep-pak column and therefore sample volumes should not be greater than about 100 ml. Low recoveries were also obtained from analysis of tap water samples. It was suspected that this may be due to the reaction of phthalimide with residual chlorine in the water. This hypothesis was confirmed by carrying out experiments on the chlorination of phthalimide.

b) Laboratory leaching experiments

Four sections of MDPE service pipe (50 cm x 22 mm id, 200 ml volume) were filled with water or water plus sodium hypochlorite as outlined in Table 23. Two sections of glass tubing of equivalent volume were used to provide chlorinated and unchlorinated blank samples.

Water was stored in each section of pipe for successive periods of 2 days, 2 days and finally 3 days. At the end of each period the pipe was emptied and refilled with fresh water. Water which had been stored in each pipe section was analysed for phthalimide using the Sep-pak/HPLC method. The results are provided in Table 24.

Table 23 - Details of laboratory leaching experiments

Pipe section	Water sample
MDPE 1	Deionised, activated-carbon-cleaned
MDPE 2	Deionised, activated-carbon-cleaned
Glass (Blank 1)	Deionised, activated-carbon-cleaned
MDPE 3	Deionised, activated-carbon-cleaned with addition of sodium hypochlorite (equivalent to 1.2 mg l^{-1} FAC)
MDPE 4	Deionised, activated-carbon-cleaned with addition of sodium hypochlorite (equivalent to 1.2 mg l^{-1} FAC)
Glass (Blank 2)	Deionised, activated-carbon-cleaned with addition of sodium hypochlorite (equivalent to 1.2 mg l^{-1} FAC)

Table 24 - Results from laboratory leaching experiments on MDPE pipe - concentration of phthalimide

Sample	Phthalimide concentration (µg l^{-1})		
	Period 1 (2 days)	Period 2 (2 days)	Period 3 (3 days)
MDPE 1	1.9*	0.6	0.7
MDPE 2	1.5	0.8	-
MDPE 3	0.9*+	0.1+	0.05+
MDPE 4	0.8+	0.1+	-

* Presence confirmed by GCMS

\+ A small peak was observed in the chlorinated blank which interfered with phthalimide. These results have been adjusted accordingly

\- Not determined

The results show that phthalimide was detected in all samples of water stored in MDPE pipe. The highest concentrations, about 2 µg l^{-1}, was found in the initial 2 day sample from the pipe section filled with unchlorinated water. This indicates that phthalimide was being leached from MDPE regardless of whether chlorine was present in the water in contact with the pipe. Thus it would appear that decomposition of copper phthalocyanine to phthalimide can occur by a mechanism other than aqueous chlorination, possibly during extrusion of the pipe.

Analysis of unchlorinated water following the second two-day storage period, showed a reduction in the concentration of phthalimide which indicated depletion of phthalimide from the surface of the pipe. This trend was continued in the sample following the final three day storage. The concentration of phthalimide leached by chlorinated water was consistently lower than that found in unchlorinated water. This indicated that phthalimide itself may undergo reaction with aqueous chlorine (see Section 3.2.5). A similar trend in reduction of phthalimide concentration with storage time was observed.

c) The chlorination of phthalimide

From the experiments described in b) above it was suspected that phthalimide could react with aqueous chlorine. A series of chlorination experiments were carried out to verify this hypothesis.

In the first experiment an aqueous solution of phthalimide (100 $\mu g\ l^{-1}$) was chlorinated (10 $mg\ l^{-1}$ FAC) for four hours with sodium hypochlorite.

Analysis of the chlorinated sample showed that all of the phthalimide had been consumed. This was confirmed by GCMS analysis. The experiment was repeated using less sodium hypochlorite (1 $mg\ l^{-1}$ FAC). Samples were taken from the reaction mixture at intervals of 15 min, 30 min, 1 hour and 2 hours and the phthalimide concentration determined in each sample. The results are presented in Table 25, and showed that a rapid and virtually complete consumption of phthalimide had taken place. A corresponding chlorinated blank (ie no addition of phthalimide) was also processed and analysis of water samples spiked with phthalimide (100 µg l^{-1}) showed a mean recovery from three repeat samples of 88% (standard deviation, 5.7). Thus it was concluded that phthalimide rapidly reacts with aqueous chlorine.

Table 25 - Results from laboratory chlorination of phthalimide

Reaction time (min)	Phthalimide (µg l^{-1})
0	100
15	26
30	13
60	2.5
120	0.4
240	0.1

Initial concentration of free chlorine = 1 mg l^{-1} FAC

Separation of the Sep-pak extracts using HPLC with diode array detection did not reveal any major products from the chlorination of phthalimide. GC analysis of a sample of water taken after 30 min chlorination showed that no trihalomethanes (less than about 0.2 µg l^{-1}) were produced in the reaction.

To attempt to identify the products from the chlorination of phthalimide a further experiment was carried out using an increased concentration of phthalimide, ie 1 mg l^{-1} of phthalimide, chlorinated using sodium hypochlorite (0.8 mg l^{-1} FAC). The consumption of phthalimide with time was again measured using the Sep-pak/HPLC method. As before, this showed the rapid reaction of phthalimide with chlorine, with virtually all of the phthalimide consumed after 2 hours (see Table 26). After 2 hours the water was divided into two equal portions. One half was adjusted to pH 2 and extracted with dichloromethane (2 x 100 ml), and the other extracted with dichloromethane (2 x 100 ml) without pH adjustment.

Table 26 - Results from laboratory chlorination of phthalimide (increased concentration)

Reaction time	Phthalimide ($\mu g\ l^{-1}$)
0	1000
15	680
30	500
60	330
120	100

Initial concentration of chlorine = 0.8 mg l^{-1} FAC

Analysis of the dichloromethane extract by capillary GC-FID showed a large peak eluting at a retention time of 20.5 min (under the same conditions phthalimide eluted at 19.3 min) which was not present in DCM extracts of the chlorinated blank. Analysis by GCMS showed that this peak was due to a monochloro-phthalimide. It was not certain from the mass spectrum at what position in the molecule the chlorine was substituted but N-chlorophthalimide was considered to be likely. No further products were indicated from the GC or GCMS analysis and no difference was observed between the pH 2 and neutral pH extracts.

HPLC analysis of the Sep-pak extracts indicated that N-chlorophthalimide was not extracted from water using the Sep-pak HPLC method.

3.2.6 Laboratory and field trials on leaching of phthalimide and related compounds from blue MDPE pipe into drinking water

Previous work had shown that phthalimide could leach from the blue pigment in blue MDPE pipe, copper phthalocyanine, into drinking water. In addition, phthalimide may react with chlorine in drinking water to produce a chlorinated phthalimide, probably N-chlorophthalimide. Laboratory and field trials were therefore carried out on the leaching of these compounds from blue MDPE pipe into water.

a) Laboratory experiments

It was decided to standardise on a 24 hr leaching period to enable comparison of leaching data. The following experiments were undertaken:

1) Reaction of phthalimide with chlorine

Two sections of blue MDPE service pipe (185 cm x 2.2 cm id) were filled with deionised-carbon-treated water and buffered to pH 7 with 10 mM phosphate buffer. Two sections were filled also with deionised-carbon-treated water, buffered to pH 7 with 10 mM phosphate buffer, but chlorinated at 1 mgl^{-1} free available chlorine. The pipes were stored for 24 hours at room temperature after which the volume of water from the pipes was measured, the water filtered and extracted with 2 x 75 ml of dichloromethane (DCM). The extracts were then concentrated by Kuderna Danish apparatus to 10 ml, further concentrated under nitrogen to 1 ml, halved and each portion taken to 100 µl for GC and LC analysis. System blanks were processed in the same way and also analysed by GC and LC.

The results of the LC analysis were as follows:

Sample	Phthalimide Concentration (μgl^{-1}) (adjusted for 59% recovery)	Leaching Rate ($\mu gm^{-2}h^{-1}$)
MDPE unchlorinated 1	2.4	0.54
MDPE unchlorinated 2	2.4	0.54
MDPE chlorinated 1	*0.11	0.04
MDPE chlorinated 2	*0.13	0.04

* Presence confirmed by GCMS

Chlorophthalimide was not found in the chlorinated pipe extracts on examination by GC/FID and GCMS but a lower concentration of phthalimide was found in the chlorinated water compared to the unchlorinated water. This indicates that phthalimide reacts with chlorine. No phthalimide was found in the blanks.

2) Leaching of phthalimide at higher pH (9)

The recovery of phthalimide (1 μgl^{-1}) at pH 9 was found to be 33%; at pH 7 the recovery was around 59%. If the pH was adjusted to 7 just prior to extraction the recovery was still low (35%) which suggests that at the higher pH, phthalimide may be unstable.

Two sections of blue MDPE pipe (185 cm x 2.2 cm id) were filled with 10 mM phosphate buffer (pH 7) and sealed. A further 2 sections of similar dimensions were filled with 10 mM phosphate buffer (pH 9) and also sealed. The pipes were stored for 24 hours at room temperature, and then the water from the pipes was treated as described above before analysis by LC. The results were as follows:

Sample	Phthalimide Concentration * (μgl^{-1})	Leaching rate * ($\mu gm^{-2}h^{-1}$)
MDPE (pH 7) 1	2.59	0.58
MDPE (pH 7) 2	2.38	0.53
MDPE (pH 9) 1	0.03	-
MDPE (pH 9) 2	0.02	-

* adjusted for 59% recovery at pH 7 and 35% at pH 9

The very low concentrations of phthalimide after 24 hrs in the water at pH 9 may be due to substantial degradation of leached phthalimide and/or inhibited leaching. However, the evidence obtained already (see above) suggests the former mechanism.

3) Leaching of phthalimide from blue MDPE pipe obtained from different manufacturers

For this work analysis was based upon C_{18} Sep-pak since this was simpler and quicker. However, it was not possible to monitor for N-chlorophthalamide using this method.

Two sections of each pipe were flushed with deionised-carbon-treated water and then filled with buffered 10 mM phosphate (pH 7) deionised-carbon-treated water and sealed. The pipes were stored for 24 hours at room temperature and then the volume of the water from the pipes was measured, the water filtered and 100 ml eluted through a Sep-pak cartridge, followed by elution by 2 ml of methanol. The methanol extracts were concentrated to 100 µl under nitrogen at 40 °C prior to analysis.

The results were as follows:

Sample	Dimensions of pipe	Phthalimide conc ($\mu g l^{-1}$)*	Leaching rate ($\mu g m^{-2} h^{-1}$)*
MDPE-C	1 m x 2.0 cm id	2.03	0.40
MDPE-U	1.1 m x 2.0 cm id	0.37	0.07
MDPE-P	0.93 m x 1.5 cm id	4.07	0.62
MDPE-B	1.85 m x 2.2 cm id	3.22	0.75
MDPE-B	1.33 m x 2.2 cm id	2.37	0.52
MDPE-S	1 m x 2.0 cm id	0.90	0.18

* adjusted for 59% recovery

The results showed that the concentration of phthalimide varied from about 0.2 µg l^{-1} to 4 µg l^{-1} depending on the manufacturer of the pipe. All pipes leached detectable amounts of phthalimide.

The effect of flushing the MDPE pipe over an extended time on the rate of leaching was assessed. Since blue MDPE pipe P leached the highest concentration of phthalimide, two fresh sections of this pipe were used for this experiment. Two pipes were flushed with deionised/carbon-treated water and then filled with 10 mM phosphate buffer (pH 7). The pipes were emptied and refilled with the same water at approximately 48 hour intervals for a week before taking a 24 hour leached sample and extracting it by the Sep-pak method for LC analysis. This was repeated after a further, similar weekly flushing periods. The results were as follows:

Sample (time)	Phthalimide (µg l^{-1})*	Leaching rate (µg $m^{-2}h^{-1}$)*
MDPE-P pipe (after 1 week)	0.64	0.1
" (after 1 week)	0.73	0.1
" (after 2 weeks)	0.17	0.03
" (after 2 weeks)	0.17	0.03
" (after 3 weeks)	0.37	0.06
" (after 3 weeks)	0.34	0.05
" (after 4 weeks)	0.56	0.09
" (after 4 weeks)	0.46	0.07

* adjusted for 59% recovery

The results indicate that the initial rate of leaching (about 0.6 $\mu g m^{-2}h^{-1}$) fell quickly but then apparently levelled out.

4) Chlorophthalimide and phthalic acid

Various experiments were carried out to develop a method for chlorophthalimide and measure its formation under realistic conditions. The conclusion of the work was that chlorophthalimide could be formed. However, its analysis proved erratic and unreliable and, in addition, it is probable that chlorophthalimide is unstable. Its concentration in drinking water based on typical levels of phthalimide, is unlikely to be more than a few μgl^{-1}. If such contamination is deemed to be significant then further investigations, which are likely to be difficult, should be considered.

Experiments have also indicated that phthalic acid is leached from blue MDPE pipe, or is produced by degradation of phthalimide. Indications are that typical levels may be around a few μgl^{-1} at most. However, no further work on this contaminant was carried out since phthalic acid did not appear to pose a particular hazard.

b) Field trials on the leaching of phthalimide into water from MDPE pipe

Work in the laboratory had shown that phthalimide could leach from the blue pigment added to MDPE pipe into drinking water. Laboratory experiments found that levels leached into drinking water from new MDPE pipe following 24 hour leaching periods were in the range of 0.4 to 4 μgl^{-1}. Phthalimide had also been detected in water samples taken from MDPE systems during field trials described in Section 3.4. Concentrations were unknown, but in the few samples examined were probably $<1\ \mu gl^{-1}$. To gain information on typical concentrations of phthalimide in water from MDPE distribution systems, a small survey was therefore undertaken.

Previous work to determine typical levels of antioxidants and other additives leached into drinking water from MDPE distribution systems had been carried out at specific sites. A large proportion of the new pipe installed at these sites was blue MDPE. It was therefore decided to carry out the survey for phthalimide in the same area.

Twelve sites were selected covering a range of pipe diameters (63-125 mm). Generally, sampling points were on a dead-end section of pipe so that water samples taken would have a relatively long contact time with the pipe. Sampling was carried out between 0600 and 1240, with some early morning samples taken to ensure that some had been subjected to overnight stagnation (see Table 27). All samples were taken from hydrants.

Table 27 - Results from the analysis of phthalimide in water sampled from blue MDPE pipe

Sample No (time taken)	Time the pipe had been in service (weeks)	Diameter of pipe (mm)	Phthalimide concn ($\mu g\ l^{-1}$)	Recovery of 5 $\mu g\ l^{-1}$ spike
1 (0950)	4	63	ND	-
2 (0950)	4	90	ND	-
3 (1010)	6 - 8	63	ND	44, 36
4 (1035)	10 - 12	63	ND	-
5 (1055)	12	125	ND	-
6 (1220)	8	90	ND	44, 36
7 (1240)	10 - 12	90	ND	-
8 (0720)	12	63	ND	-
9 (0720)	12	63	ND	54, 36
10 (0650)	2 - 3	63	ND	-
11 (0600)	2½ - 3 (years)	63	0.12, 0.38	-
12 (0610)	1	125	ND	-

ND = Not detected (<0.1 $\mu g\ l^{-1}$) in either sample

All sampling sites selected, except one, involved relatively new MDPE pipe installations (<12 weeks in service), since highest levels were expected from new pipes. One sample was taken from a pipe which had been in service for about 2½ years to provide some information on long-term leachate concentrations.

All samples were extracted immediately (ie on site) using the Sep-pak extraction method described in Section 3.2.5(a). Although this technique gave a less efficient recovery compared to solvent extraction methods, it was chosen for this survey because it is simple and rapid and could therefore be employed on site, immediately after the sample was taken. Duplicate samples (100 ml) were extracted at each site. At three sites (see Table 27), duplicate samples were also spiked with phthalimide (5 $\mu g\ l^{-1}$) in order to check recovery.

Sep-paks were eluted with methanol (2 ml) and the extracts returned to the laboratory for analysis by HPLC.

Results from the analysis of phthalimide in water samples from a series of MDPE distribution systems are shown in Table 27. Detectable levels of phthalimide were found in only one of the water samples taken. Although it had been anticipated that the highest concentrations would be found in samples from the newer installations, the only site with detectable levels was the one which had been in use for 2½-3 years. The reason for this is unknown, however, it may reflect batch-to-batch changes in production of blue MDPE pipe.

Results from analysis of the three spiked samples indicated an acceptable recovery of phthalimide although the results were lower than had been obtained in laboratory spiking experiments (mean recovery 65%, standard deviation 5.7). However, it is known that phthalimide can react rapidly with chlorine in drinking water and this may have caused the lower recoveries found in this series of experiments.

The results from this survey indicated that typical concentrations of phthalimide in drinking water from blue MDPE distribution systems were probably <0.1 μgl^{-1}. However, one system appeared to be leaching low levels of phthalimide (probably <1 $\mu g\ l^{-1}$) into drinking water for a long period of time.

To confirm this result another small survey was undertaken in the same area; this focused on pipes that had been in service for 2-3 years. Four sites were selected covering a range of pipe diameters (65-125 mm). Sampling was carried out in the early morning from hydrants situated on dead-ends so that the water sampled had a long residence time in the pipe.

The Sep-pak extraction method was used on site (see Section 3.2.5 (a)) and the extracts were returned to the laboratory for analysis by HPLC. Duplicate samples (100 ml) were taken at two sites (see Table 28) with one sample spiked with phthalimide (5 µg l^{-1}) to estimate recovery.

Table 28 - Leaching of phthalimide

Sample No (time taken)	Time pipe in service (years)	Diameter of pipe (mm)	Phthalimide (µg l^{-1})	% Recovery of 5 µg l^{-1} spike
1 (6.15 am)	3	63	ND	49,42
2 (6.40 am)	3	63	ND	-
3 (8.10 am)	2	125	ND	-
4 (8.00 am)	2-3	63	ND	45,24

ND = Not detected (<0.1 µg l^{-1}) in duplicate samples

The results are shown in Table 28; no phthalimide was detected at any of the sites, including the site (No 4) where phthalimide (at 0.25 µg l^{-1}) had been detected previously.

The results indicated that while phthalimide could leach from new blue MDPE pipe (demonstrated in laboratory experiments) its detection in water distributed through blue MDPE pipes was very sporadic. This may have been due to its reaction with free chlorine which was demonstrated in earlier studies.

3.3 THE LEACHING OF ORGANIC COMPOUNDS INTO WATER FROM UNPLASTICISED POLYVINYLCHLORIDE (u-PVC) PIPE

3.3.1 Introduction

Considerable use has been made of u-PVC for the installation of new mains, but very little has been laid as service pipes owing to its lack of flexibility in comparison with PE(6). Certain organic and inorganic compounds are added to u-PVC during manufacture of the final product; these are heat stabilisers, lubricants and UV stabilisers. The use of u-PVC pipes for water distribution has been shown to lead to some water quality problems(20,22,23). In particular the leaching of lead(8) and organo-tin compounds from heat stabilisers(9) has been investigated.

However, little information was available on the range of other contaminants which may leach from u-PVC pipe into water.

3.3.2 Compounds used during manufacture of u-PVC pipe

Certain organic and inorganic compounds are added to uPVC during manufacture of uPVC pipe, such as heat stabilisers, lubricants and UV stabilisers. Compounds commonly used are:

a) heat stabilisers - inorganic lead (usually lead carbonate), organotin compounds (mainly dialyltins eg dimethyl, dibutyl or dioctyl) tin esters (eg of lauric, maleic and thioglycolic acids) and tin mercaptides,

b) lubricants - stearic acid stearates and polyethylene waxes,

c) UV stabilisers - benzophenones and benzotriazoles.

3.3.3 Laboratory leaching experiments

The range of organic contaminants leaching from u-PVC pipe into water has been investigated in a series of laboratory experiments.

Three types of water a) deionised-distilled water, b) tap water and c) deionised-distilled water plus 1 ppm free chlorine, were stored in sections of uPVC pipe for 3 days. Blanks consisted of the same type of water stored in glass tubes for an equivalent time. After storage, water samples were filtered and a) extracted with dichloromethane at pH 2, b) passed through a C_{18} Sep-Pak cartridge followed by methanol elution of adsorbed components and c) passed over on XAD-2 resin column followed by diethyl ether elution. GCMS was used to analyse the dichloromethane extracts and XAD-2 resin/diethyl ether extracts and fast atom bombardment mass spectrometry (FAB-MS) was used to analyse Sep-Pak extracts and dichloromethane extracts. Details of the leaching experiments carried out are provided in Table 29.

3.3.4 Results and discussion

GCMS analysis of the dichloromethane extracts detected only low levels of organics leaching from the u-PVC pipe. No significant differences were observed from analysis of dichloromethane extracts from the different types of water. Compounds identified included benzyl alcohol, phenylacetaldehyde, benzothiazole, tris-chloroethylphosphate and a series of phthalates. GCMS analysis of XAD-2 extracts provided similar results, with the exception that bisphenol A diglycidyl ether (Bis A) was detected at low concentrations (probably $<1\ \mu g\ l^{-1}$) in all extracts. Bis A was not thought to be employed in the manufacture of the u-PVC pipe used for this experiment. However, epoxy compounds have been reported to be used as stabilisers during u-PVC production(24).

As found with GCMS analysis, only low concentrations of organic compounds could be detected using +ve and -ve ion FAB-MS and consequently few identifications were possible. Compounds identified consisted of a series of fatty acids, ie palmitoleic, palmitic, lauric, myristic and stearic. These were detected in dichloromethane extracts from the tapwater and chlorinated water samples. Stearic and other fatty acids plus their esters are used as lubricating agents during u-PVC pipe manufacture. Thus their presence in these extracts would be expected.

Table 29 - Details of laboratory leaching experiments (u-PVC pipe)

Type of water	Duration of storage in u-PVC	Volume (litres)	Extraction method	Analytical technique
Deionised/activated Carbon cleaned	3 days	1	Dichloromethane solvent extraction	GCMS, FAB
		0.1	Sep-pak-methanol elution	FAB
		7.0	XAD-2 Et_2O elution	GCMS
Tap water	3 days	1	Dichloromethane solvent extraction	GCMS, FAB
		0.1	Sep-pak-methanol elution	FAB
		7.0	XAD-2 Et_2O elution	GCMS
Deionised/activated carbon cleaned plus 1 mg l^{-1} chlorine	3 days	1	Dichloromethane solvent extraction	GCMS, FAB
		0.1	Sep-pak-methanol elution	FAB
		7.0	XAD-2 Et_2O elution	GCMS

The laboratory leaching experiments carried out therefore indicated that a variety of organic contaminants can be leached from new u-PVC pipe into water. However, the observed concentrations were very low and these would be expected to be gradually reduced following installation and use of the pipe.

3.4 THE LEACHING OF ORGANIC COMPOUNDS FROM GLASS REINFORCED POLYESTER (GRP) PIPE

3.4.1 Introduction

The use of GRP pipe for potable water supply is increasing, although it is generally restricted to large diameter trunk mains. GRP is a composite material which consists primarily of glass fibres embedded in a polymerised resin matrix. Unsaturated polyester resins are most commonly used for the manufacture of GRP pipe for potable applications in the UK.

As far as we are aware, very little work has been carried out on the nature of organic compounds leaching into water from GRP pipe. Work carried out at WRc concluded that GRP pipes could introduce substantial quantities of organic substances into water but levels decreased with time. The concentration of styrene and dimethylphthalate was monitored but these were reported to be a small fraction of the general organic leachate.

A laboratory experiment was therefore carried out to investigate the range and concentration of organic contaminants leached from GRP pipe in current use.

3.4.2 Experimental

Pieces of GRP were cut from a section of pipe (40 cm id, thickness 0.9 cm) and placed in a glass thin layer chromatography tank. Leaching experiments were carried out using deionised water and buffered deionised water with 1 mgl^{-1} Cl_2 added. The sections of pipe were submerged in the test water and left for successive periods of 24 hours, 48 hours and finally 96 hours. At the end of each period the water was removed for analysis and the tank refilled with fresh water.

Water samples were adjusted to pH2 and extracted with dichloromethane (2 x 100 ml), which had been spiked with deuterated internal standards for analysis by mass spectrometry. Extracts were concentrated using a Kuderna-Danish evaporator and finally under nitrogen for analysis by GC and GCMS.

3.4.3 Results and discussion

Analysis of extracts by capillary GC indicated that a wide range of organic contaminants were leached from the GRP pipe. Analysis of water from the successive leach periods ie 24, 48 and 96 hours showed that concentrations, and therefore leaching rates, were reduced significantly over this period. This followed the expected pattern of leaching of contaminants from materials in contact with water. Analysis by GC with FID and ECD detection indicated some differences in the extracts from GRP leached with deionised water and chlorinated, deionised water. 24 hour leached samples from both types of water were analysed by GCMS. A list of the compounds identified in the unchlorinated leachate is provided in Table 30.

Table 30 - Compounds leaching into deionised water from GRP pipe

Phthalic acid ester
Dimethyl phthalate
Benzaldehyde
Acetophenone
Dialkoxy phthalate ester
Unknowns: possible mol wt 240
Dioctylphthalate
Styrene
Tris-chloroethylphosphate
Benzoic acid
Nonanal
2-ethyl hexanoic acid

A range of contaminants were detected with the major components being, dimethylphthalate, a phthalic acid ester, benzaldehyde, acetophenone, tris-chlorethylphosphate, two unknown isomeric compounds of possible molecular weight 240 and styrene.

The approximate concentration of contaminants in the extract was calculated based on the response of an internal standard (D_{10}-xylene) added to the extract. These are provided in Table 31, which gives the estimated concentration leached into 1 l of water over the first 24 hour period in the laboratory experiment. From this concentration a figure was calculated for the leaching rate per sq metre of pipe and the concentration expected in water in a typical GRP pipe (40 cm dia), assuming the water had been stagnant in the pipe for 24 hours.

Table 31 - Concentration of organic contaminants leached from GRP pipe

Compound	Concentration in laboratory experiment$^+$ (µg l^{-1})	Leaching rate (µg m^{-2} hr^{-1})	Estimated concentration in # water from a 40 cm dia pipe (µg l^{-1})
Phthalic acid ester	271	109	26
Dimethyl phthalate	212	85	21
Benzaldehyde	45	18	4
Acetophenone	32	13	3
Styrene	7	3	0.7
Tris-chloroethyl-phosphate	32	13	3

\+ 24 hour static leachate experiment
\# Assuming the water is stagment in the pipe for 24 hours

The highest concentrations found were for the phthalic acid ester and dimethyl phthalate, with about 25 µg l^{-1} estimated to be leached into water from a 40 cm pipe following a 24 hour leaching period. Concentrations of the other contaminants, benzaldehyde, acetophenone, styrene and tris-chloroethylphosphate were estimated to about 1-5 µgl^{-1}.

SECTION 4 - THE PERMEATION OF POLYETHYLENE PIPES BY ORGANIC COMPOUNDS

4.1 INTRODUCTION

The phenomenon of permeation through a water pipe implies the penetration of compounds through the wall of the pipe without causing the pipe to leak. For a water pipe in contaminated soil, the driving force for permeation is the difference in concentration of a contaminant in the soil surrounding the pipe and the concentration of the contaminant in the water inside the pipe.

The problem of organic solvents permeating plastic pipes was reported in the mid-1950's(11). Since then a wide variety of taste and odour incidents have been attributed to spillage of organic substances (particularly petrol and other oil products) in the vicinity of plastic supply pipes. Evidence emerged in the late 1970s that contamination of drinking water can occur by permeation of plastic pipes in polluted soil in situations other than gross contamination. In the Netherlands, methyl bromide was detected in a drinking water supply in the vicinity of a number of greenhouses(25). It had been used as a soil fumigant, and it had contaminated the soil surrounding the pipe. In 1978, a highly contaminated site was discovered at a housing estate in Lekkerkerk near Rotterdam. In addition to many cases of severe contamination, several organic compounds were found to have permeated plastic distribution pipes and contaminated the drinking water supply(26,27).

A review of the effects of soil contamination on materials used for the distribution of water has recently been published(28). A detailed discussion of the phenomenon of permeation of plastic pipes by organic compound can be found in this report.

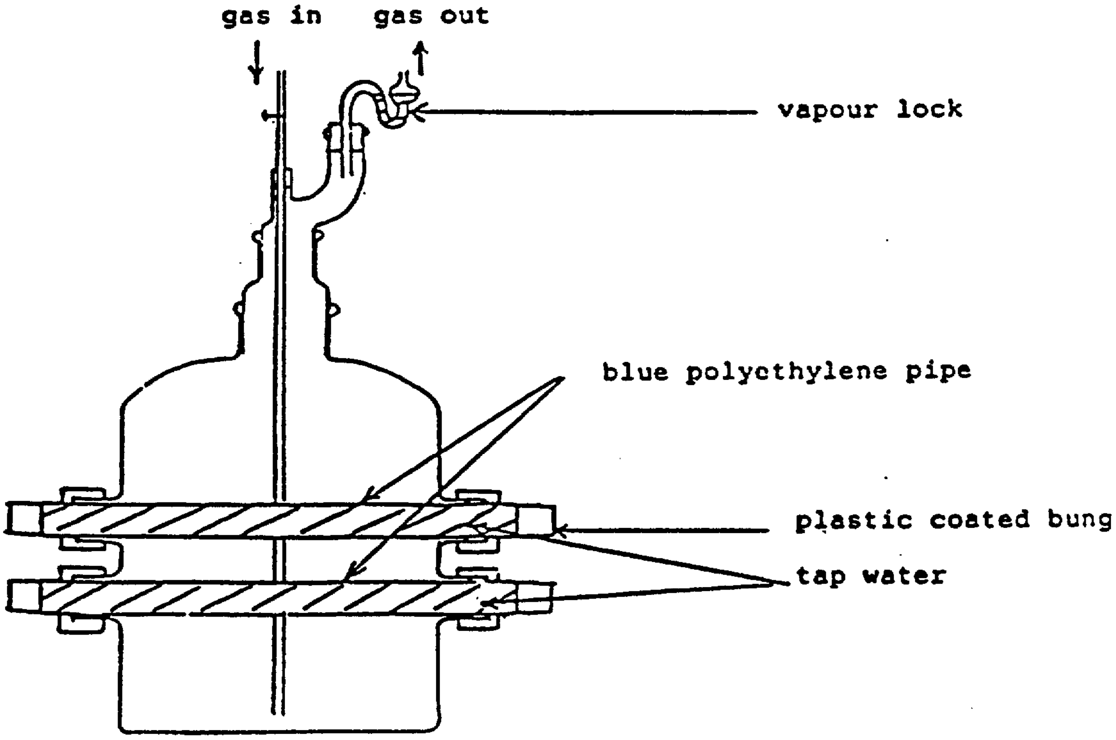
4.2 THE PERMEATION OF POLYETHYLENE BY NATURAL GAS ODORANTS

4.2.1 Introduction

British Gas and Regional Water Authorities are currently considering the double-trenching of polyethylene pipe for use with water and natural gas (ie laying new MDPE gas and water pipes in the same trench). As the two pipes would be in close proximity, the possibility of the natural gas (ie and in particular the odorants added to natural gas; ethylmercaptan, tert-butylmercaptan, diethylsulphide and methyl ethylsulphide) causing taste and odour problems in the water should there be a leak from the gas pipe, was raised. An experiment was therefore devised in which it was determined how long it took for natural gas odorants to permeate through a PE pipe filled with water and give rise to a detectable taste and odour.

4.2.2 Experimental design

A glass vessel was constructed in which short lengths of pipe were held in a gas atmosphere. This is shown in the diagram below.



The pipes were sealed into the glass vessel using screw fittings and rubber gaskets and then filled with drinking water and sealed with polyethylene-coated rubber bungs. The vessel was then connected to the gas supply and the air displaced from the system. A vapour lock was fitted and the flow of gas adjusted to maintain a constant slow flow through the system. In this way a slight positive pressure of gas was kept in contact with the pipe.

4.2.3 Taste and odour testing

The water from both lengths of pipe was collected and taste and odour testing carried out using a taste panel. This usually consisted of four people but occasionally a panel of five was employed. Water stored in similar lengths of pipe not exposed to gas was used as the control for the taste and odour tests. The pipes were refilled with fresh water as soon as possible after emptying.

4.2.4 Sampling

Taste and odour testing was carried out on samples taken as follows:

1, 2, 9, 12, 16, 19, 23, 26, 30, 33, 40, 52, 54, 61, 68, 75, 78 and 94 days after exposure to gas.

4.2.5 Results and discussion

Natural gas odorants were not detected by any of the panel members in samples taken up to 33 days after the pipe was exposed to natural gas. After 40 days one of the panel members was able to detect a slight off-taste. In the sample taken after 52 days, three out of four panel members detected an off-taste in the sample water. These results indicated that the breakthrough of natural gas odorants through blue MDPE pipe took place after a contact time with the pipe of 40-50 days. Results from samples tested after the breakthrough of odorants (ie after 52 days) indicated that the length of time the water is in the pipe will determine whether a discernible taste and odour is transmitted to the water. Thus in the case of the sample taken after 54 days (ie the water had been in the pipe for 2 days) two of out five panel members detected a very slight taint. In the sample taken after 61 days (ie the water was in the pipe for 7 days) a taste was observed by three out of our panel members.

Further experiments confirmed these findings; thus after 78 days (ie the water was in the pipe for 3 days) one out of four panel members discerned a slight off-taste, but after 94 days (the water was in the pipe for 16 days) four out of five reported a strong off-taste.

A final sample was taken after 109 days (15 days in the pipe) and analysed for methane. A level of 1.8 mg l^{-1} of methane was found in the sample compared to a level in the blank water of <0.5 mg l^{-1} (ie below detection limit).

4.3 THE PERMEATION OF POLYETHYLENE BY POTENTIAL SOIL CONTAMINANTS

4.3.1 Introduction

The ability of a wide range of organic compounds to permeate PE has been known for a number of years. For example it has been shown that low molecular weight, relatively non-polar compounds such as benzene, toluene, trichloroethylene, chlorobenzene etc will readily permeate PE. However, the number of compounds tested is small and no data were available on the possible penetration of PE by more complex, polar organic compounds, such as the commonly used pesticides, which could occur as soil contaminants.

The permeation of MDPE pipe by a range of organic chemicals has been studied in a series of laboratory experiments carried out by Pipeline Consultants Limited, Manchester, in two sub-contracts to the main contract. Pipeline Consultants employed a radiotracer technique for this work in which a ^{14}C labelled analogue of a compound of interest is used to monitor movement of the compound through the polymer. A summary of the work carried out and the results obtained are provided in this section. Full reports on the work undertaken are provided in Appendix A and B.

4.3.2 The first series of experiments

The compounds studied were paraquat, malathion, atrazine, phenol and toluene. The first three are widely used pesticides and thus could occur as soil contaminants; phenol is a commonly found soil contaminant on industrial sites and toluene was included as a 'positive control' ie it was expected to permeate MDPE rapidly.

Paraquat, malathion and atrazine did not permeate into polyethylene after exposure for up to nine weeks. Some absorption onto the surface layer was noted but there was no evidence for transport through the polymer. However, small amounts of phenol appeared to be permeating through the polymer. Thus after nine weeks exposure, phenol could be detected in a layer approx 2 mm into a 6.25 mm thickness pipe. As expected, toluene rapidly permeated polyethylene and transport through the pipe was complete after 1 week exposure.

Thus, as expected from previously reported work, the relatively high molecular weight, polar molecules studied, ie paraquat, malathion and atrazine, did not permeate polyethylene. Phenol was found to permeate at a slow rate and in small quantities and polyethylene was shown to be highly permeable to toluene. These findings agreed with laboratory permeation experiments carried out independently by KIWA(29,30).

4.3.3 The second series of laboratory experiments

Five chemicals were investigated in the second series of experiments. These were selected because they represented classes of organic compound which may be present as soil contaminants and for which no information was available on their potential for permeating polyethylene pipe:

2-chloroaniline
cyclohexane
nitrobenzene
m-cresol
4-chlorobenzoic acid

The full results are reported in Appendix B, but the salient findings were as follows.

The observed penetration of the chemicals into MDPE can be summarised as follows:

Chemical	Penetration of MDPE in mm		Concentration ($x10^2$) in polymer at maximum penetration (mg g^{-1})	
	4 weeks	13 weeks	4 weeks	13 weeks
chloroaniline	0.5	0.5	1.35	2.50
m-cresol	1	3	0.26	0.78
nitrobenzene	3	3	0.11	0.11
chlorobenzoic acid	1	2.5	0.14	0.08
cyclohexane	1	3	0.21	0.92

Thus, substantial penetration occurred in the case of m-cresol, nitrobenzene, chlorobenzoic acid and cyclohexane, especially if one bears in mind the thickness of small diameter MDPE service pipes.

These compounds were selected to cover a range of chemical and physical properties to enable a comparison of penetration characteristics with these properties to ascertain any relationships. However, no clear-cut relationships were found, although there was a possible correlation between the diffusion coefficients and the solubility of the chemical in water. The diffusion coefficient decreased with time to some extent for all compounds except m-cresol. Although this phenomenon has been reported previously for other polymers, it is not clear why it happens.

Although the data showed that a range of potential soil contaminants could permeate MDPE pipe it is difficult to predict accurately the rate of permeation of a compound from physical/chemical data on the compound and the usual polymer parameters.

4.4 AN INVESTIGATION OF A CONTAMINATED LAND SITE

4.4.1 Introduction

A substantial amount of laboratory work has been carried out for example, by KIWA in the Netherlands and as part of this contract, on the permeation of PE by organic compounds. Several compounds have been examined to estimate their rate of travel through PE. This laboratory work has involved the measurement of permeation rates from either concentrated aqueous solutions or from the vapour phase. As a result we now have an understanding of the type of compound likely to permeate PE and the time required for that compound to pass through a PE pipe. However, this information cannot be easily translated to a level of soil contamination which will give rise to permeation. This is because compounds absorbed onto soil particles do not behave in the same way as in aqueous solution or in the vapour phase. In order to investigate this problem, it was decided to examine a redeveloped old industrial site in which MDPE and u-PVC pipe had been laid. The work was designed to provide information on the degree of soil contamination which may give rise to contamination of the water supply. An outline of the potential problem of permeation of MDPE arising from soil contamination was presented to a WRc/Water Authority MDPE Steering Group meeting. Following this meeting we were contacted by a water authority concerning a site which might be suitable for our work. While laying a service pipe (MDPE) to a new building, workmen excavating the trench complained of 'oily liquids' on their hands and clothing. Although the pipe was installed and the trench back-filled, the Authority, concerned about the possibility of permeation of the MDPE by organics in the soil, would not allow the service to be used. The Authority laid an alternative supply (in u-PVC sleeved copper) to the new building. WRc was offered use of the redundant pipe for experimental purposes. A 4" diam u-PVC fire main had been installed in the same trench.

4.4.2 History of the site selected

The site has been used for several years for production of a wide range of chemicals. Current products are mainly organic esters (butyl stearates, palmitates), fatty acids and lactate esters but well over 400 compounds were manufactured on site at various times. The area adjacent to the new building had been used for storage of waste products (in drums) for many years. This area was recently concreted over. Formerly, a canal ran across the site and the whole area was subject to waterlogging. The canal, and that part of the site subject to flooding, were backfilled with domestic waste prior to covering with concrete. During a visit to the site at the start of the work (May 1986), it was apparent that many of the drums on the site were in poor condition and some were leaking.

4.4.3 Sampling programme

In order to determine the nature of the organic contaminants in the soil in contact with the pipe, soil samples were taken at regular distances along a trench near to the MDPE pipe. A sample of groundwater was also taken from the bottom of the excavated trench. Since the MDPE pipe had already been laid and the trench backfilled when this work was undertaken, soil and water samples were taken from the trench excavated for the new copper service pipe (about 1 m from the MDPE pipe).

A series of water samples were then taken from the pipe at regular intervals to determine if permeation of the plastic pipes had occurred. Sampling was initially focused on the MDPE pipe since PE is known to be more susceptible to permeation effects than u-PVC. However, subsequent samples were also taken from the u-PVC pipe to investigate the permeation of this material. All sampling exercises were carried out using the following procedures. One week before sampling the water in the test pipe was discharged to waste so that fresh mains water filled the pipe. In this way it was ensured that the water sampled had been in contact with the pipe (and any organic contaminant permeating the pipe) for a known period of time. In order to ascertain whether any permeation had occurred, control samples were taken at the same time from either the copper service pipe, a hydrant on the water mains inlet to the site or another hydrant on the feeder main to the site.

A number of different control samples were used during the study to try to clarify whether permeation of the MDPE service pipe had occurred. In particular, interpretation of the data was difficult due to the range of organic contaminants in the water taken from the copper service pipe adjacent to the MDPE test length, originally used for the control. Hydrant samples were therefore taken from two points feeding the site to provide additional 'clean' inlet samples.

Table 32 - Sampling programme

Date	Soil samples/ groundwater	MDPE test length	u-PVC fire main	Copper service pipe (control)	Hydrant inlet (control)
02.05.86	*	-	-	-	-
26.05.86	-	*	-	-	*
29.05.86	-	*	-	*	-
05.06.86	-	*	-	*	-
18.06.86	-	*	-	*	-
16.07.88	-	*	-	*	-
03.11.88	-	*	-	*	-
17.12.86	-	*	-	*	-
11.03.87	-	*	-	*	-
03.11.87	-	*	*	*	-
26.01.88	-	*	-	*	*

* - sample taken

4.4.4 Extraction and analysis

Soil samples were extracted using Soxhlet extraction with dichloromethane. The organic extract was concentrated using a Kuderna-Danish evaporator and analysed by gas chromatography-mass spectrometry. Duplicate water samples (one was adjusted to pH 2 with concentrated hydrochloric acid) were extracted with dichloromethane (2 x 100 ml) and the organic extract concentrated using a Kuderna-Danish evaporator and finally under nitrogen for analysis by GCMS.

4.4.5 Results and discussion

Table 33 shows a list of the major organic contaminants identified in the samples of soil and groundwater analysed. A wide range of other compounds were found to be present at lower concentrations, illustrating the high degree of contamination of soil from the site. The major contaminants were mainly alcohols, ketones and esters, and which reflects the main products manufactured on the site.

Table 33 - Major contaminants identified in soil and groundwater samples

Methyl butanone
Carbon tetrachloride
Hexanol
Hexanal
2 - Heptanone
4 - Methylcyclohexanol
2 - Ethyl-1-hexanol
Nonanol
Isopropyl butyrate
Isopropyl laurate
Isopropyl palmitate
Oleic acid
Dioctyl adipate

Water samples from the MDPE test length of pipe, taken for up to 20 months after the pipe was installed (see Table 32 for details) were analysed. None of the samples showed any evidence for extensive permeation of the MDPE pipe. Some samples were found to contain very low concentrations of organic contaminants which may have been due to permeation. However it was not possible to confirm the source of such contaminants at very low concentrations without undertaking a much more detailed investigation. In particular further analytical work to investigate the nature and concentration of contaminants in the water feeding the site would have to be undertaken to confirm that permeation had occurred. No evidence for permeation of the u-PVC pipe was found in the sample taken.

Tables 34 and 35 provide lists of compounds identified in water samples taken from the MDPE service pipe and from the u-PVC pipe respectively but which were not identified in control samples.

Table 34 - Compounds identified in the MDPE service pipe

Carbon tetrachloride
Alkoxy compound
Hexanoic acid
Heptanoic acid
Ethyl hexanoic acid
Phenyl acetaldehyde
Octanoic acid
Nonanoic acid
t-butylthiophene
n-alkanes
C_4-alkylbenzenes
di-t-butyl-p-benzoquinone
2,6-di-t-butyl-4-ethylphenol
2,6-di-t-butyl-4-propylphenol
Tetrahydrofuran

Table 35 - Compounds identified in the u-PVC pipe

1,6-dichlorocylo-octa-1,5-diene
2,6-di-t-butyl-4-methylphenol
9,10-dihydro-9,9-dimethylacridine
dibutylphthalate

Approximate quantitation, based on deuterated internal standards, showed that most of the compounds listed were present at concentrations of less than 1 $\mu g\ l^{-1}$. The major components in each water sample were n-alkanes, di-butylphthalate, dioctylphthalate and, in the samples from the MDPE pipes, phenolic compounds. These were found at a concentration of about 1 $\mu g\ l^{-1}$. The phenolic compounds and the benzoquinone probably arise from leaching from the pipe materials. It is possible that the

C_4-benzene isomers and tetrahydrofuran were present as a result of permeation. However, only very low concentrations of these compounds were observed and further work would have to be undertaken to confirm this. C_4-benzenes and tetrahydrofuran were not amongst those compounds identified as major contaminants in soil from the site. However, since relatively few soil samples were analysed it is possible that a localised, but significant, area of the soil was contaminated with these compounds.

The GCMS data on contaminants identified in soil from the site and on contaminants identified in water samples from the MDPE test length of pipe has been examined to try to establish any links. No evidence was found to indicate that permeation had occurred.

SECTION 5 - THE EFFECT OF THE DISTRIBUTION SYSTEM ON ORGANIC COMPOUNDS IN DRINKING WATER

5.1 INTRODUCTION

Much of the analytical work on drinking water has been carried out on finished water samples, ie water from a treatment works immediately before distribution. GCMS has provided much data on the range of compounds present in such samples. However, little work has been reported on distributed water, and consequently not much is known about the behaviour of organic compounds during distribution. Studies have been made(31,32) on the variation in the concentration of haloforms during transport in the distribution system and these results have shown some increase in levels. Some work was therefore carried out to determine changes, during distribution, in the nature of organic compounds present in finished water and also try to identify any compounds arising from the distribution system itself.

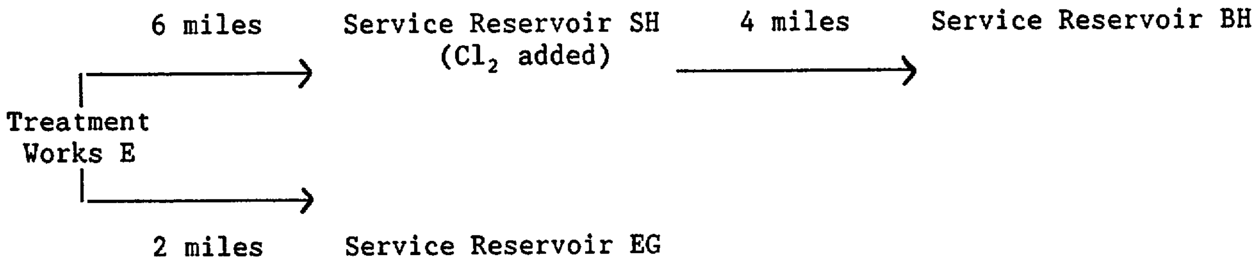
Studies focussed on one distribution system where an attempt was made to assess the day-to-day variability in the range of organic compounds present in water leaving the treatment works and in water taken from selected points along the distribution system.

The organic compounds present in each sample were determined using GCMS. In addition, an extract from each sample was separated by reversed-phase HPLC with a diode array detector. A comparison of chromatograms was then used to indicate changes in the compounds present in each sample. Subsequently further experiments were carried out on the same distribution system in which the concentration of specific compounds was measured in water leaving the treatment works and in water samples taken from various points in the distribution system.

5.2 VARIATION IN THE RANGE OF ORGANIC CONTAMINANTS PRESENT IN WATER SAMPLES TAKEN FROM VARIOUS POINTS IN THE DISTRIBUTION SYSTEM

5.2.1 Introduction

The distribution system selected was fed with water derived from a lowland river source. A map of the section of the system selected for study is shown below:



The reservoirs marked on the map were covered service reservoirs in the distribution system. The volumes of these reservoirs was, SH, 2 million gallons; EG, 6 million gallons; and BH, 3 million gallons. This initial study used such reservoirs as sampling points since it was considered that they would provide 'composite' water samples, ie better representative of water leaving the treatment works over a considerable time period than grab samples. The distribution system between the treatment works and the reservoirs consisted essentially of ductile iron or cast-iron pipes probably coated with coal-tar pitch or possibly bitumen. It is not known precisely how long it took water leaving the treatment works to reach each reservoir, however, residence times were estimated as follows:

Treatment Works E to EG - 1 day
Treatment Works E to SH - 1 - 1.5 days
Treatment Works E to BH - 3 days

At Reservoir SH the water received 'booster' chlorination with sodium hypochlorite, before distribution.

5.2.2 Sampling

Sampling was designed to enable estimation of day-to-day variability in the range of organic compounds present in water leaving the treatment works and in water at selected points in the distribution system. Two sampling exercises were carried out, in which samples from the treatment works and the reservoirs were taken on successive days over a 3 or 4 day period. Details are provided in Table 36. In the initial exercise duplicate samples were taken to check on process variability. Since all duplicates were found to be virtually identical, single samples were taken in the subsequent exercise.

5.2.3 Extraction and analysis

Samples were extracted using XAD-2 resin adsorption, C_{18} Sep-pak cartridges and solvent extraction.

For XAD-2 resin adsorption, a 2 litre sample (no pH adjustment) was passed through the resin which was then eluted with diethyl ether (30 ml). Prior to GCMS the diethyl ether extract was concentrated to 1 ml for analysis using a Junk vessel with a 3-ball micro-Synder column. Final concentration to 100 μl was carried out with a stream of N_2. Samples for XAD-2 extraction were spiked with deuterated internal standards to enable approximate quantification of any compounds present.

Table 36 - Details of samples taken from the distribution system

(a) Sampling Exercise 1

Date	Sample point	Sample volume*
16.2.87	Treatment Works E	2 x 2.5 litres
17.2.87	Treatment Works E	2 x 2.5 litres
	Reservoir BH	2 x 2.5 litres
18.2.87	Treatment Works E	2 x 2.5 litres
	Reservoir BH	2 x 2.5 litres
19.2.87	Reservoir BH	2 x 2.5 litres

* Duplicate samples were processed in this series of experiments

(b) Sampling Exercise 2

Date	Sample point	Sample volume
16.3.87	Treatment Works E	5 litres
17.3.87	Treatment Works E	5 litres
	Reservoir EG	5 litres
	Reservoir SH	5 litres
18.3.87	Treatment Works E	5 litres
	Reservoir EG	5 litres
	Reservoir SH	5 litres
19.3.87	Reservoir EG	5 litres
	Reservoir SH	5 litres

For C_{18} Sep-pak extraction, a 100 ml water sample (neutral pH) was passed through the cartridge. This was followed by elution with methanol (2 ml), which was concentrated to 100 µl under a stream of N_2 prior to analysis by HPLC.

For solvent extraction, a 1 litre sample (neutral pH) was extracted with dichloromethane (2 x 100 ml) which was then concentrated to 100 µl using a Kuderna-Danish apparatus. Final adjustment of volume was made under a stream of N_2.

XAD-2 resin extracts were analysed using GCMS. HPLC was used to analyse Sep-pak extracts and dichloromethane solvent extracts. In addition, total organocarbon (TOC), adsorbable organohalogen (AOX) and trihalomethanes (THM) were determined in all samples.

5.2.4 Results

a) GCMS analysis

Those compounds identified that appeared to be present at greater than about 0.5 µg l^{-1} in the samples taken from Treatment Works E and Reservoir BH in the first sampling exercise (see Table 36) are listed in Table 37. Duplicate samples were taken from both of these sites for three consecutive days.

Good agreement was obtained in the range and concentration of organic substances found in duplicate samples. This indicated acceptable repeatability in the process of sampling, concentration and analysis. Repeat samples on three consecutive days showed that the composition of water leaving the treatment works exhibited small differences. The same conclusion could be drawn from the samples taken from the distribution system. In addition, only small differences between samples leaving the treatment works and the samples at Reservoir BH were observed.

The compounds identified in the samples taken from Treatment Works E and Service Reservoirs SH and EG in the second sampling exercise (see Table 36) are listed in Table 38. As with the first exercise good agreement was found in the range and concentration of organic compounds identified in duplicate samples.

Total ion current traces from the GCMS analysis of one sample from each site are illustrated in Figures 9-11. Small differences only were observed in samples taken from each of the sites although an unkown substance was found in the distribution samples.

Table 37 - Compounds identified by GCMS analysis of water from treatment works E and Reservoir BH taken over a three-day period

Compound	Treatment Works E			Service Reservoir BH		
	Mon	Tues	Wed	Tues	Wed	Thurs
Chloroform	V	V	V	V	V	V
Dichloroacetonitrile	V	V	V	V	V	V
Dichlorobromomethane	V	V	V	V	V	V
Trichloroethylene	V	V	V	V	V	V
Toluene	V	V	V	V	V	V
Dibromochloromethane	V	V	V	V	V	V
1,1,1-trichloroacetone	V	V	V	V	V	V
Dibromoacetonitrile	V	V	V	V	V	V
Xylene isomer	V	V	V	V	ND	V
Bromochloroiodomethane	V	V	V	V	ND	V
Multi-halo acetone	V	V	V	V	V	V
Dichlorobenzene	V	V	ND	ND	ND	ND
Nonanal	V	ND	V	V	ND	ND
Aldehyde	V	ND	ND	V	V	ND
Dimethylphthlate	V	V	V	ND	ND	V
Carboxylic acid	ND	V	ND	V	V	V
Diethyl phthalate	V	V	V	V	V	V
Tributyl phosphate	V	V	V	V	V	V
Atrazine	V	V	V	V	V	V
Myristic acid	V	V	V	V	V	V
N-butylbenzene sulphonamide	V	V	V	V	V	V
Dibutyl phthalate isomer	V	V	V	V	V	V
Dibutyl phthalate isomer	V	V	V	V	V	V
Palmitic acid	V	V	V	V	V	V
Stearic acid	V	V	V	V	V	V
Tris (butoxyethyl) phosphate	V	V	V	V	V	V
Dioctyl phthalate	V	V	V	V	V	V

V = detected (ie greater than about 0.5 $\mu g\ l^{-1}$)
ND = not detected

The main conclusion to be drawn from GCMS analysis is that over a three-day period, only very small differences are likely in the range and concentration of organic compounds in water samples from the treatment works and the distribution system reservoirs.

Table 38 - Compounds identified by GCMS analysis of water from Treatment Works E and Reservoirs SH and EG over a three-day period

Compound identified	Treatment Works E			Service Reservoir SH			Service Reservoir EG		
	Mon	Tues	Wed	Tues	Wed	Thurs	Tues	Wed	Thurs
Chloroform	✓	✓	✓	✓	✓	✓	✓	✓	✓
Dichloroacetonitrile	✓	✓	✓	✓	✓	✓	✓	✓	✓
Dichlorobromomethane	✓	✓	✓	✓	✓	✓	✓	✓	✓
Trichloroethylene	✓	✓	✓	✓	✓	✓	✓	✓	✓
Dibromochloromethane	✓	✓	✓	✓	✓	✓	✓	✓	✓
1,1,1-Trichloroacetone	✓	✓	✓	✓	✓	✓	✓	✓	✓
Multi-halo acetone	✓	✓	✓	✓	✓	✓	ND	✓	✓
Lauric acid	✓	✓	✓	✓	✓	✓	✓	✓	✓
Diethyl phthalate	✓	✓	✓	✓	✓	✓	✓	✓	✓
Tributyl phosphate	✓	✓	✓	✓	✓	✓	✓	✓	✓
Atrazine	✓	✓	✓	✓	✓	✓	✓	✓	✓
Myristic acid	✓	✓	✓	✓	✓	✓	ND	✓	✓
Dibromoacetonitrile	✓	✓	✓	✓	✓	✓	✓	✓	✓
Dibutyl phthalate isomer	✓	✓	✓	✓	✓	✓	✓	✓	✓
Dibutyl phthalate isomer	✓	✓	✓	✓	✓	✓	✓	✓	✓
Palmitic acid	✓	✓	✓	✓	✓	✓	✓	✓	✓
Stearic acid	✓	✓	✓	✓	✓	✓	ND	✓	✓
Tris (butoxyethyl) phosphate	✓	✓	✓	✓	✓	✓	✓	✓	✓
Dioctyl phthalate	✓	✓	✓	✓	✓	✓	✓	✓	✓
N-butylbenzene sulphonamide	✓	✓	✓	✓	✓	✓	ND	✓	✓

✓ = detected (greater than about 0.5 µg l^{-1})
ND = not detected

b) HPLC analysis

In the first sampling exercise a C_{18} Sep-pak extract from each water sample (100 ml) was obtained. Separation of these extracts was carried out using a reversed-phase gradient (10% acetonitrile in 0.1% aqueous acetic acid to 90% acetonitrile in 0.1% aqueous acetic acid over 20 min). Under these conditions, HPLC profiles from all samples were virtually identical. However only low levels of organic compounds could be detected in these extracts thus making it difficult to compare the range of compounds present in each sample. In the second sampling exercise, a larger volume of water (1 litre) was therefore extracted (using solvent extraction) so that a more concentrated extract was available for HPLC analysis. HPLC profiles from the separation of extracts of samples taken from the same site on consecutive days were virtually identical with only minor differences being detected. Thus, analysis by HPLC confirmed the general conclusions from analysis by GCMS.

Chromatograms (derived from dichloromethane extracts) from each site are presented in Figure 12. The profiles from each site were very similar, although some minor differences could be observed. A close examination of the chromatograms show some small changes in the types and amounts of components. However it was not possible to identify the components involved and evaluate the significance and likely source of the components.

c) Total organocarbon (TOC), adsorbable organohalogen (AOX) and trihalomethane (THM) analysis

All water samples were analysed for TOC, AOX and THMs. Results for the first sampling exercise are given in Table 39 and for the second sampling analysis exercise in Table 40. In general the results obtained for TOC and AOX were similar for all samples. TOC varied between 3.4 and 4.1 mg l^{-1} and there was no significant difference between water leaving the treatment works and water in distribution. AOX results were more varied, with a maximum of 190 µg l^{-1} in one of the samples at Treatment Works E. The remainder of the results varied between 74 µg l^{-1} and 172 µg l^{-1} but showed no clear trend when comparing water leaving Treatment Works E and water in distribution.

Table 39 - TOC, AOX and THM results from the first sampling exercise

Sample	Date	TOC (mg l^{-1})	AOX (µg l^{-1})	Total* THM (µg l^{-1})
Treatment Works E	16.2.87	3.7	172	42
	17.2.87	3.7	190	42
	18.2.87	3.9	115	31
Service Reservoir BH	17.2.87	4.1	127	41
	18.2.87	3.5	96	43
	10.2.87	3.3	104	40

* Sum of four determinands - chloroform, dichlorobromomethane, dibromochloromethane and bromoform. Chloroform was invariably present in the largest amount (usually about 50% of the total).

Table 40 - TOC, AOX and THM results for the second sampling exercise

Sample	Date	TOC (mg l^{-1})	AOX (µg l^{-1})	Total* THM (µg l^{-1})
Treatment Works E	16.3.87	3.8	87	19
	17.3.87	3.6	102	15
	18.3.87	3.4	84	22
Service Reservoir EG	17.3.87	3.6	128	33
	18.3.87	3.6	102	41
	19.3.87	3.6	74	44
Service Reservoir SH	17.3.87	3.7	118	30
	18.3.87	3.5	109	36
	19.3.87	3.4	108	34

* Sum of four determinands - chloroform, dichlorobromomethane, dibromochloromethane and bromoform, chloroform was invariably found in the largest amount (about 50% of the total)

The level of THMs (ie chloroform, dichlorobromomethane, dibromochloromethane and bromoform) for all samples varied between 15 μg l^{-1} and 44 μg l^{-1} . Of the four, chloroform was invariably found in the highest concentration, usually being about 50% of the total. There was an increase in total THM in the distributed water compared to the water leaving the treatment works. This phenomenon has been observed previously and is likely to be due both the presence of chlorine in water leaving the treatment works (which reacts with other organic compounds present in the water during distribution to form THMs) and THM intermediates which decompose to form THMs.

5.3 VARIATION IN THE RANGE OF ORGANIC CONTAMINANTS PRESENT IN WATER SAMPLES TAKEN FROM THE EXTREMITIES OF THE DISTRIBUTION SYSTEM

The objective of this investigation was to identify any changes in organic compounds in the water due to passage through the distribution system (a combination of 15", 9", 6" and 4" diameter pipes - probably iron, lined with bituminous material). Further samples (5 l), from the distribution system outlined in Section 5.2.2, were therefore collected from service reservoir BH and from hydrants near the ends of three distinct branches on the distribution system fed by the reservoir (see Section 5.4.2 for a diagram of the system). The details of the samples were as follows:

Date/time	Sample
9.6.87/10.30 am	BH Reservoir A
10.6.87/9.30 am	BH Reservoir B
10.6.87/10.15 am	BH 1A: Hydrant SL
10.6.87/10.43 am	BH 2A: Hydrant BG
10.6.87/11.25 am	BH 3A: Hydrant WC
11.6.87/9.26 am	BH 1B: Hydrant SL
11.6.87/9.51 am	BH 2B: Hydrant BG
11.6.87/9.38 am	BH 3B: Hydrant WC

The samples were extracted using XAD-2 and dichloromethane and examined by GCMS and HPLC respectively, as described in Section 5.2.3. The data obtained was complex, but very little difference was observed in the nature of the organic compounds identified in different samples. Some small differences could be found on close examination of the GCMS data but it was not possible to ascertain whether the differences were real or due to variability of the analytical method when measuring trace concentrations of organic contaminants in water.

Of all the compounds detected, only four (three trace unknowns and a phthalate) were found in hydrant samples but not in the service reservoir water samples. All compounds found in the service reservoir samples were found in at least one of the hydrant samples.

Overall, the data from the two exercises described in Section 5.2 and 5.3 on all samples taken from the distribution system and the water leaving the treatment works, showed that there was little qualitative difference between the samples. Two unidentified compounds were observed in the treated water leaving the works but not in any samples taken from the distribution system:

unknown (MS ions of 71, 43, 56 ... 173)
unknown (71, 43, 56, 89)

In addition, a few compounds were found only in distribution system samples:

tetrachloroethylene
dichlorobenzene
triallyl isocyanate
caffeine
chlorobromoiodomethane
unknown (MS ions of 43, 55, 57, 68)
phenylacetaldehyde

Without further studies it is not possible to explain (or confirm) the origin of such contaminants.

However, the large majority of compounds were found in both treated water and distribution samples - although some compounds, which apparently were present at extremely low concentrations, did not appear in all distribution system samples. This was probably due to analytical variations. In general, no clear-cut quantitative differences could be observed. The herbicides atrazine and simazine did not appear to be affected by distribution.

5.4 VARIATION IN THE CONCENTRATION OF SPECIFIC ORGANIC COMPOUNDS IN WATER SAMPLES TAKEN FROM VARIOUS POINTS IN THE DISTRIBUTION SYSTEM

5.4.1 Introduction

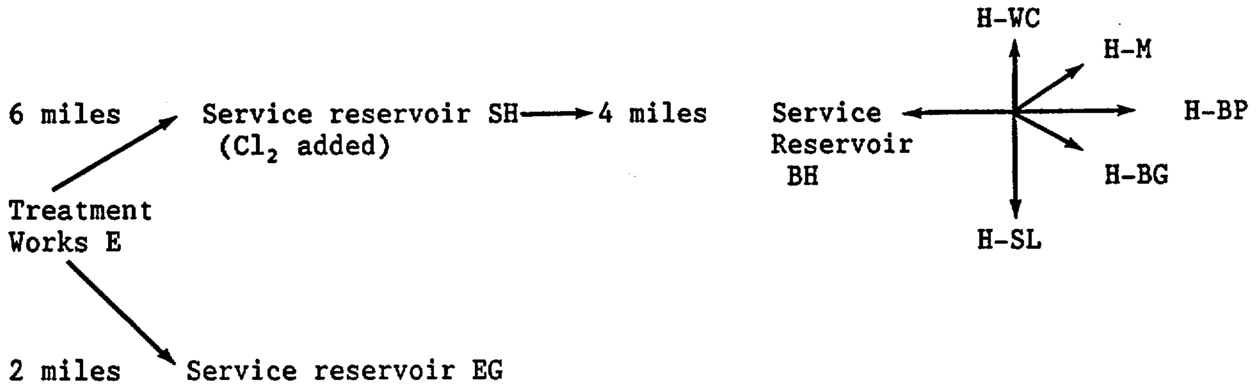
To conclude the work on the potential effects of distribution on organic contaminants in water, quantitative analytical work was carried out for a range of selected compounds in water samples from the same system. Thus the concentration of these compounds in water leaving the treatment works has been compared to concentrations in water taken from different parts of the distribution system. Selection of compounds was based on GCMS analyses carried out as part of earlier investigations (see Sections 5.2 and 5.3) and included the following:

Dibutyl phthalate
Dimethyl phthalate
Diethyl phthalate
Dioctyl phthalate
Tributyl phosphate
Tris (2-butoxyethyl) phosphate
Atrazine
Simazine

In addition, TOC, AOX and volatile halogenated compounds were determined in all samples.

5.4.2 Sampling and analysis

Samples were collected from treatment works E, service reservoir BH and from hydrants on the distribution system WC, M, BP, BG and SL as shown below.



To attempt to determine the maximum levels of organic contaminants at consumers taps, first draw samples were collected (ie after overnight stagnation). Details of samples taken are shown in Table 41.

Table 41 - Details of samples taken from the distribution system

Date	Time	Sample point
16.2.88	10.00 am	Treatment works E
16.2.88	10.30 am	Reservoir BH
17.2.88	06.50 am	Hydrant WC
17.2.88	06.55 am	Hydrant M
17.2.88	07.05 am	Hydrant SL
17.2.88	07.15 am	Hydrant BG
17.2.88	07.25 am	Hydrant BP

Samples (1 l) adjusted to pH2 with concentrated hydrochloric acid were spiked with deuterated internal standards and extracted with dichloromethane (2 x 100 ml) which was concentrated to about 5 ml using a Kuderna-Danish apparatus. Final adjustment of volume to 100 µl was made with a stream of N_2, for analysis by GCMS.

5.4.3 Results and discussion

Results from the analysis of water samples for the range of selected compounds are provided in Table 42. These show that little variation in concentration was detected in water from different parts of the distribution system and also compared to water leaving the treatment works. For example, water at the treatment works contained 1.4 µg l^{-1} of tris (2-butoxyethyl) phosphate with a range in concentration within the distribution system of 1.5 to 2.8 µg l^{-1}.

Results from the analysis of water samples for TOC, AOX, trihalomethanes, trichloroethylene and tetrachlorethylene are provided in Table 43. Both TOC and AOX do show a small, but consistent increase when comparing results from water leaving the treatment works to water in the distribution system. For example, an AOX of 65.9 µgl^{-1} was recorded in the finished water while concentrations ranged from 67.9 to 83.5 µg l^{-1} in distribution. While this increase is barely significant, it may be due to the reaction, during distribution, of aqueous chlorine with other organic compounds in the finished water to produce halogenated organic reaction products. However, no significant difference was found in the concentration of individual volatile halogenated compounds in the series of water samples analysed. This contrasted with an earlier sampling exercise where total THM concentration increased from about 19 µg l^{-1} at the treatment works to about 39 µg l^{-1} in distribution. However, since the residence time of water in the system is difficult to estimate, such small differences may still be due to the varying quality of water entering the treatment works.

Previous work had indicated that tetrachloroethylene was only present in distributed water samples and therefore may have been entering the distribution system at some point. However, in this series of

Table 42 - Results from the analysis of water samples for selected organic compounds

	Treatment works E	Service Reservoir BH	Hydrant WC	Hydrant M	Hydrant SL	Hydrant BG	Hydrant BP
Diethyl phthalate	0.1	0.2	0.1	0.1	0.1	0.1	0.1
Dimethyl phthalate	0.01	0.03	0.02	0.01	0.02	0.02	0.02
Dibutyl phthalate	0.4	0.2	0.2	0.2	0.2	0.1	0.2
Dioctyl phthalate	0.7	1.3	1.0	0.9	1.6	1.0	2.6
Tributyl phosphate	0.01	0.08	0.07	0.04	0.07	0.06	0.1
Tris (2-butoxyethyl) phosphate	1.4	1.5	1.9	1.5	2.1	1.6	2.8
Atrazine *	0.1	0.1	0.1	0.1	0.1	0.1	0.2
Simazine	<0.01	0.02	0.01	0.01	0.04	ND	0.02

* Interferences present
ND Not detected
All concentrations in $\mu g l^{-1}$

Table 43 - Results from the analysis of water samples for TOC, AOX and volatile halogenated compounds

Sample	TOC	AOX	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	C_2HCl_3	C_2Cl_4	Total THM
Treatment works E	1.99	65.9	14.8	13.2	10.1	1.1	0.6	11.2	39.2
Service res BH	2.26	71.1	* -	* -	* -	* -	* -	* -	-
Hydrant WC	2.24	73.7	* -	* -	* -	* -	* -	* -	-
Hydrant M	2.51	72.4	14.4	13.5	11.9	1.0	0.9	15.2	40.8
Hydrant SL	2.05	79.2	15.2	10.7	8.0	0.9	0.8	12.3	34.8
Hydrant Bq	2.07	83.5	15.6	12.8	7.3	1.0	0.4	6.4	36.7
Hydrant BP	2.48	67.9	15.7	14.3	11.1	0.9	0.7	12.4	42

* Samples lost

All concentrations are in μgl^{-1} apart from TOC in mgl^{-1}

experiments, tetrachloroethylene was detected in the water leaving the treatment works at about the same concentration as was found in distributed water samples.

SECTION 6 - THE EFFECT OF MAINS RENOVATON TECHNIQUES ON WATER QUALITY

6.1 INTRODUCTION

The problem of internal corrosion of water mains leading to consumer complaints and eventual failure of the pipe is well-known. As an alternative to the high cost of replacing corroded pipes, water undertakings are making increasing use of a variety of relatively cheap pipe renovation techniques. Such techniques involve the removal of corrosion products, cleaning the pipe and, in some cases, relining to improve water quality and flow.

As part of this contract, an extensive study was undertaken on the leaching into water of organic contaminants from a water mains relining technique using epoxy resins (See Section 2). However, several other renovation techniques are in current use and the simplest and cheapest of these involves straightforward scraping or boring to remove corrosion products with no subsequent relining of the pipe(33). Three such techniques are power-boring, polly-pigging and water-jetting which are regarded as aggressive renovation or cleaning techniques. Power-boring is often used before non-structural lining and on some occasions, water mains are power-bored and returned to service overnight before being lined. Some water undertakings carry out polly-pigging and water-jetting to improve the carrying capactiy of the main without subsequent lining. These methods are distinct from non-aggressive cleaning techniques such as air scouring, swabbing and flushing which remove loose deposits from water mains, usually to improve water quality and reduce discoloration.

Concern has been expressed about the possible adverse effects on water quality following the application of such aggressive cleaning techniques. In particular, it is possible that following the removal of corrosion products the exposure of a 'fresh' surface of pipe will give rise to the leaching into water of organic (eg from coal tar pitch or bitumen linings) and inorganic contaminants such as iron. For example, it is known that PAH can leach into water from coal tar pitch linings(2).

In order to investigate these potential problems, a study of three renovation processes was undertaken in conjunction with WRc Engineering.

6.2 RENOVATION METHODS TESTED

a) Power-boring

The principle of powerboring is to mechanically scrape the inside surface of the pipe to produce a clean finish. A rod is fitted with a type of flail which is slowly pushed into the pipe and the rod rotated. When that particular length of rod has been pushed into the pipe another section of rod is added, and the process repeated. At the same time water is allowed to flow in the opposite direction to the powerboring to wash the scrapings out of the pipe.

b) Polly-pigging

Polly-pigs are shaped pieces of foam which, using water pressure, are forced along the length of pipe scraping it clean in the process. The surface of the pig can be smooth plastic or plastic coated with a variety of abrasive materials (eg carborundum, metal combs, or studs). The contractors claim that careful choice of the diameter and type of pig allows cleaning to leave a thin layer of corrosion products, to leave the original protective layer or to remove any coating to leave the metal.

c) Water-jetting

A high pressure water hose fitted with a cleaning nozzle is slowly pushed along the pipe. Water under pressure is forced through the nozzle, cleaning the corrosion products from the pipe. The nozzle is also fitted with small water jets so that corrosion products are washed away as the hose is pushed through the pipe.

6.3 DESIGN OF THE FIELD TRIALS

With the co-operation of a water utility, a programme of work was undertaken to assess the efficiency and effects on water quality of the three mains cleaning techniques described in Section 6.2. The criteria for judging the effectiveness of the cleaning procedure was to be internal inspection of the pipe and monitoring of water quality before, during and after cleaning. The individual parameters monitored were conductivity, pH, dissolved oxygen, colour, metals (ie iron, manganese, aluminium), PAH and a microbiological examination.

It was agreed by the water utility and WRc Engineering that if any of the above parameters exceeded EC directive limits, or consumer complaints after one month were unacceptably high irrespective of water quality, then the pipes were to be relined with a suitable material (eg cement mortar).

In setting up the trial WRc Engineering consulted WRc Environment and with the prior agreement of DoE it was decided that a series of samples would be taken to investigate, using GCMS, the range of organic contaminants in the water arising from the cleaning techniques.

The selected site formed a corner of a zone boundary, so work on the pipes would avoid disturbance to the remaining distribution system. The four test lengths of pipe (3 to be cleaned, 1 control) were supplied by a 4" mains pipe. Two of the test lengths were supplied by a common 4" loop (returning to the mains) which was cut to give two 4" dead-ends. After discussion with the pipe cleaning contractors and close-circuit television (CCTV, fiberscope) examination, the following cleaning programme was agreed.

Pipe	Mains size (diam in)	Selected cleaning method	CCTV observation
1	3	power-boring	Pipe showed little sign of corrosion at the ends but was poor in the middle.
2	4	polly-pigging	20% reduction in pipe diameter due to corrosion.
3	4	water-jetting	50% reduction in pipe diameter due to corrosion.
4	4	control	Little corrosion, inside surface black.

A typical daily schedule for the field work was:

8:30-9:00 - Consumer stop-taps closed
- Isolating valve closed
- Pipe cut

9:00-11:00 - Cleaning

11:00-11:30 - CCTV survey

11:30-12:00 - Chlorinate

12:00-13:00 - Flush, followed by return to service

All the preliminary work of digging holes, fitting valves for washouts etc was carried out by the water utility several weeks before the work commenced.

6.4 WATER QUALITY INVESTIGATIONS

In the course of the field trials samples were taken for the following analyses;

Conductivity
pH
Dissolved oxygen
Colour
Iron, manganese, aluminium
PAH
Microbiological examination
General organics using GCMS

The conductivity, pH and dissolved oxygen were all measured (using hand held meters) on site prior to and immediately after cleaning. Separate water samples were taken for PAH analysis and microbiological examination, carried out by the utility and general organics analysis and metals, carried out at WRc Environment.

Water sampling for colour and metal analysis was carried out using equipment designed by WRc Engineering ie an automatic liquid filtration instrument (ALFI). The ALFI is a programmable automatic device for collecting water samples (up to 36) at pre-determined times over several days. ALFI's were installed to collect samples for monitoring the water quality one week before and up to one month after renovation. The ALFI is fitted with a filter paper through which the water sample is pushed into a sample container. Any particulate material is retained by the filter paper and the colour of the filter paper compared with previous samples or standard charts. The water sample was retained for metal analysis at WRc Environment.

The sampling frequency adopted for general organics and PAH analysis was as follows:

Day	Pipe 1	Pipe 2	Pipe 3
1	Inlet	-	-
2	After return to service	Inlet	-
3	After overnight stagnation	After return to service	Inlet
4	After overnight stagnation	After overnight stagnation	After return to service
5	-	After overnight stagnation	After overnight stagnation

Inlet samples were taken from the main upstream of the renovation work.

6.5 ANALYTICAL METHODS

6.5.1 Polycyclic aromatic hydrocarbons (PAH)

Samples were analysed by the utility for the six PAH specified in EC drinking water directive ie fluoranthene, benzo(a)pyrene, benzo(k)fluoranthene, benzo(b)fluoranthene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene. Water samples (1 l) were extracted with cyclohexane (2x50 ml) and the extract dried with sodium sulphate. The cyclohexane was removed using a vacuum rotary evaporator, and finally to dryness with nitrogen gas. The residue was dissolved in methanol (200 µl), and analysed by HPLC using fluorescence detection.

6.5.2 General organics analysis

The water sample (1 l) was acidified to pH2 (with concentrated hydrochloric acid), and extracted with dichloromethane (2x100 ml). This was carried out in the utility laboratory as soon as possible after sampling. Deuterated internal standards were added to the initial aliquot of dichloromethane. The solvent extracts were returned to Medmenham and dried by freezing out any water before concentration using a Kuderna-Danish evaporator and nitrogen gas (final volume 100 µl) for analysis by GC/MS.

6.5.3 Metals analysis

The water samples collected by the ALFI's were returned to WRc Environment. They were acidified to give a nominal acid concentration of 0.1 M (concentrated nitric acid), and left overnight before analysis by plasma emission spectroscopy.

6.6 RESULTS AND DISCUSSION

Results from the analysis of water samples for PAH are provided in Table 44, and show that large increases in concentration followed application of each of the renovation processes. Since fluoranthene was always by far the most abundant of the six PAH monitored, concentrations of this compound only have been included in the Table. On pipe 1, after application of power-boring, the concentration of fluoranthene increased from less than 10 ngl^{-1} to over 1 µg l^{-1}, with a peak concentration of about 5 µg l^{-1} in a sample taken 15 hours after the pipe was returned to supply. The high initial concentration did not decrease significantly with time. About 3 weeks after renovation, the concentration of fluoranthene was still about 2 µg l^{-1}. Similar increases in the concentration of fluoranthene were recorded following the use of scraping (pipe 2) and waterjetting (pipe 3), although slightly lower peak concentrations were detected.

Results from the analysis of water samples for metals indicated a large increase in the concentration of iron following renovation, but less significant trends with other metals. Result from the determination of iron are presented in Table 45. For example, the concentration of iron increased from about 0.05 mg l^{-1} before power-boring, to over 1 mg l^{-1} immediately after renovation. However, in contrast to the leaching of fluoranthene, the concentration of iron did decrease with time. Thus, after 20 days the concentration had reduced to less than 0.1 mg l^{-1}.

Table 44 - Results for the analysis of fluoranthene in water samples following the application of mains renovation techniques

Time after renovation (hrs)	Inlet	Control	Concentration (ng l^{-1}) Pipe 1	Pipe 2	Pipe 3
Before renovation	<3	<3	6	3	4
0	<3	<3	1170	750	430
1	-	-	1070	680	100
15	-	-	5100	2660	150
40	<3	<3	3650	2850	2140
62	4	10	1310	2410	-
86	<3	5	1710	-	2160
134	<3	4	1510	1560	1760
206	<3	6	1660	1940	-
326	<3	<3	2690	2280	1700
398	<3	<3	3290	1830	1660
518	<3	<3	4200	1980	1290
686	<3	<3	2050	720	1130

- = no sample taken

Plots of the concentration of fluoranthene, iron and colour against time are provided in Figures 13, 14, and 15; these show high values immediately after renovation and then, usually, a slow decrease with time. The levels before renovation and maximum levels after renovation (about 24 hours) are shown in Table 46. This illustrates the dramatic increase observed in these three parameters following renovation.

Table 45 - Results from the analysis of iron in water samples following the application of mains renovation techniques

Time after			Concentration (mg l^{-1})		
renovation (hrs)	Inlet	Control	Pipe 1	Pipe 2	Pipe 3
Before renovation	-	-	0.05	0.07	0.08
0	0.05	0.08	1.36	1.66	2.11
8	0.11	0.05	1.72	1.94	4.45
16	0.07	0.11	-	2.24	-
24	0.05	0.06	1.20	0.83	-
30	0.08	0.06	0.95	2.19	-
38	-	0.09	1.99	2.50	-
44	0.05	-	0.85	-	0.31
50	0.06	0.23	-	1.98	-
58	0.06	-	1.23	-	-
75	0.05	0.08	1.06	0.91	0.18
99	0.06	0.07	1.03	0.90	0.27
123	0.08	0.07	0.84	1.29	0.21
147	0.06	0.11	0.66	1.13	0.26
171	0.07	0.12	0.67	-	0.26
195	0.07	0.04	0.85	0.92	0.21
215	0.09	0.11	1.02	0.90	0.37
235	0.08	0.11	1.00	0.70	-
259	0.06	0.11	0.51	-	0.13
317	0.05	-	0.49	0.87	0.16
340	0.07	-	0.42	-	0.15
365	0.08	-	0.32	0.61	0.11
390	0.04	-	0.18	0.47	1.44
413	0.04	-	0.13	0.36	-
437	0.17	-	0.08	-	-

For the other five PAH monitored levels were <10 ng l^{-1} before, during and after renovation - sampling being carried out in the week before, during and five weeks after renovation. Since fluoranthene is the most water soluble of the six PAH monitored, these results indicate that the observed increase in PAH levels was due to dissolution from the exposed coal-tar lining rather than particles of coal-tar from the lining being present in the water. If particles of coal-tar pitch had been present, much higher levels of the other five PAH monitored would also have been expected.

Table 46 - **Levels of fluoranthene, iron and colour before and after renovation**

Sample*	Fluoranthene ng l^{-1}	Iron mg l^{-1}	Colour **
Pipe 1			
before renovation	6	0.06	3.0
after renovation	5100	6.2	6.5
Pipe 2			
before renovation	3	0.06	2.0
after renovation	2850	4.1	6.0
Pipe 3			
before renovation	3	0.07	2.5
after renovation	2159	5.2	5.5

* Before and after (24 hr) renovation
** Determined subjectively by estimating filterable colour

The levels of aluminium and manganese also increased after renovation; aluminium rising from about 0.05 mg l^{-1} to a maximum of 0.15 mg l^{-1}, and manganese 0.01 mg l^{-1} to 0.05 mg l^{-1}.

Results from the analysis of water samples by GCMS are provided in Table 47. These results showed that numerous PAH and related chemicals were present in the drinking water. The predominant PAH was phenanthrene and, in addition, high levels of pyrene were evident. Note that these PAH are not included in the PAH specified in the WHO , Guidelines, the EC Directive and the UK Water Regulations. Both phenanthrene and pyrene also have relatively high water solubility which supports the hypothesis that the increased PAH levels were due to dissolution from a freshly exposed surface of coal-tar pitch.

It is only possible to make a preliminary comparison of the three renovation techniques tested based on only one set of trials. However, the fact that all the techniques lead to levels of PAH exceeding the EC Directive and Water Regulations for a substantial time is of concern.

Table 47 - Compounds identified by GCMS after mains renovation

	Sample	Inlet			Pipe 1 (power boring)			Pipe 2 (polly pigging)			Pipe 3 (water jetting)	
Compound	Day	1	2	3	1	2	3	2	3	4	3	4
Terpene (Limonene C10H16)		N	N	N	Y	Y	Y	N	N	N	N	N
Naphthalene		Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
		*<.1	<.1	<.1	0.1	0.4	0.3	0.6	1.4	1.4	<.1	<.1
Methyl naphthalene (isomers)		N	N	N	Y	Y	Y	N	N	N	N	N
Biphenyl		N	N	N	N	N	N	N	Y	Y	N	N
Dimethyl naphthalene (isomer)		N	N	N	Y	Y	Y	N	Y	Y	N	N
Acenaphthene		N	N	N	Y	Y	Y	N	N	N	N	N
Dibenzofuran		N	N	N	Y	Y	Y	N	N	N	N	N
C3-naphthalene		N	N	N	N	N	Y	N	N	N	N	N
Phenalene		N	N	N	Y	Y	N	N	N	N	N	N
Fluorene		N	N	N	Y	Y	N	N	N	N	N	N
Methyl biphenyl isomer		N	N	N	Y	Y	Y	N	N	N	N	N
4-Methyl dibenzofuran (182-M$^+$)		N	N	N	Y	Y	Y	N	Y	Y	N	N
4-Methyl dibenzofuran (isomer)		N	N	N	Y	Y	Y	N	Y	Y	N	N
Mixture includes:												
Dimethyl dibenzofuran (196-M$^+$)												
Trimethyl naphthalene and others		N	N	N	Y	Y	Y	N	Y	Y	N	N
Fluorenone		N	N	N	Y	Y	Y	Y	Y	Y	N	N
Dibenzothiophene		N	N	N	Y	Y	Y	Y	Y	Y	Y	Y
Phenanthrene/Anthracene		Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
(mainly phenanthrene)		*<.1	<.1	0.1	5.2	10.7	9.7	3.4	7.9	8.5	0.4	0.8
Carbazole		N	N	N	Y	Y	Y	Y	Y	Y	Y	Y
Unknown MWt 194		N	N	N	?	Y	Y	N	N	N	N	N
Methyl phenanthrene (isomer)		N	N	N	?	Y	Y	N	N	N	N	N
Methyl carbazole (isomer)		N	N	N	?	Y	Y	N	N	N	N	N
C17H16 PAH?		N	N	N	Y	Y	Y	N	N	N	N	N
C14H8N2? (204-M$^+$)		N	N	N	Y	Y	Y	N	N	N	N	N

Table 47 - continued

	Sample	Inlet			Pipe 1 (power boring)			Pipe 2 (polly pigging)			Pipe 3 (water jetting)	
Compound	Day	1	2	3	1	2	3	2	3	4	3	4
Fluoranthene		Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
		*<.1	0.1	0.1	1.0	2.5	2.3	1.0	2.3	2.5	0.2	0.2
Pyrene		Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
		*<.1	0.1	0.1	0.9	2.7	2.5	1.0	2.3	2.5	0.2	0.2

N = not detected
Y = detected
* semi-quantitative analyses by GCMS, results quoted as µg/l

Presumably these techniques remove corrosion products from the inside of the mains but uncover fresh coal tar pitch surfaces. Subsequent work carried out by WRc Engineering at this site indicated that relining with epoxy resin reduced the PAH to acceptable levels. Clearly, use of the cleaning or renovation techniques described in this section without relining the pipe cannot be recommended at the present time. Further studies on this phenomenon would be advisable.

SECTION 7 - THE LEACHING OF ORGANIC COMPOUNDS INTO WATER FROM RESERVOIR/TANK LININGS

7.1 INTRODUCTION

A wide range of linings are used by water undertakers as protective coatings for reservoirs and water tanks. Many products have been approved under the WBAS scheme and are listed in the Water Fittings and Materials Directory. However, as far as we are aware none of these products have been approved for use by the Committee on Chemicals and Materials for use in Public Water Supplies and Swimming Pools (CCM). Therefore, it is likely that insufficient information is available on leaching into water of organic chemicals used in formulating these products. A limited investigation has been undertaken of one protective coating in common use in the water industry.

7.2 SELECTION OF THE COATING TO BE TESTED

The following groups of products appear to be in use in the water industry although epoxy resin based products are probably the most common.

a) Epoxy resin coatings

These are two component products, comprising resin and hardener, which are mixed before use. Application is either by brush or spray. Products widely used by the water industry include: Nitocote EP405, Thoroseal and Febcure Sealcote.

b) Other types of coating

Product types used include polyurethane (usually factory applied), siloxanes (not in widespread use), polysulphides and bitumens.

c) Loose linings

These usually consist of sheets or membranes anchored to the reservoir/tank by internal water pressure. Common products include low density and high density PE sheets and linings made from butyl rubber.

d) Cement-based coatings

These are essentially concrete linings formulated with various additives to improve waterproofing. Commonly used additives include styrene-butadiene copolymers.

Because of the widespread use of epoxy resin coatings for reservoirs and water tanks it was decided to carry out experiments on a product from this group of materials. One of the most popular products in this range was selected and the manufacturer provided details on the formulation and supplied samples of the resin and hardener components.

The resin was based on a mixture of bisphenol A diglycidyl ether and bisphenol F diglycidyl ether while the hardener contained two curing agents, 2,2,4-trimethylhexamethylenediamine and isophorone diamine.

7.3 EXPERIMENTAL

Two glass plates (20 cm x 20 cm) were coated on both sides with the pre-mixed epoxy resin, the resin cured in the dark at room temperature for 24 hours and the coated plates placed in a glass tank. The total surface area of the epoxy resin was 1280 cm^2. Sufficient water (local borehole water, known to have a very low concentration of background organic contaminants) was added to cover the coated area (3 l), to provide a surface area to volume ratio of 0.4. This ratio is much larger than would normally be encountered in the routine use of these products. After 24 hours the water was removed for analysis. This was repeated for 48 hours and 96 hours, refilling on each occasion with fresh borehole water.

The above procedure was repeated (with freshly coated glass plates) using borehole water containing 1 mg l^{-1} chlorine.

The water samples were analysed for the trimethylhexamethylenediamine and isophorone diamine, determined as a combined concentration (method given in WRc Report PRD 896-M(15)), bisphenol A diglycidyl ether and bisphenol F diglycidyl ether (method given in WRc Report PRD 897-M(14)).

The chlorinated water samples (1 mg l^{-1} chlorine added: >90% free chlorine) were also analysed for free and bound chlorine before and after the leaching experiments.

7.4 RESULTS AND DISCUSSION

Neither bisphenol A diglycidyl ether or bisphenol F diglycidyl ether was detected in any of the samples (limit of detection about 2 µg l^{-1}). The concentration of total amine (trimethylhexamethylenediamine and isophorone diamine) was initially high, but fell rapidly over successive leaching periods. The results are shown in Table 48.

Analysis of the chlorinated water samples for free and total chlorine after each of the leaching periods showed that no free chlorine could be detected.

In the 24 hour sample, 1.0 mg l^{-1} bound chlorine was detected, but only a small amount of bound chlorine was found in the 48 and 96 hour samples (0.19 mg l^{-1} and 0.06 mg l^{-1} respectively). The apparent lower leaching rate in the presence of chlorine may be due to some of the leached amine reacting to form chloramines.

Table 48 - Concentration of amines leached from epoxy resin reservoir coating

Sample	24 hr		48 hr		96 hr	
	Conc+	Leaching rate*	Conc+	Leaching rate*	Conc+	Leaching rate*
Unchlorinated	2057	1531	78	29	52	10
Chlorinated	966	719	68	25	49	9

+ $\mu g\ l^{-1}$ measured as trimethylhexamethylenediamine
* $\mu g\ m^{-2}\ hr^{-1}$

A high initial leaching rate of organic amines from the coating was observed. In drinking water reservoirs the possibilities for extensive flushing, to remove the high amounts of amine that leach initially, may be limited. Consequently, the practice of lining reservoirs and tanks should be reviewed in the light of these results. If practical it would appear to be prudent to fill the reservoir, leave for at least 24 hours and then flush this water to waste before refilling and putting the reservoir back into public supply.

SECTION 8 - CONCLUSIONS AND RECOMMENDATIONS

8.1 EPOXY RESIN RELINING OF CAST IRON WATER MAINS

8.1.1 Four hour cure process

The results from the laboratory and field trials on the original process involving 4 hour cure prior to return to service showed that relatively high levels of organic contaminants were leached into water during the first 24 hours after relining. A full report on the laboratory and field investigations was submitted to the DoE Committee on Chemicals and Materials of Construction for use in Public Water Supply and Swimming

Pools (CCM), who were considering an application for approval of in situ applied epoxy resin linings. The Committee concluded that the high levels of organic contaminants leached from the resin were unacceptable on health grounds. However, the process was considered to be sufficiently promising to encourage the development of a modified epoxy-resin-based relining procedure to try to reduce the high level of leaching.

8.1.2 Sixteen hour cure process

Extending the curing period of the applied epoxy resin lining was considered to be the simplest way of reducing the levels of organic contaminants leaching from the resin into the water. Extending the cure time to 16 hours ensured that a greater proportion of the ingredients used in formulating the resin (unreacted monomers, cross linking agents etc) was incorporated into the cured resin and therefore unavailable for leaching into water.

Results showed that the degree of leaching was substantially reduced and consequently details of the process and results from leaching trials were submitted for consideration by the CCM. At this stage one of the epoxy resin formulations was withdrawn by the manufacturers. On the basis of the results obtained, the Committee concluded that the remaining resin system could be used by the Water Industry, on a limited basis, in order that the process could be further developed. In particular, developments in control and inspection equipment were needed so that procedures could be implemented to assure the quality of applied linings. In addition, further leachate data were requested to provide information on factors such as relining in areas of different water quality, the effect of different water temperatures and long-term leaching rates.

While these data were being gathered, the manufacturers of the resin and hardener components and the resin formulator commissioned detailed toxicological studies on the resin and hardener ingredients. This information, together with the additional data - described in the text and produced in studies outside of this work, enabled approval to be given for an epoxy resin formulation for the in situ relining of water mains. One requirement was that the epoxy resin must be applied in accordance with various stipulations (as described in the text).

8.2 ORGANIC COMPOUNDS INTRODUCED INTO DRINKING WATER BY PLASTIC PIPES

8.2.1 Leaching of organic contaminants from PE pipe

The work in the laboratory showed that a variety of organic chemicals can leach into drinking water in low concentrations from blue MDPE pipe. These were generally substances used in the manufacture of the pipe such as antioxidants, UV stabilisers and their degradation products. The same substances were detected at very low levels in several field studies particularly with newly laid blue MDPE mains. In particular, Irganox 1010 and 1076 were found to leach from MDPE pipe and their degradation product, 2,6-di-tert-butyl-p-benzoquinone, was found to be a common contaminant in water distributed by MDPE pipe. After six months the concentrations were reduced and often non-detectable. This degree and type of leaching is not believed to be significant in relation to possible risks to health. However, further information on the toxicology of these compounds would be needed to confirm this. However, some alkylated-p-benzoquinones have a strong tendency to cause tastes in water and there is some indication of an ability to cause sensitisation. 2,6-di-tert-butyl-p-benzoquinone was tested and found to have a taste threshold considerably in excess of the concentrations of this compound detected in drinking water during field trials. However, further investigation of this quinone would be prudent. Phthalimide has also found to leach from blue MDPE and this proved to be due to its presence as an impurity related to the blue pigment copper phthalocyanine, probably formed during pipe extrusion. All blue MDPE pipes studied leached phthalimide in the laboratory. However, field work showed that while phthalimide could leach from new MDPE pipe its presence in water distributed through MDPE systems was very sporadic. This may have been due to rapid depletion or reaction with free chlorine. Evidence for the latter (which indicated the production of a chlorophthalimide) was obtained but accurate quantitative analysis of chlorophthalimide proved difficult due to its instability. There is little toxicological data for phthalimide and none for chlorophthalimide.

8.2.2 Leaching of organic contaminants from u-PVC pipe

Studies showed that a range of organic chemicals leach from new u-PVC pipe into water. However, the levels were very low and do not appear to pose any risks to health based on available toxicity data. Although no work on u-PVC pipes in the field was carried out, it is expected that these very low levels would reduce gradually following installation.

8.2.3 Leaching of organic contaminants from GRP pipe

A wide range of contaminants were found to leach into drinking water from the GRP pipe examined, including a range of phthalates and styrene. The leaching rates were appreciable and although depletion with time would be expected, further studies are needed.

8.3 PERMEATION OF PE PIPES BY ORGANIC CHEMICALS

8.3.1 Permeation by natural gas odorants

A contact time of at least 40 days was required for natural gas odorants to permeate blue MDPE and produce a discernible taste/odour in a water sample. Once breakthrough had occurred it appeared that at least two days were required for a sufficient amount of odorants to permeate the pipe and cause a slight off-taste. For a strong taste to be transmitted to the water a 7 day exposure to the pipe was required.

With the use of PE gas pipes which are much less likely to leak than iron gas pipes, the likelihood of PE water pipes being exposed to natural gas for long periods seems remote. However, PE water pipes could be permeated by natural gas odorants if such contamination of the surrounding soil by gas did occur.

8.3.2 Permeation of PE by potential soil contaminants

The laboratory experiments demonstrated that blue MDPE was readily permeated by non-polar chemicals such as toluene, slowly permeated by phenol, a more polar substance, but not permeated by more complex polar molecules such as the pesticides paraquat, malathion and atrazine. In additional experiments significant penetration of MDPE occurred with m-cresol, nitrobenzene, chlorobenzoic acid and cyclohexane. Although attempts were made, accurate prediction of the rate of permeation by chemicals from physical/chemical data could not be made. PE pipe is clearly very vulnerable to permeation by certain chemicals which could lead to significant contamination of supplies, at least on a local basis. The contaminants could arise in the soil by spillage (after laying of the pipes) or by inadvertently laying pipes in contaminated ground.

8.3.3 Permeation of PE pipe laid in contaminated ground

No significant permeation of a MDPE service pipe (and a u-PVC fire main) installed in a contaminated land site was encountered. The MDPE pipe may have been permeated by C_4-benzenes and tetrahydrofuran in the last samples taken, however, the concentrations of these compounds were very low and it was not possible to be certain that their presence in water from the MDPE pipe was indicative of permeation. Further work to determine the typical concentration of C_4-benzenes and tetrahydrofuran in the water supply to the site, would have to be carried out to confirm that permeation had occurred.

In view of the known susceptibility of MDPE to permeation by certain organic compounds, the experimental results appear surprising, but the following factors could have influenced the results. The site was contaminated mainly with compounds which would not be expected to readily permeate MDPE or u-PVC. Another important factor is likely to be the effect of soil particles on the permeation behaviour of organic chemicals. In general, data on the permeation of MDPE and u-PVC by organic chemicals has been obtained in the laboratory with experiments using either a concentrated aqueous solution of the test compound or the vapour phase in contact with the plastic. Very little information is available on the effect of the presence of soil particles on permeation behaviour. It is possible that compounds bound onto soil particles will not be 'available' for permeation. The results from the investigation of a contaminated site indicate that the effect of soil particles on permeation behaviour may be significant. This is a subject needing further investigation. Since the soil contaminants were specific to this particular site it was not possible to draw broad conclusions covering other sites, with different contaminant. A better understanding of the mechanism of permeation is required to be able to predict the permeation potential of a contaminated soil with any accuracy.

8.4 THE EFFECT OF THE DISTRIBUTION SYSTEM ON ORGANIC COMPOUNDS IN DRINKING WATER

The work carried out to determine any changes, during distribution, in the nature of organic contaminants present in finished water and also to identify any contaminants arising from the distribution system itself, showed that few changes took place. However only one treatment works/distribution system was studied and it is possible that other systems may give different results. Matching the water samples taken in the distribution systems to the same water leaving the treatment works was difficult and small changes could have been due to this problem.

A wide range of organic contaminants were always present in the finished water and virtually all of these were found in distributed samples, even at the extremities of the system. Contaminants such as phthalates, atrazine, simazine and organic phosphates showed no marked changed in levels during distribution. THMs increased, markedly on one occasion, through the distribution system. However this is a known phenomenon and is due to further chlorination reactions or breakdown of chlorinated THM precursors. TOC and AOX did no show any significant changes.

A small number of organic contaminants were found only in samples from the distribution system. However, the source of these is difficult to explain in terms of our knowledge of distribution materials and other potential sources. The information gathered suggests that for some contaminants, monitoring in relation to the Water Supply (Water Quality) Regulations 1989, could be undertaken at supply points (treatment works, service reservoirs etc) rather than from consumer's taps. For example, this should be the case for atrazine and simazine.

8.5 EFFECT OF MAINS RENOVATION TECHNIQUES ON WATER QUALITY

The comparison of the three renovation techniques tested was based on only one set of trials. However, it is of concern that all the techniques led to PAH levels in excess of maximum values specified in the Water Supply (Water Quality) Regulations 1989, for a substantial period of time. These techniques remove corrosion products from the inside of the mains and this probably uncovers fresh coal-tar pitch surfaces from which leaching takes place. Subsequent work carried out by WRc Engineering at the same site indicated that relining with epoxy resin reduced the PAH to acceptable levels. Clearly, use of the cleaning/renovation techniques described in the report without relining the pipe cannot be recommended at the present time. Further studies on this phenomenon are recommended.

8.6 LEACHING OF ORGANIC COMPOUNDS INTO WATER FROM RESERVOIR/TANK LININGS

Only a limited amount of experimental work was possible on the leaching of organic contaminants from tank or reservoir linings. However the one product examined (an epoxy-resin based coating) did illustrate that a relatively high concentration of one of the ingredients used in the formulation could leach into water in the short term, although this level did rapidly reduce with time. Although it is difficult to use the results from the epoxy resin coating studied to predict the behaviour of other coatings, it does appear likely that some ingredients in the coating will leach into water, particularly in the first few hours following the first contact with water after application.

It is recommended that such products receive more detailed study of leaching potential before being used in contact with potable water.

8.7 GENERAL CONCLUSIONS

The work has shown that the distribution system is a potential source of organic contamination of drinking water. This is important bearing in mind that distributed water goes directly to the consumer. Thus it is vital to ensure that distribution materials and processes do not lead to significant organic contamination of supplies. Currently this is covered mainly by the Committee on Chemicals and Materials of Construction for use in Public Water Supply and Swimming Pools (CCM) and to some extent the Water Byelaws Advisory Scheme.

Organic substances can enter supplies in several ways, ie leaching from plastic materials, application of renovation processes and permeation of certain plastic pipes. Some introduction of organic chemicals from such sources is inevitable at some level, particularly in the early stages - ie with a newly laid pipe or after a recent renovation. This is not significant in itself. However, it is important to fully evaluate materials and processes prior to use with respect to any potential to introduce, or cause, significant levels of organic contamination. Such evaluation inevitably requires complex trace organic analysis for known substances (formulation components) and unsuspected components (formulation impurities, byproducts etc) - the latter needing techniques such as gas chromatography - mass spectrometry (GC-MS). An assessment of the possible effect of chlorine (or any other disinfectant in supply) is essential in many cases. This is because new chemicals could be formed.

An outcome of this work has been that the CCM has largely incorporated several of the methods or approaches developed into their approval scheme for materials and chemicals for use in contact with potable water.

At the present time the testing of materials is being considered by several EEC Committees with a view to establishing standard methods for EEC countries. In many ways the UK systems for evaluating materials is more stringent than the schemes operated in other countries. Such schemes rarely include any evaluation of unsuspected chemicals. Consequently the strength of the UK approach needs to be included in any future EC protocol.

8.8 SUMMARY OF RECOMMENDATIONS

General

It is recommended that materials, chemicals and processes connected with the distribution system are rigorously evaluated before use for any potential to cause significant levels of organic contamination. This assessment requires complex trace organic analysis, not only for the known formulation constituents but also for unsuspected impurities and byproducts using techniques based on mass spectrometry. In addition, the effect of chlorine (or any other disinfectant in supply) needs to be evaluated. Such evaluations need to be carried out where appropriate under realistic conditions. It should be noted that during the duration of this project these recommendations have been largely incorporated into the approval scheme operated by CCM. The Water Bill has added mandatory power to the UK approved scheme and the CCM is under revision. It is recommended that the vigorous approach of CCM is maintained and that the new revised scheme is made more 'visible' to industry. The more stringent UK approach should be incorporated in any new scheme, developed by the EEC Committees. Possibly the data in this report could help in assuring this.

Specific

1. Recommendations associated with the work on in situ applied epoxy resin have been made to CCM during the progress of the work and have been acted upon. With the emergence of an approved relining system

the only recommendation now is that the associated stipulations aimed at assuring the quality of the applied lining are strictly followed.

2. With respect to leaching from plastic pipes;

   - more toxicological data on phthalimide and 2,6-di-tert-butyl-p-benzoquinone (impurities in blue MDPE pipe) would be of value in assessing their significance. Further investigation of the taste potential of the latter would be prudent.

   - more investigation of the leaching of organic substances from GRP pipe is needed.

3. PE pipe is vulnerable to permeation by certain organic chemicals when they contaminate soil. However, it is difficult to accurately predict the degree of permeation and subsequent contamination of drinking water; further work in the area is needed.

4. The application of the aggressive pipe renovation techniques described in the text led to significant contamination by PAH. Consequently, is it recommended that further investigations are carried out on water quality effects arising from these and other renovation techniques. The renovation techniques studied in this work should not be used without subsequent relining of the mains.

5. Further work is needed on the leaching of organic contaminants from reservoir/tanks linings. While new products are covered by the CCM scheme (and probably its successor), older products may need some re-evaluation.

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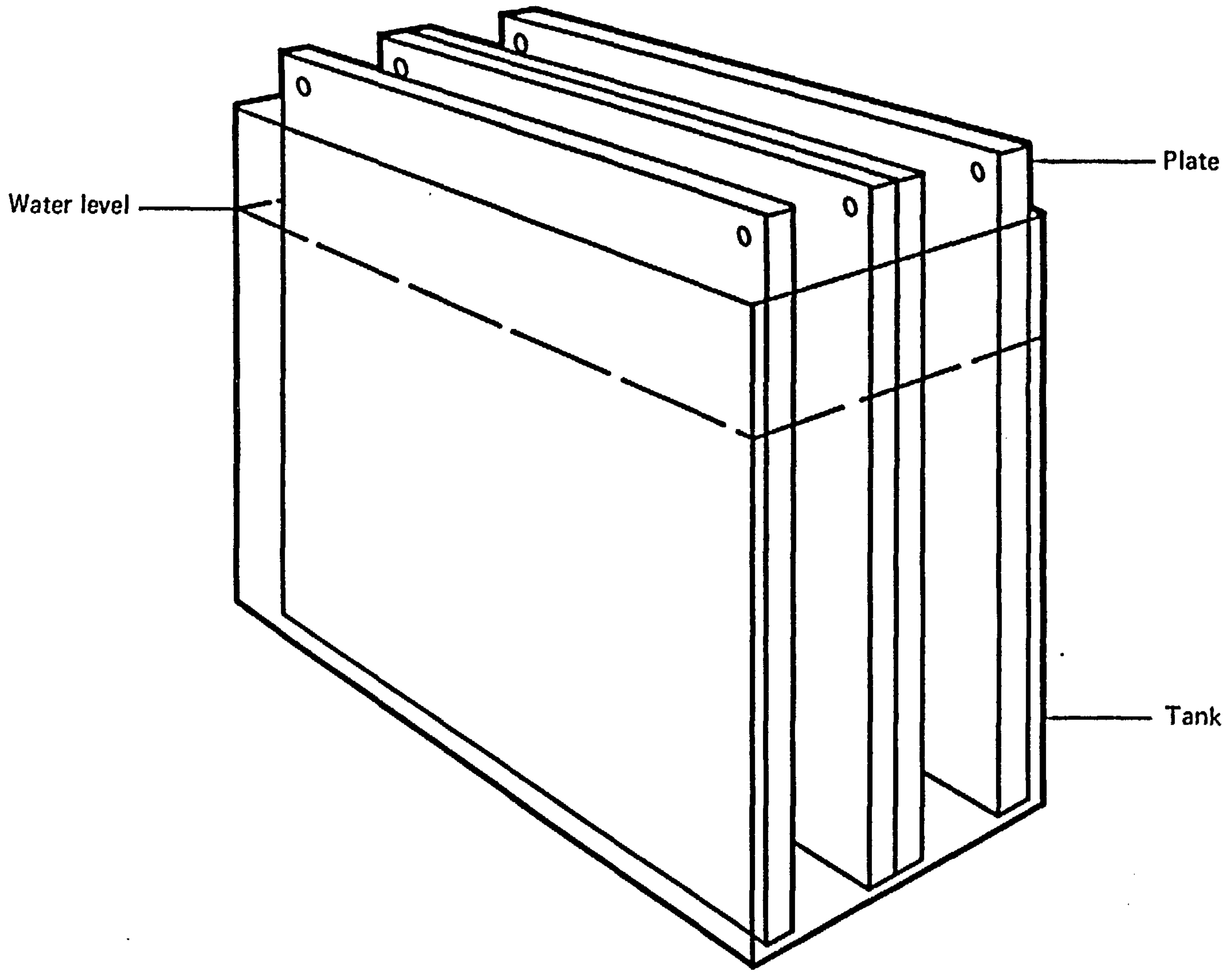


Fig. 1 Organic leachate rig

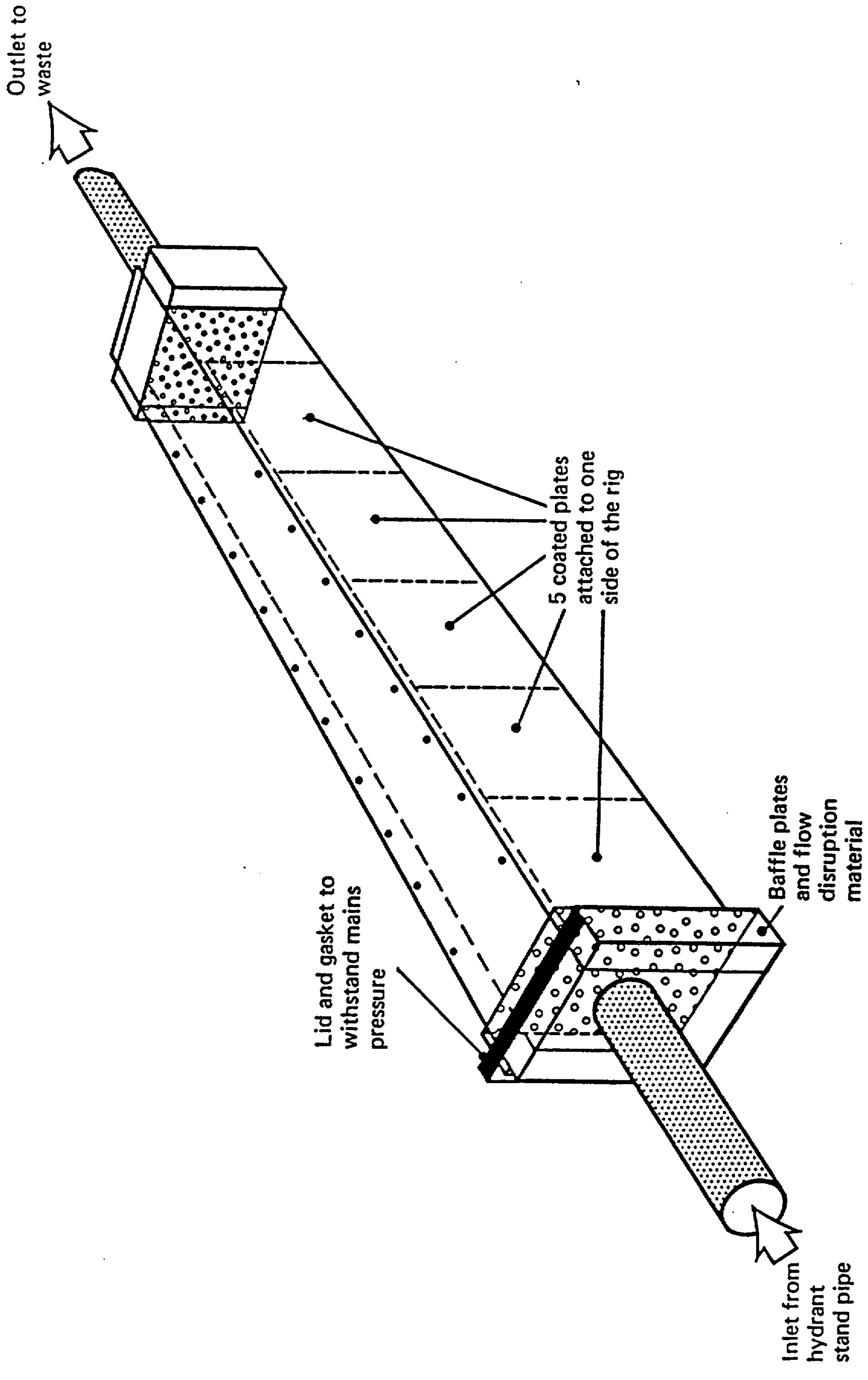

Outlet to waste
Lid and gasket to withstand mains pressure
5 coated plates attached to one side of the rig
Baffle plates and flow disruption material
Inlet from hydrant stand pipe

Figure 3. Results from Laboratory experiments

Plot of leaching rate versus time for trimethylhexamethylene diamine

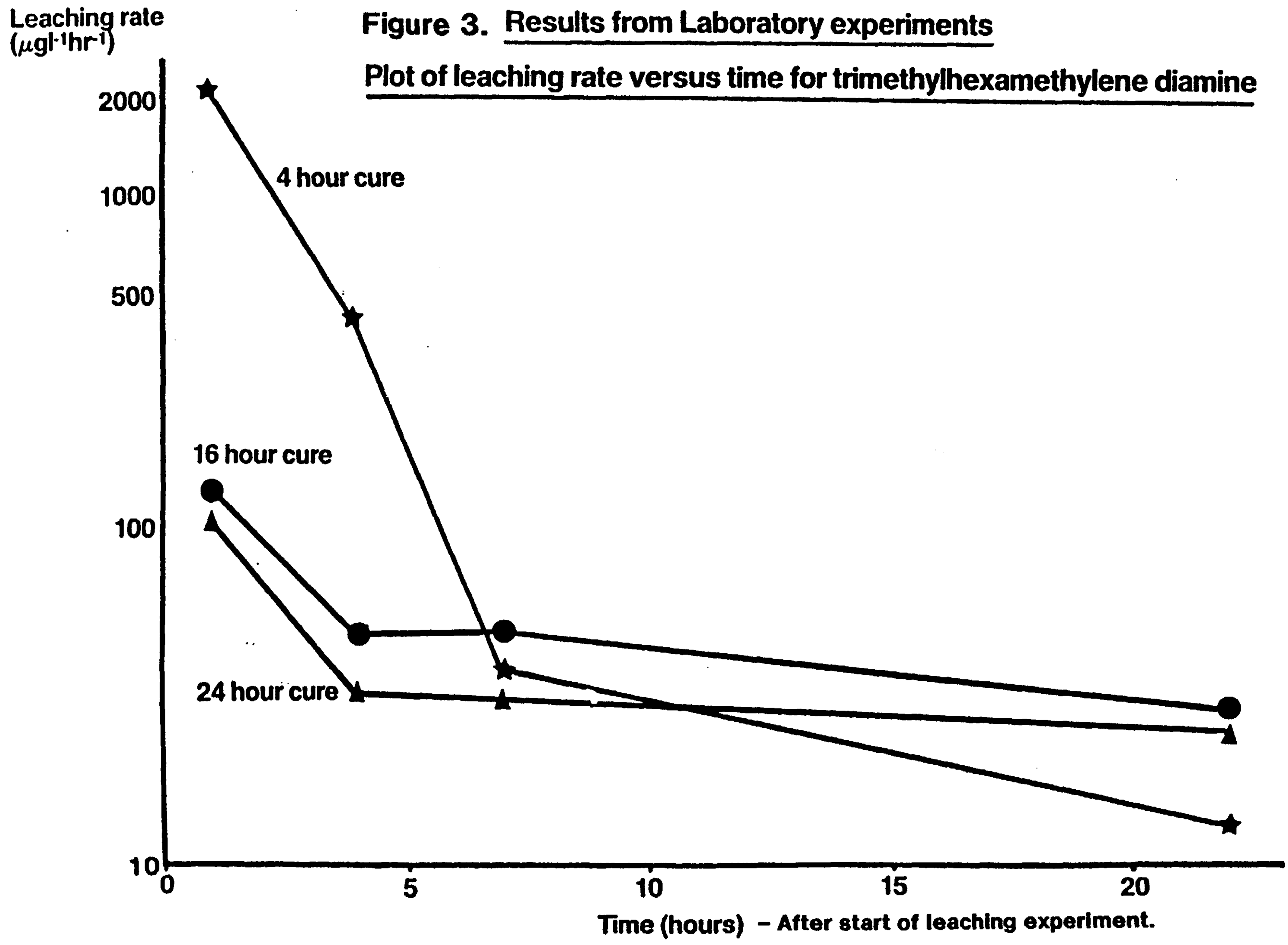


Figure 4.

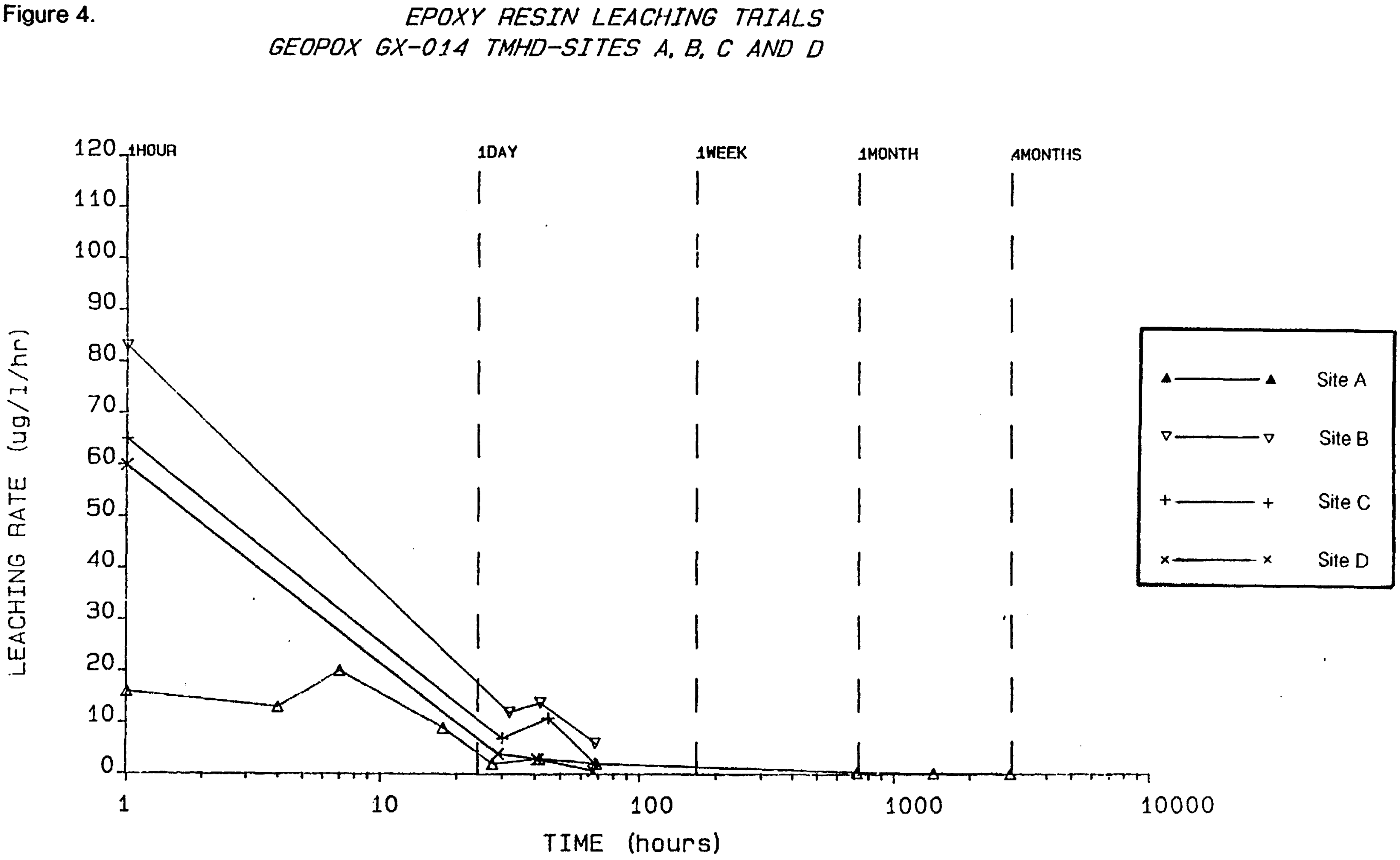

EPOXY RESIN LEACHING TRIALS
GEOPOX GX-014 TMHD-SITES A, B, C AND D
LEACHING RATE (ug/l/hr)
120
110
100
90
80
70
60
50
40
30
20
10
0
1HOUR
1DAY
1WEEK
1MONTH
4MONTHS
1
10
100
1000
10000
TIME (hours)
Site A
Site B
Site C
Site D

Figure 5.

EPOXY RESIN LEACHING TRIALS
GEOPOX GX-014 BISPHENOLS-SITES A, B, C AND D

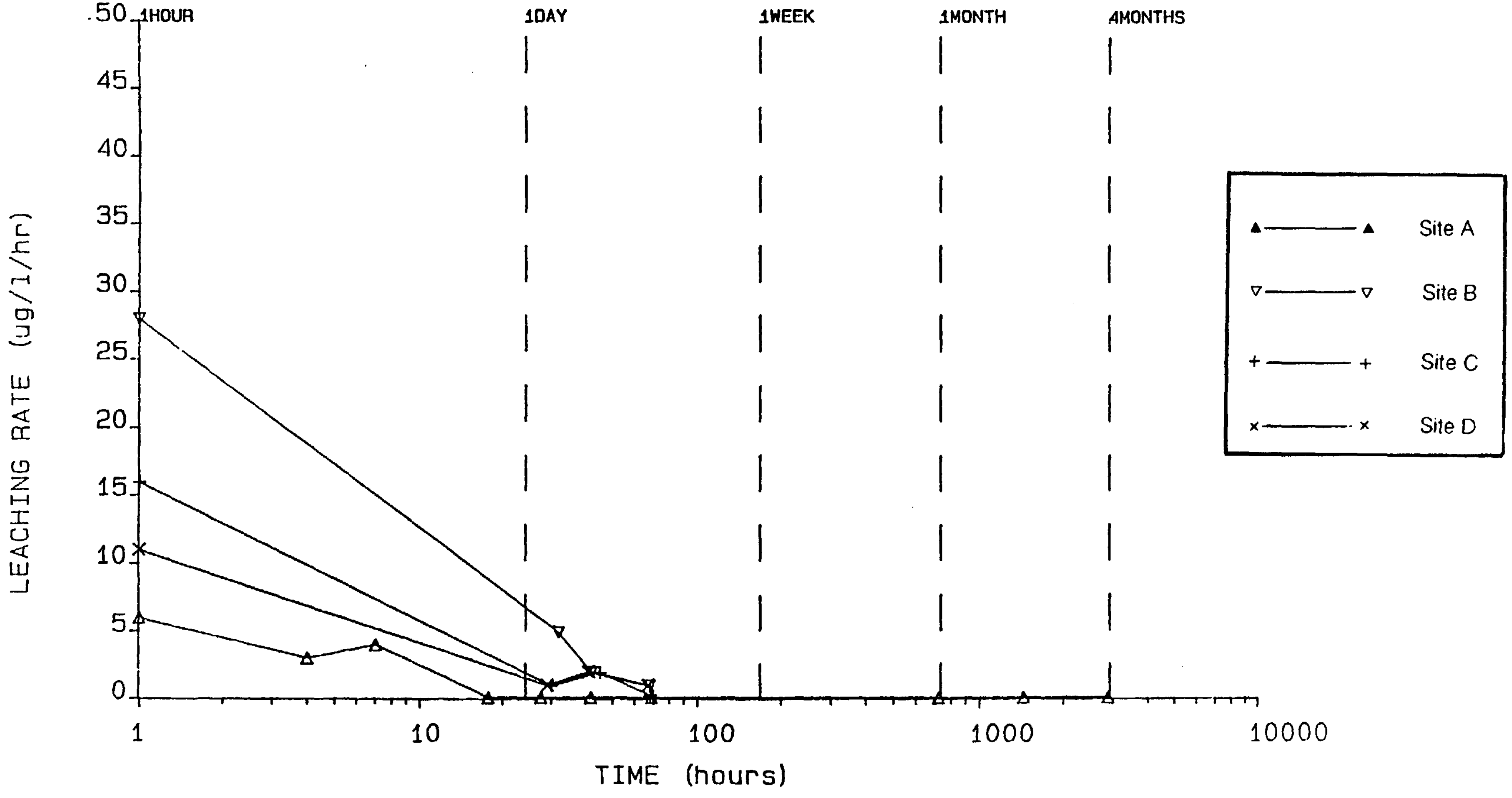
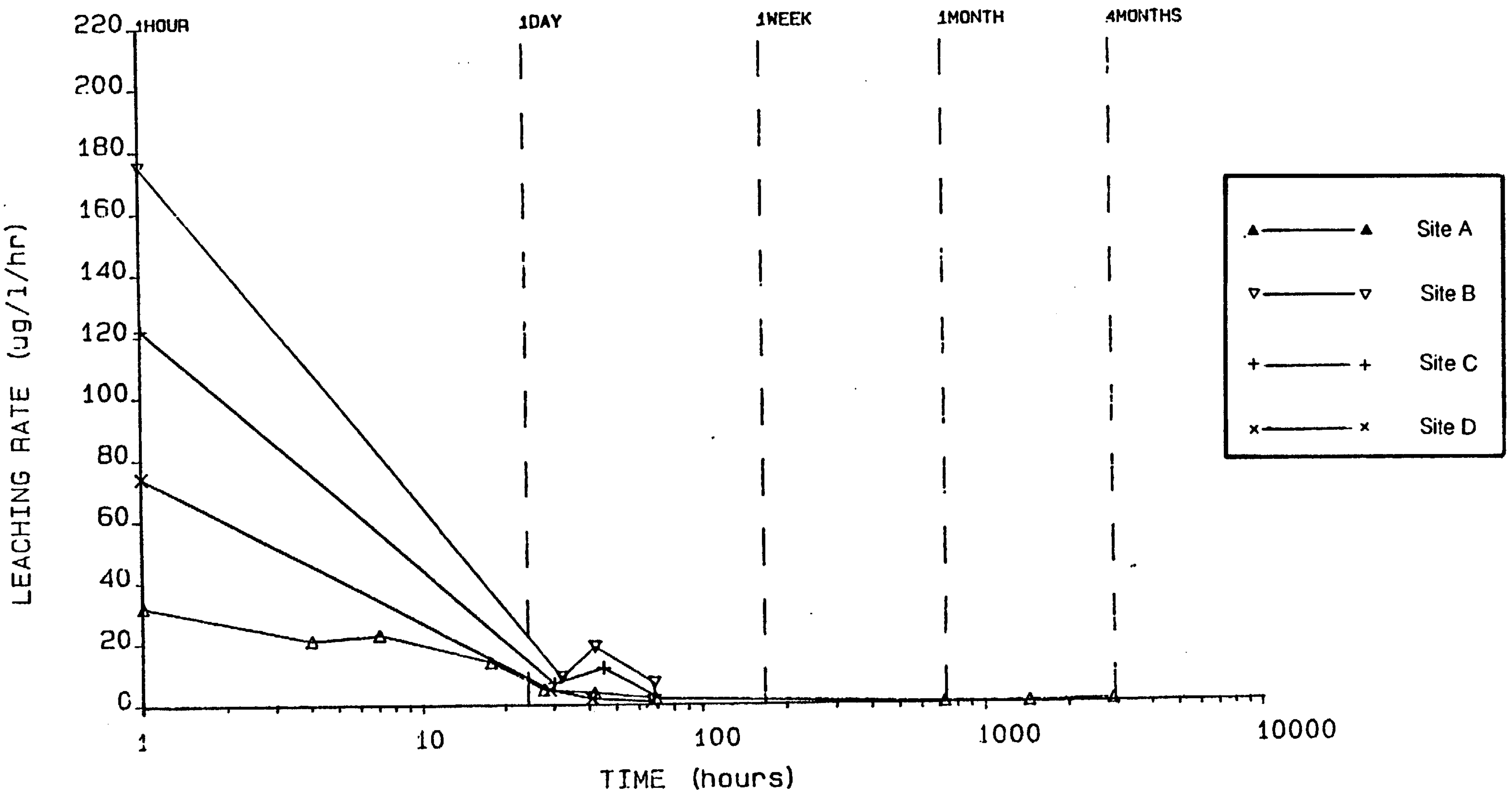


Figure 6.



EPOXY RESIN LEACHING TRIALS
GEOPOX GX-014 PTSA-SITES A, B, C AND D

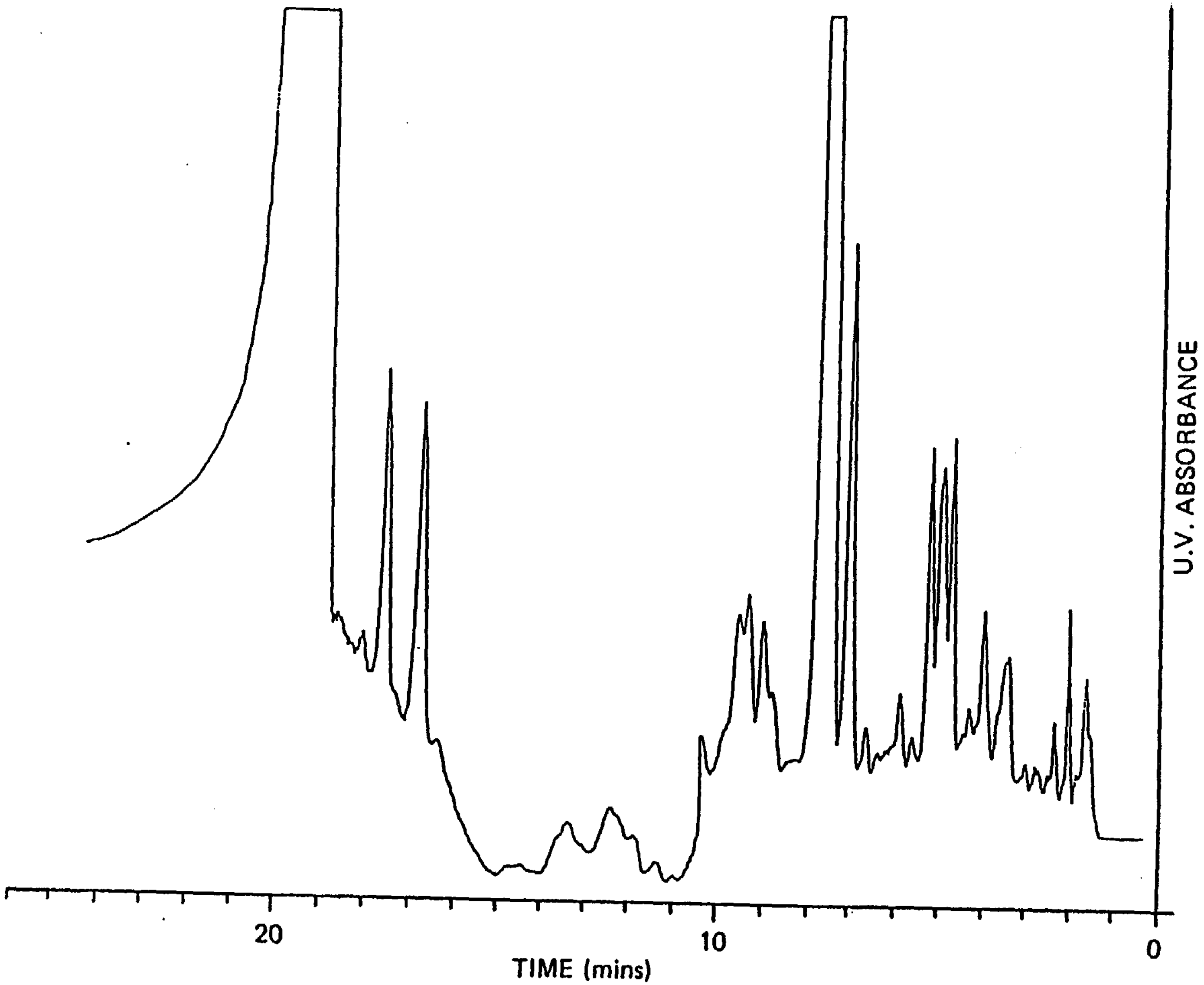


Fig. 7. Chromatogram from the HPLC separation of an extract from medium density blue polyethylene.

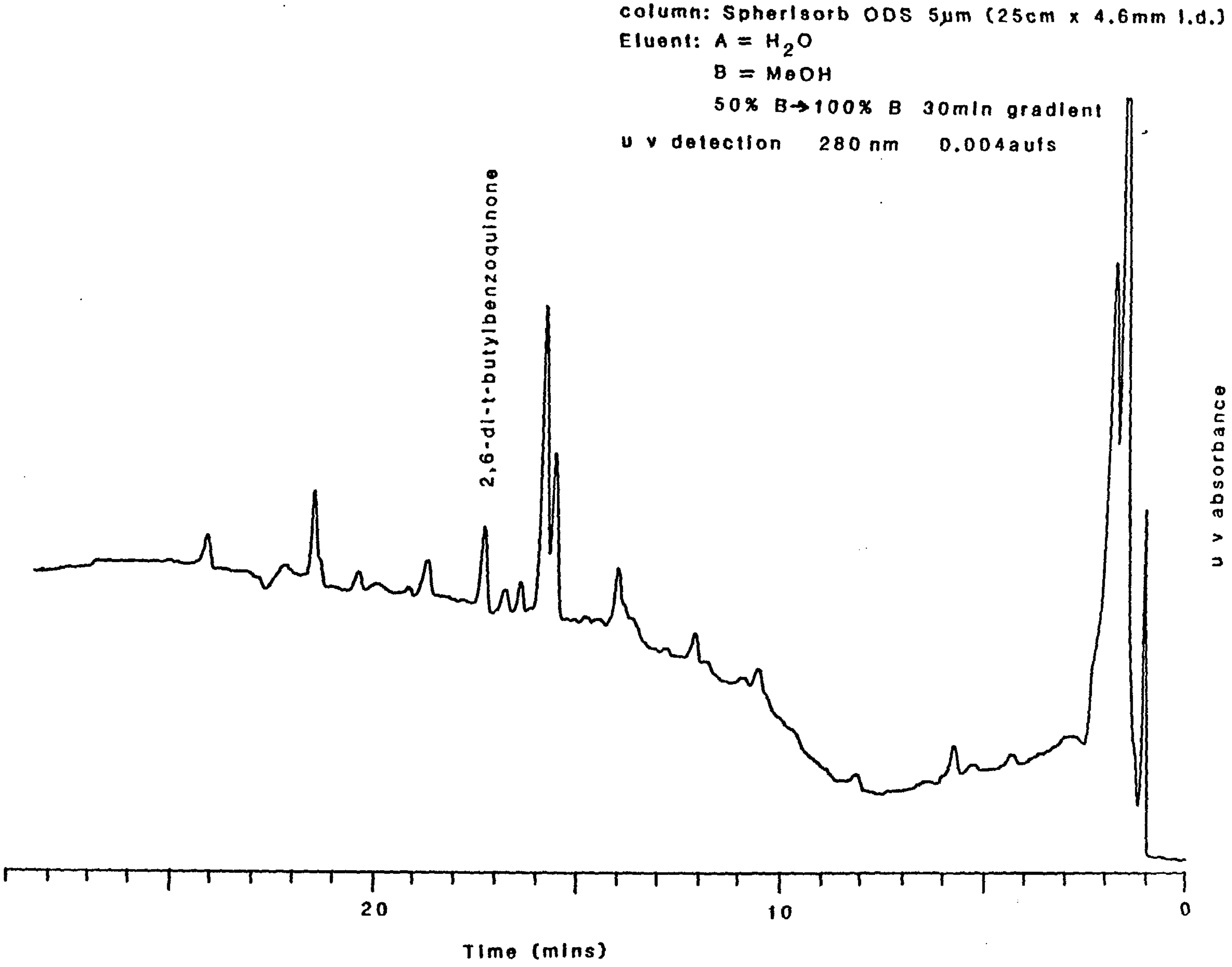


Figure 8. Chromatogram from the HPLC separation of an extract of water distributed by MDPE pipe.

Figure 9. Total ion current chromatogram from GCMS analysis of water from treatment works E

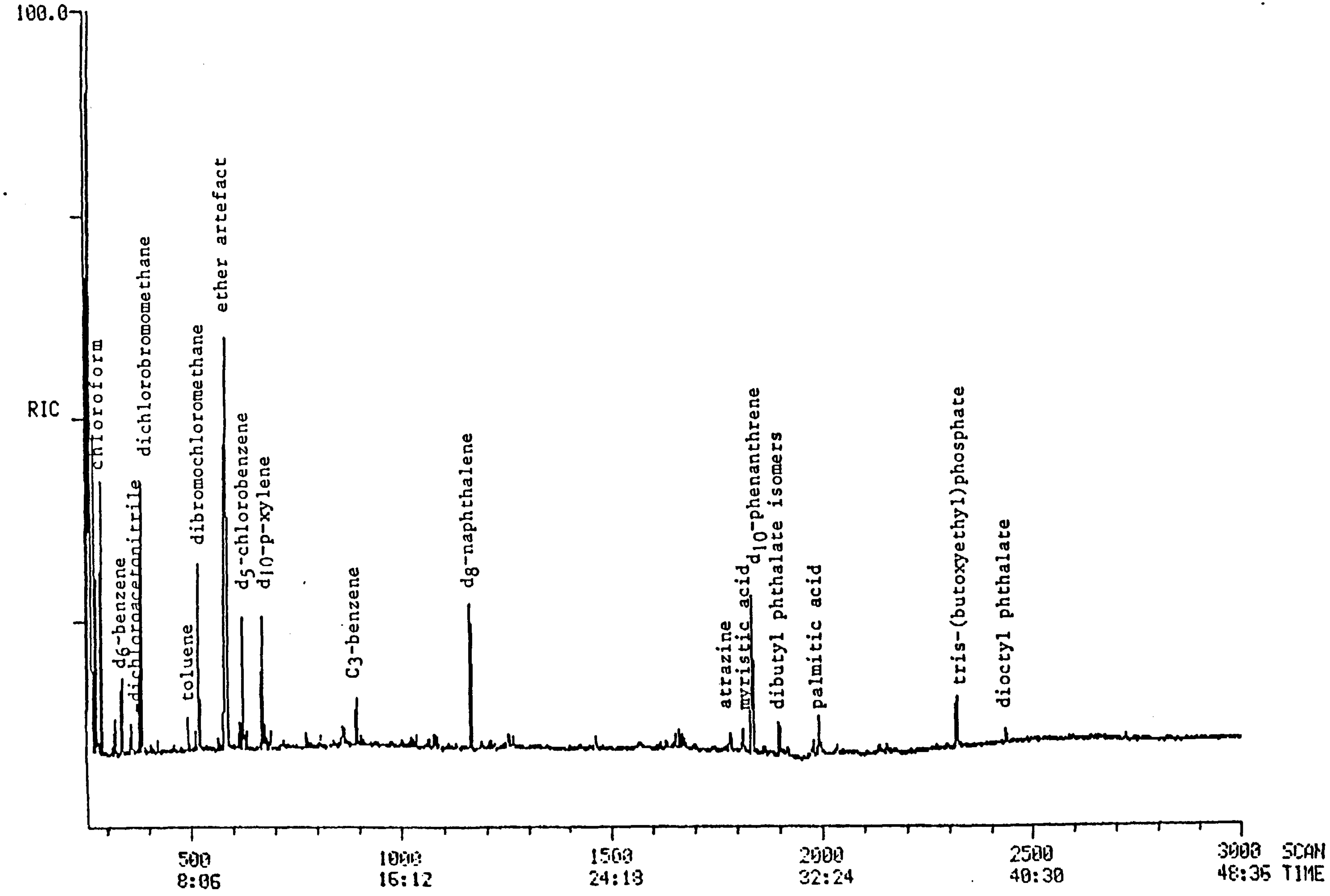


Figure 10. Total ion current chromatogram from GCMS analysis of water from distribution system reservoir EG

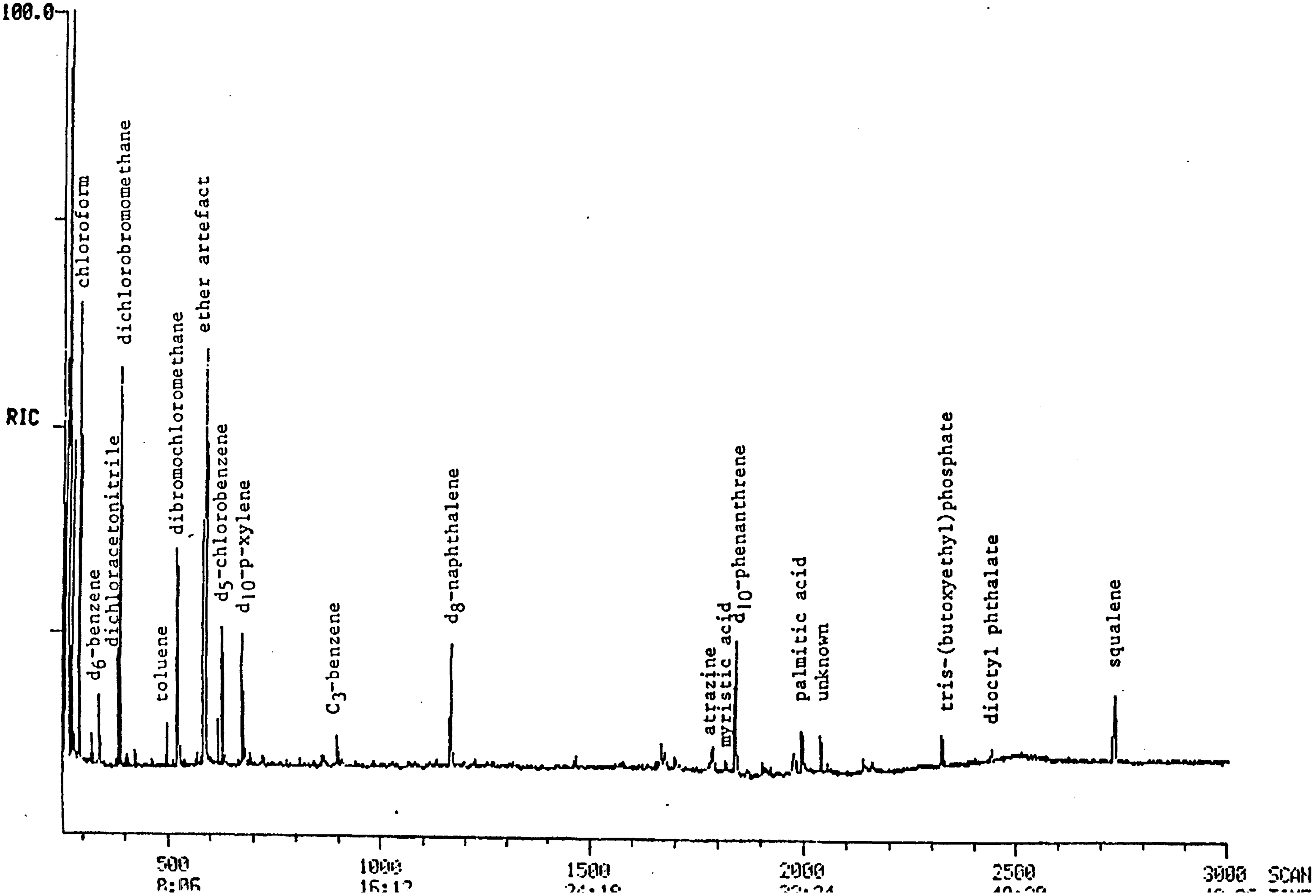


Figure 11. Total ion current chromatogram from GCMS analysis of water from distribution system reservoir SH

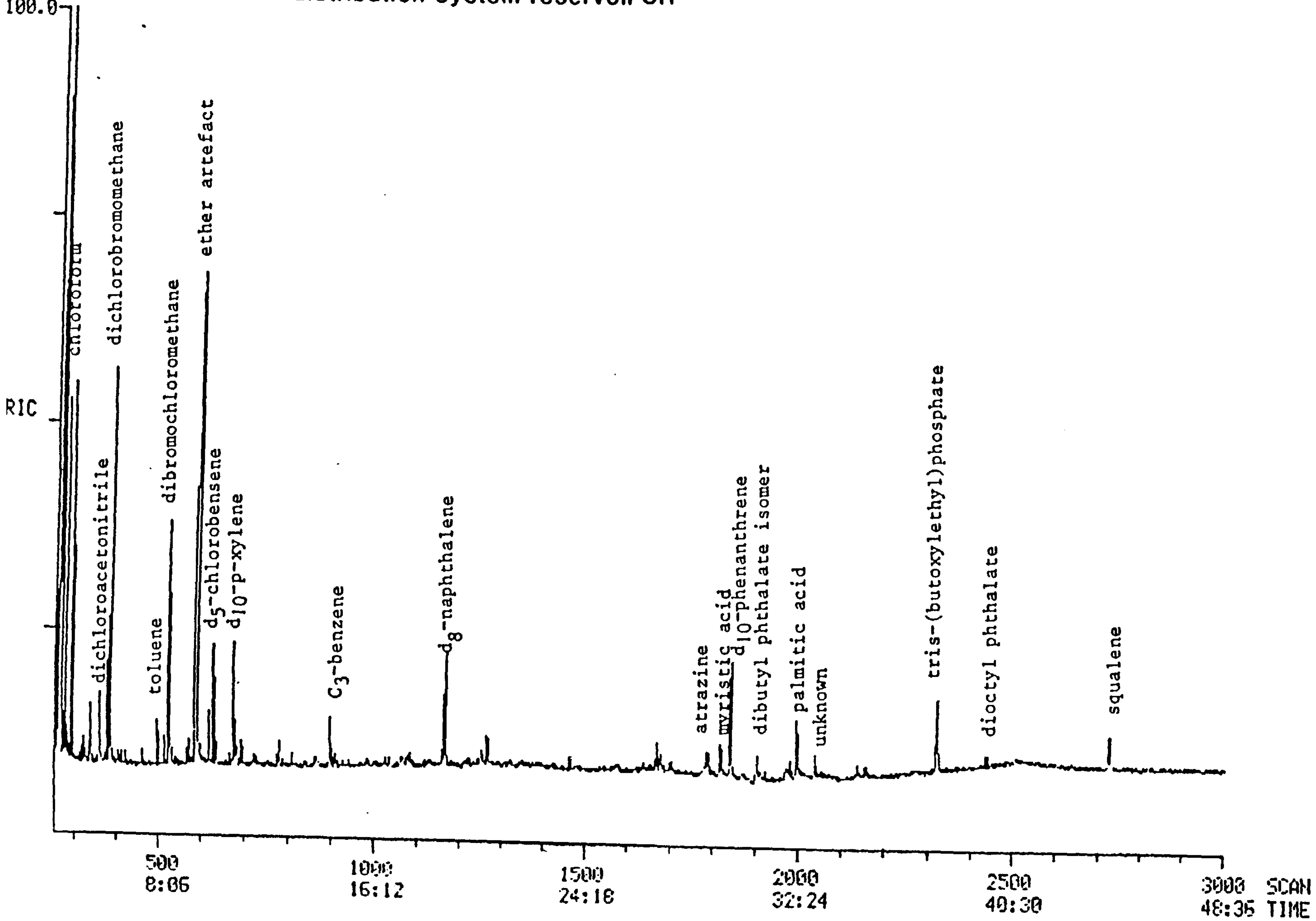
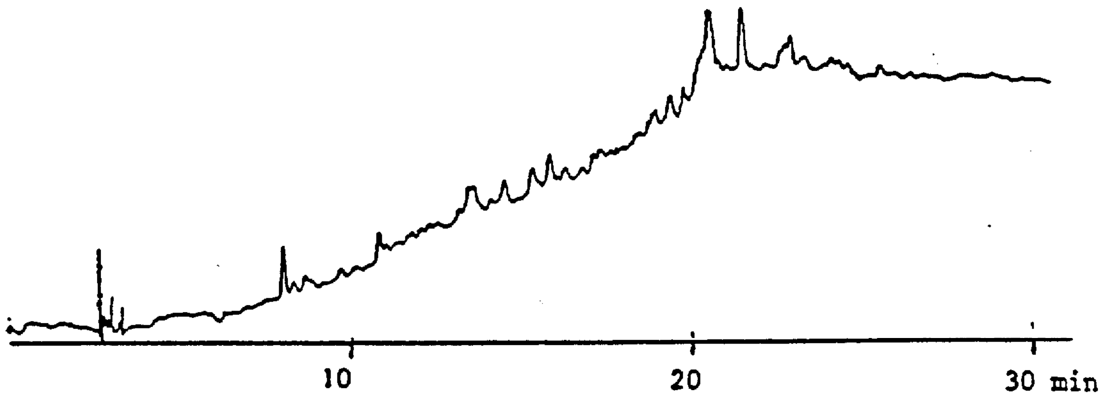
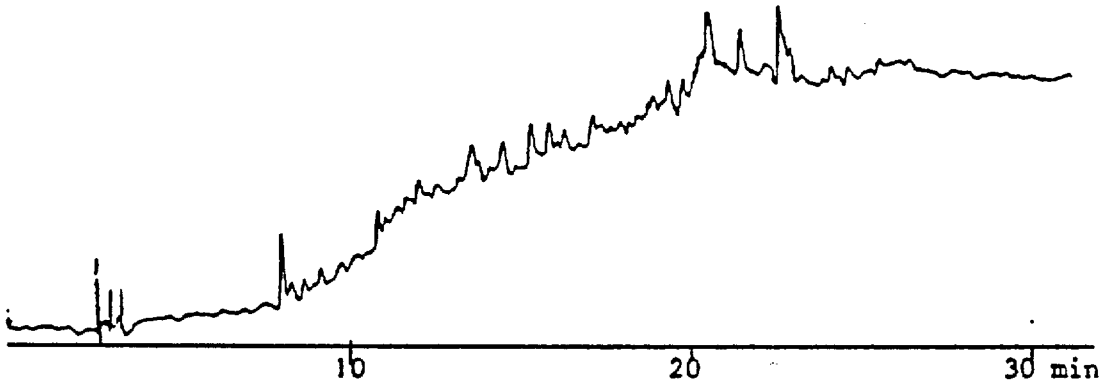


Figure 12. HPLC separation of dichloromethane extracts from water samples taken from a treatment works and from two points in the distribution system

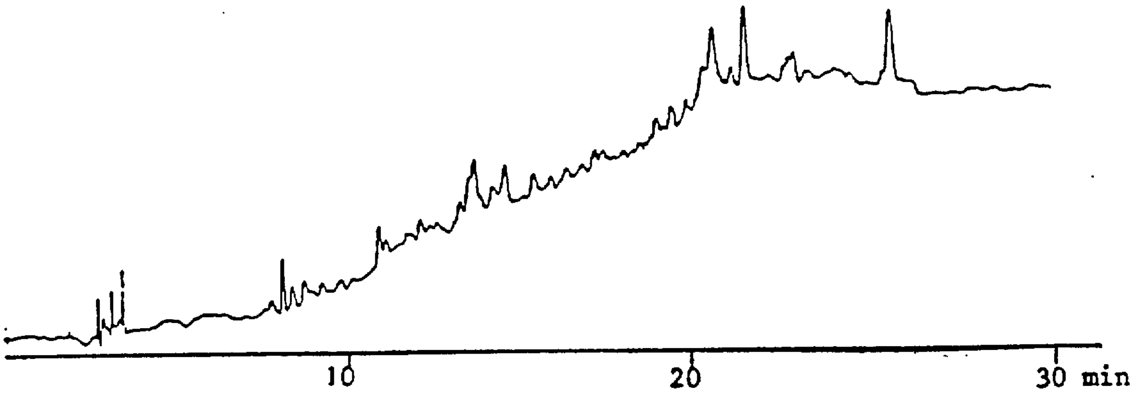
(i) Works E



(ii) Distribution Reservoir EG



(iii) Distribution Reservoir SH



LC conditions: Column: ultratechsphere 5.005 25 cm x 4.6 mm ID
Eluent: acetonitrile/water - 0.1% acetic acid
Flow: 1 ml min^{-1}
20 minute gradient from 10% ACN to 90% ACN with 10 minute hol
λ = 254 mm range = 50 mAU

Figure 13. Variations of fluoranthene, iron and colour: length 1 (power boring)

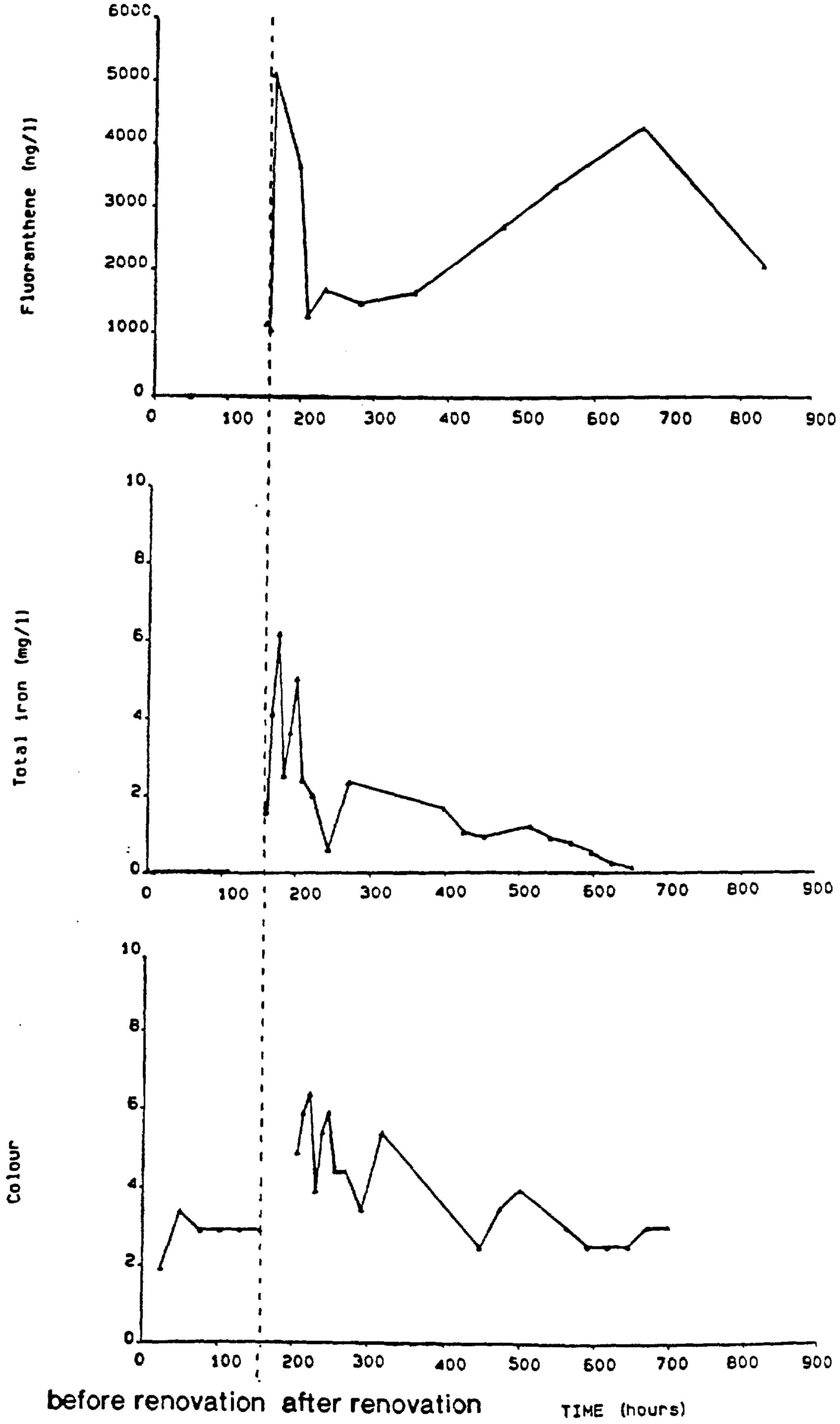


Figure 14. Variations of fluoranthene, iron and colour: length 2 (pollypigging)

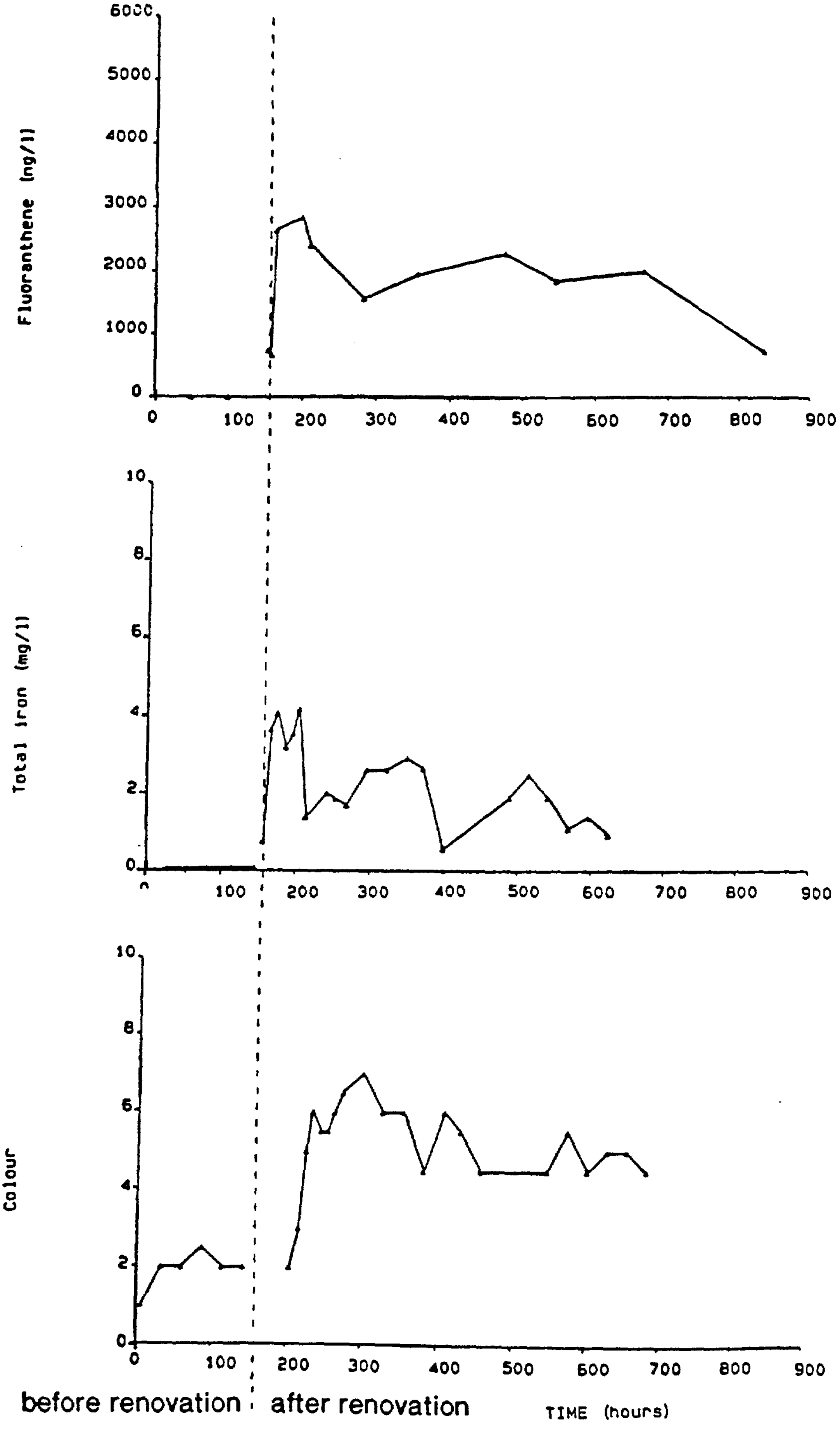
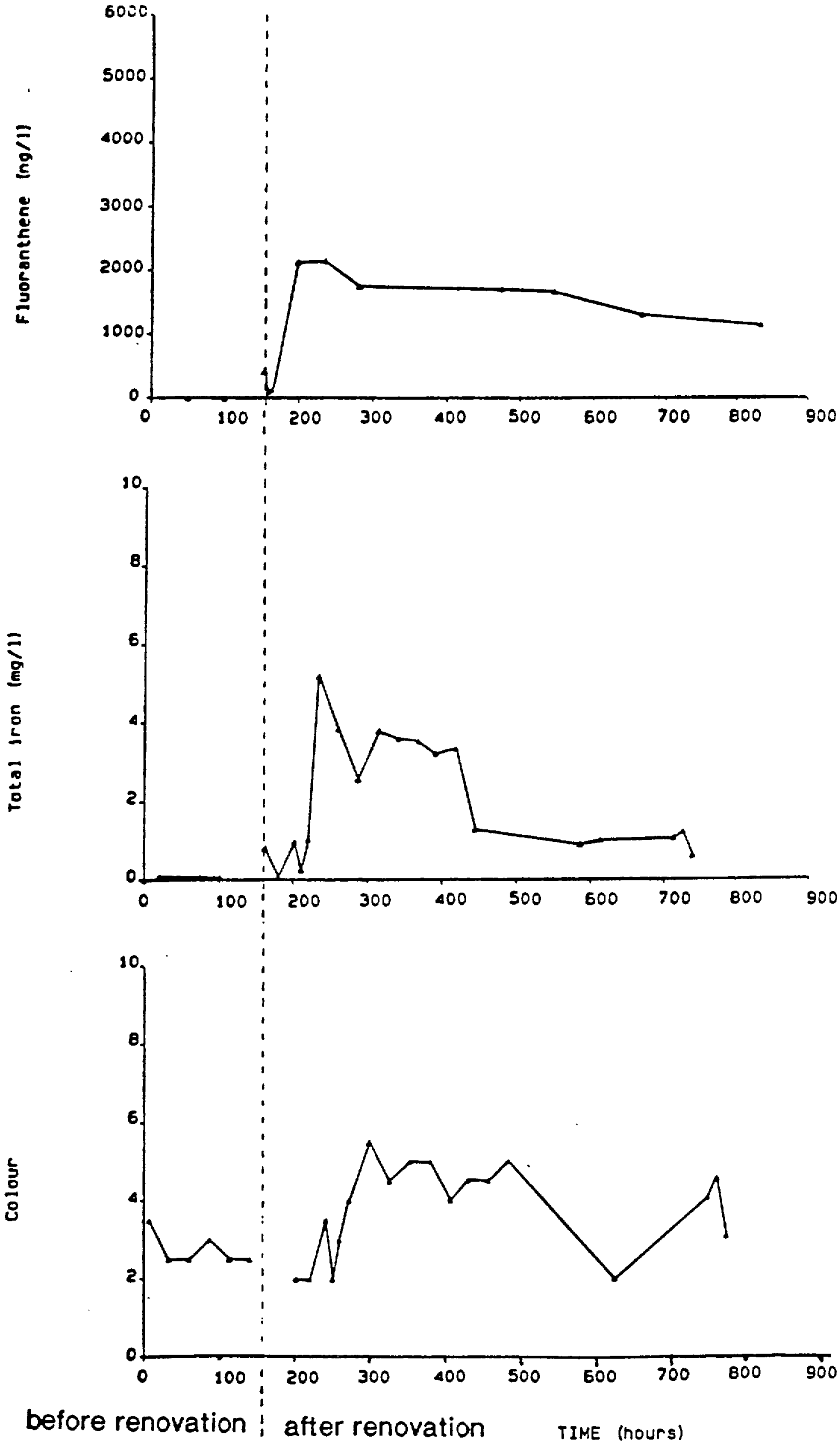


Figure 15. Variation of fluoranthene, iron and colour: length 3 (water jetting)



APPENDIX A

THE DIFFUSION OF HAZARDOUS CHEMICALS INTO MEDIUM DENSITY POLYETHYLENE PIPE

Manchester Polytechnic
Director K Green BA MA

John Dalton Faculty of Technology
Department of Polymer Technology
Head P C Powell BSc MSc DIC FPRI
John Dalton Building Chester Street
Manchester M1 5GD
Telephone 061-228 6171

REPORT ON:

THE DIFFUSION OF HAZARDOUS CHEMICALS INTO MEDIUM DENSITY POLYETHYLENE PIPE

by

J. M. MARSHALL

D. M. EYRE

1. INTRODUCTION

Medium density polyethylene (MDPE) pipes are being increasingly used for the transport of potable water. The ductile iron pipes used previously could be considered essentially impermeable to any liquids or vapours they may have encountered. All plastics, however, are permeable to some extent. It is known that some organic solvents such as toluene, chlorobenzene and methanol do penetrate polyethylene (1). Nothing is known about the possible penetration of MDPE by more complex chemicals such as herbicides and pesticides which may be found as aqueous solutions in agricultural areas.

There are several factors to be considered before deciding whether a polymer will act as an effective barrier to any contaminants:

1. Does the substance diffuse into the polymer at all?
2. At what rate and at what temperatures will it diffuse completely through the pipe wall?
3. Will the substance be released into the water at all?
4. Will the amount of contaminant passing into the water be sufficient to cause taste and odour or toxicity problems?

For the purposes of the present study it was decided to consider only the first point as this was seen as being the logical place to start any investigation. WRC selected five substances which might possibly be present in ground through which water pipes could pass. There were:

Phenol (1- hydroxybenzene) - used by farmers as a disinfectant.

Malathion (s-1, 2-di(ethoxycarbonyl)ethyl o-o-dimethylphosphorodithioate) - an isecticide.

Atrazine - (2-chloro-4-(ethylamino)-6-(isopiopylamino)-S-triazine))
Paraquat chloride (1, 1-dimethyl -4, 4-dipyridilium dichloride)) herbicides.

Toluene (1-methyl benzene) - a common organic solvent.

The first four substances were studied as saturated or near-saturated aqueous solutions and toluene was used alone in order to try to simulate the worst possible case.

2. EXPERIMENTAL

This radiotracer technique is a modification of one used successfully for a number of different polymer-diffusant systems over the past six years. Several papers have been published (1 - 4) and a detailed description of the technique is to be found in reference 5.

2.1 Diffusants

2.1.1 Radioisotopes

Approximately 50 u Ci each of carbon-14 labelled phenol, malathion, paraquat chloride and toluene were obtained from Amersham International. The details of the labelling are as follows:

[U- ^{14}C] phenol: specific activity 98m Ci/m mol.

[methyl- ^{14}C] paraquat chloride: specific activity 111 m Ci/m mol.

[ethyl- 1 -^{14}C] atrazine: specific activity 25 m Ci/m mol.

[^{14}C] malathion: specific activity 27m Ci/m mol.

[methyl- ^{14}C] toluene: specific activity 46m Ci/m mol.

Copies of the batch analysis sheets supplied by Amersham International are included in Appendix 1.

2.1.2 Other Materials

Pure samples of atrazine and paraquat chloride were supplied by WRC and malathion was obtained from the Laboratory of the Government Chemist. "Scintran" grade toluene and Analar phenol were purchased from BDH Chemicals Limited.

2.1.3 Solution preparation

The radioactive solutions were prepared as follows:

(a) Atrazine, Malathion.

The solvents in which these samples were supplied was allowed to evaporate and the whole of the radioactive sample was then dissolved in distilled water. The solution was made up to 250 cm^3 and sufficient inactive compound added to ensure saturation.

Since saturated solutions had been prepared, final concentrations were assumed to be:

Malathion, 0.15 mg/cm^3
Atrazine, 0.03 mg/cm^3

(b) Phenol, Paraquat chloride.

The radioactive compound was dissolved in distilled water and the soluttion made up to 250 cm^3. A known quantity of inactive compound was then added. Final concentrations were:

Phenol: 8 mg/cm^3
Paraquat chloride: 0.31 mg/cm^3

(c) Toluene

The radioactive toluene was made up to 250 cm^3 with "Scintran" grade inactive toluene.

2.1.4 Determination of radioactive concentrations

The radioactive concentrations of the solutions were determined by first diluting 10 cm^3 aliquots of the solutions to 1000 cm^3. The activity of 1 cm^3 of each solution was then measured using liquid scintillation counting. The activities were found to be:

Phenol:	0.173 μ Ci/cm^3
Malathion:	0.190 μ Ci/cm^3
Paraquat Chloride:	0.23 μ Ci/cm^3
Atrazene:	0.22 μ Ci/cm^3
Toluene:	0.165 μ Ci/cm^3

2.2 Polymer

Ring samples (1.5mm wide) were cut from one length of 63mm diameter SDR11 blue MDPE pipe produced by Stewarts & Lloyds Plastics.

2.3 Exposure to Diffusant

Each pipe sample was cemented to a glass petri dish using a silicone sealing compound The radioactive solution (25 cm^3) was then pipetted into the ring and a second petri dish cemented on top. The samples were left at room temperature (20°C ± 2°C) for periods of one, two, three and four weeks. In some cases samples were exposed for nine weeks.

After soaking the top dish was removed, the liquid decanted off, the second dish removed and the sample rinsed thoroughly before analysis.

2.4 Cutting

The pipe sample was then pushed tightly onto a metal mandrel and placed in liquid nitrogen for a time to halt further diffusion. When the sample was cold the mandrel was fitted onto a watchmakers lathe mounted in a cold box. The box was maintained at -20°C to -30°C by passing liquid nitrogen through a copper cooling coil. A jet of cold nitrogen gas was played onto the cutting tool to prevent localised heating. The sample was then cut into 0.5mm thick layers, each layer being collected and stored in card ice (solid CO_2) until required.

2.5 Preparation for Counting

Samples (0.05 g) from each layer were accurately weighed out and completely oxidised using a Biological Materials Oxidiser. In this the sample was burnt in a stream of oxygen at 900°C and the resulting gasses passed through a catalyst bed which was maintained at 700°C. The carbon dioxide produced was trapped in 15 cm^3 of a 40 : 60 mixture of carbosorb, a CO_2 trapping agent and Permafluor*, a scintillation cocktail.

Since the only source of carbon - 14 was the diffusant, determination of the amount of

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* Trade mark: Packard.

radioactivity in each sample from the oxidiser gave a measure of the amount of diffusant which must have been present in that layer of polymer.

2.6 Counting and Analysis

The activity of each sample was determined by liquid scintillation counting. The solution from the oxidiser trap was transferred to a disposable vial and this was placed in a Tracor 6892 Liquid Scintillation Counter. The number of counts per minute (cpm) were determined and this converted to disintigrations per minute (dpm) by means of a PET computer and specific software package.

A knowledge of the dpm of each sample, plus the initial radioactive and solute concentrations of the diffusant solutions, enabled the amount of diffusant present in each layer of the pipe to be calculated.

3. RESULTS

3.1 Atrazine

The data for the diffusion of atrazine from solution into MDPE are given in Table 1.

Distance through pipe wall (mm)	Concentration x 10^4 (mg solute/g polymer)				
	1 Week	2 Weeks	3 Weeks	4 Weeks	9 Weeks
0.25	-	-	-	-	-
0.75	-	-	-	-	-
1.25	-	-	-	-	-
1.75	-	-	-	-	-
2.25	-	-	-	-	
2.75	-	-	-	-	-
3.25	-	-	-	-	-
3.75	-	-	-	-	-
4.25	-	-	-	-	-
4.75	-	-	-	-	-
5.25	-	-	-	-	-
5.75	-	-	-	-	-
6.25	24	48	43	46	58

Table 1.

There was no evidence of any atrazine being present in the sample beyond the layer which was in contact with the solution during the test. The amounts were very low and relatively constant suggesting that this chemical is only absorbed by MDPE to a very low level and is not transported through the polymer.

3.2 Paraquat Chloride

The data are shown in Table 2.

Distance through pipe wall (mm)	Concentration x 10^4 (mg solute/g polymer)			
	1 Week	2 Weeks	3 Weeks	4 Weeks
0.25	-	-	-	-
0.75	-	-	-	-
1.25	-	-	-	-
1.75	-	-	-	-
2.25	-	-	-	-
2.75	-	-	-	-
3.25	-	-	-	-
3.75	-	-	-	-
4.25	-	-	-	-
4.75	-	-	-	-
5.25	-	-	-	-
5.75	-	-	-	-
6.25	5.4	3.8	4.7	3.9

Table 2.

Again there was no evidence of this substance being transported through the polymer and the amounts absorbed were extremely low. The fluctuation of the results possibly indicated that the paraquat chloride was adsorbed on the pipe surface rather than actually absorbed into the material.

3.3 Malathion

The results are given in Table 3.

Distance through pipe wall (mm)	Concentration x 10^4 (mg solute/g polymer)				
	1 Week	2 Weeks	3 Weeks	4 Weeks	9 Weeks
0.25	-	-	-	-	-
0.75	-	-	-	-	-
1.25	-	-	-	-	-
1.75	-	-	-	-	-
2.25	-	-	-	-	-
2.75	-	-	-	-	-
3.25	-	-	-	-	-
3.75	-	-	-	-	-
4.25	-	-	-	-	-
4.75	-	-	-	-	-
5.25	-	-	-	-	-
5.75	-	-	-	-	-
6.25	246	258	187	213	230

Table 3.

The quantities of malathion absorbed are greater than observed for paraquat or atrazine. There was no evidence of transport through the polymer and the irregular variation might suggest adsorption.

3.4 Phenol

The data are given in Table 4.

Distance through pipe wall (mm)	Concentration x 10^4 (mg solute/g polymer)				
	1 Week	2 Weeks	3 Weeks	4 Weeks	9 Weeks
0.25	-	-	-	-	Not Analysed
0.75	-	-	-	-	
1.25	-	-	-	-	
1.75	-	-	-	-	
2.25	-	-	-	-	
2.75	-	-	-	-	-
3.25	-	-	-	-	-
3.75	-	-	-	-	-
4.25	-	-	-	-	139
4.75	-	-	-	115	375
5.25	-	-	-	408	767
5.75	306	1013	1383	1686	1550
6.25	5111	6565	7864	7453	9307

Table 4.

Phenol appeared to diffuse through the polymer after first being absorbed to a comparatively large extent in the surface layer.

3.5 Toluene

It was possible to obtain data for soak times longer than one week when using toluene as it evaporated rapidly.

The results obtained are given in table 5.

Distance thro' pipe wall (mm)	Concentration (mg toluene/ g polymer
0.25	2.8
0.75	9.7
1.25	2.5
1.75	9.4
2.25	10.9
2.75	6.1
3.25	21.3
3.75	20.7
4.25	43.7
4.75	43.6
5.25	48.4
5.75	45.7
6.25	64.8

Table 5.

Even after one week toluene had completely penetrated the pipe wall and was present in relatively large amounts at all points in the sample.

NB: In all cases the pipe sample is cut from outside to inside and so the polymer/ liquid interface is at 6.25mm through the pipe wall.

4. DISCUSSION

As can be seen from tables 1 - 5, only phenol and toluene were found to diffuse into the pipe samples. Atrazine, malathion and paraquat chloride were found in the surface layer only and it is probable that these substances were simply adsorbed onto the surface, rather than dissolved in the polyethylene.

Polyethylene has a simple chemical structure, it is non polar and its physical structure is fairly well known. The degree of crystallinity and the orientation of the molecules will both affect the diffusion coefficients for any substance moving through it.

Several theories of diffusion phenomena have been suggested. One of the more recent was proposed by Pace & Daytyner (6-10) who consider a semi crystalline structure in which the macromolecular chains are locally almost parallel in the amporphous as well as in the crystalline phase. This would fit well when considering a pipe wall, since the extrusion process will introduce a relatively high degree of orientation of the polymer chains. Diffusion parallel to the chains is supposed to have a zero activation energy, but perpendicular diffusion requires distortion of the chains and so has a finite activation energy. Results for polyethylene for small spherical molecules, and for larger more complex species, agree well with their proposed expression for the diffusion coefficent and activation energy of the molecules, taking into account some of the characteristics of the polymer.

Klein(11-13)recently published a theory in which he proposed that in the amorphous phase, the macromolecular chains partly belong to a crystallite, be they entangled, or tied to two crystallites (tie molecules). Several fixed obstacles are also assumed to appear in this phase, these being separated by a distance h. A small molecule will diffuse without being affected by this, but a long molecule will have to avoid these obstacles. Klein concluded that the diffusion coefficient D varied as l^{-2} in molecules of length l greater than h.

The kinetics of diffusion of complex molecules in polyethylene depends therefore on parameters related to both the structure of the diffusant and to that of the polymer and it is difficult to predict diffusion behaviour for any system without direct measurement.

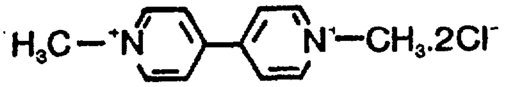
The factors of importance when considering the diffusant molecule are:

i) Size - molecular mass.
ii) Shape - diameter and stiffness.
iii) Compatibility with polymer - e.g. polarity.

If we consider each of the chemicals used, the effects of these parameters can be seen.

4.1 Paraquat Chloride (Table 2)

Chemical Structure:

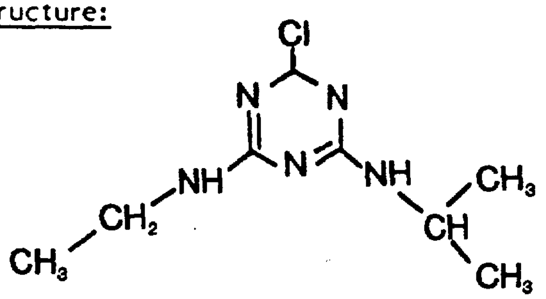


Molecular Mass: 261 (at specific activity supplied)

This is a large, stiff molecule, which is likely to have difficulty in being accommodated within the polymer. It is also polar and has little compatibility with the non-polar polyethylene. It is therefore most likely that this substance does not dissolve in the polymer but is merely adsorbed onto the surface. The very small quantities involved, and their relative inconsistency, support this hypothesis.

4.2 Atrazine (Table 1)

Chemical Structure:

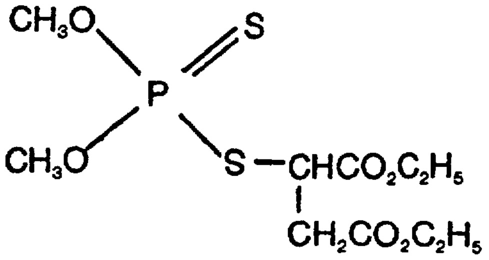


Molecular Mass: 216 (at specific activity supplied)

This is a bulky, polar molecule which will be expected to have little affinity for polyethylene. The amounts of the chemical detected in the surface layer are ten times greater than for atrazine, but it is doubtful that these represent dissolution of the polymer.

4.3 Malathion (Table 3)

Chemical Structure:

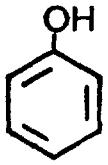


Molecular Mass: 330 (inactive)

Although this molecule is heavier than the two discussed previously, it is likely to be more flexible as it contains no benzene rings. Again, the adsorbtion of this molecule is found to be a factor of ten greater than the amount of atrazine taken up, but adsorbtion is still the more probable mechanism than dissolution in the polyethylene.

4.4 Phenol (Table 4)

Chemical Structure:

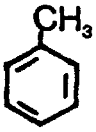


Molecular Mass: 98 (at specific activity supplied)

The amounts of phenol measured were very much greater, and there were signs that this substance was diffusing into the polymer. The molecule concerned is now very much smaller than any considered before, and in spite of being polar, is quite likely to be able to find "holes" within the polymer chains into which it can fit. The concentration of the phenol solution in contact of the pipe will now become important in determining the quantities which will diffuse through.

4.5 Toluene (Table 5)

Chemical Structure:



Molecular Mass: 92 (inactive)

This is the smallest of the molecules considered, and as it is non-polar it is the most compatible with polyethylene. Indeed, toluene is a solvent for this polymer at temperatures above 80°C. This is reflected in the data, where toluene was found to have completely penetrated the pipe wall after only one weeks exposure at room temperature (19°C). The quantities involved were found to be 10^2 - 10^4 times greater than for the other chemicals.

CONCLUSIONS

There is unlikely to be any penetration of polyethylene water pipes by Atrazine, Malathion or Paraquat Chloride.

Phenol may possibly penetrate the polymer, although in small quantities. The concentration of the Phenol solution may well be important.

Polyethylene is relatively permeable to Toluene which will diffuse through the pipe wall quite rapidly at ambient temperatures.

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APPENDIX B

THE DIFFUSION OF ORGANIC COMPOUNDS INTO MDPE PIPE FROM AQUEOUS SOLUTION

Pipeline
Consultant
Limited

Broadway, Salford, Manchester M5 2TQ
Telephone: 061-872 5641
Telex: 665264

REPORT ON:

THE DIFFUSION OF ORGANIC COMPOUNDS INTO MDPE PIPE FROM AQUEOUS SOLUTION

BY

J. M. MARSHALL

D. M. EYRE

JUNE 1987

1. Introduction

Previous studies have been carried out to look at the diffusion of pesticides and herbicides from aqueous solution into MDPE water pipe, and a report was submitted to WRC in September 1985.

This report concerns a subsequent project commissioned by WRC and the diffusants in this case were

- 2-chloraniline
- cyclohexane
- nitrobenzene
- m-cresol
- 4-chlorobenzoic acid

All the chemicals were used as 50% saturated aqueous solutions.

2. Experimental

The radiotracer technique used was described fully in the previous report, and further details can be found in reference 1.

2.1 Diffusants

2.1.1 Radioisotopes

All isotopes were obtained from Amersham International. These were:

2-chloro[U-^{14}C] aniline - 100μci
m-chloro[carboxyl-^{14}C] benzoic acid - 1000μci
[U-^{14}C] cyclohexane - 250μci
nitro [U-^{14}C] benzene - 250μci
m-[ring-U-^{14}C] cresol - 250μci

Copies of the batch analysis sheets supplied by Amersham International are included in Appendix 1.

2.1.2 Solution preparation

Approximately 50% saturated aqueous solutions of all the labelled compounds were prepared, using inert compounds of the highest available purity as carriers. All compounds were accurately weighed out using a Sartorius electronic balance capable of weighing to four decimal places. The concentration of each solution was thus known, and the radioactive concentrations were determined by liquid scintillation counting. The activities are given in Table 1.

Solution	Approximate Initial Dilution	Measured Activity
m-cresol	250μci in 250cm^3	0.97μci/cm^3
nitrobenzene	250μci in 250cm^3	1.05μci/cm^3
Chlorobenzoic acid	1000μci in 500cm^3	2.15μci/cm^3
chloroaniline	100μci in 250cm^3	0.24μci/cm^3
cyclohexane	250μci in 250cm^3	0.04μci/cm^3

Table 1: Radioactive concentrations of Initial Solutions

It is apparent that, in the case of the chloroaniline, and particularly in that of the cyclohexane, some of the initial activity has been lost. However, both these labelled compounds presented difficulties when being diluted, the cyclohexane proving especially volatile.

2.2 Polymer

Ring samples approximately 20cm wide were cut from one length of 63mm diameter SDR11 blue MDPE pipe.

3. Results

All results are the average of two sets of data.

3.1 Chloroaniline

The data for chloroaniline are given in Table 2 and shown in figure 1.

Distance through pipe wall mm	Concentration mg chloroaniline/g polymer		
	1 week	2 weeks	4 weeks
0.25 (outside)	0.18	0.39	-
0.75	0.05	0.28	-
1.25	-	-	-
1.75	-	-	-
2.25	-	-	-
2.75	-	-	-
3.25	-	-	-
3.75	-	-	-
4.25	-	-	-
4.75	-	-	-
5.25	-	-	-
5.75	-	-	-
6.25	0.80	0.97	1.35
6.75 (inside)	3.53	4.75	6.77

Table 2

The small amount of compound sometimes detected in the outer layers of the pipe is thought to arise from slight leakage which occurred in some instances, and should probably be ignored. It can be seen from the above results that although the amount of chloroaniline in the inner two layers increased with time the compound has not permeated any further into the pipe wall.

3.2 m-Cresol

These data are presented in Table 3 and shown graphically in figure 2.

Distance through pipe wall mm	Concentration mg m-cresol/g polymer		
	1 week	2 weeks	4 weeks
0.25 (outside)	0.21	0.37	0.48
0.75	0.13	-	0.15
1.25	-	-	0.13
1.75	-	-	-
2.25	-	-	-
2.75	-	-	-
3.25	-	-	-
3.75	-	-	-
4.25	-	-	-
4.75	-	-	-
5.25	-	-	-
5.75	-	0.25	0.26
6.25	0.10	2.50	1.99
6.75 (inside)	4.43	11.22	7.28

Table 3

The results are somewhat anomalous, and the results of the long term soaking experiment will indicate which of the two soak times 336h or 672h should be repeated.

3.3 Nitrobenzene

The data are shown in Table 4 and figure 3.

Distance through pipe wall mm	Concentration x 10 mg nitrobenzene/g polymer		
	1 week	2 weeks	4 weeks
0.25 (outside)	0.49	0.19	0.16
0.75	-	0.15	0.17
1.25	-	0.03	0.15
1.75	-	-	0.07
2.25	-	-	0.05
2.75	-	-	-
3.25	-	-	-
3.75	-	-	0.11
4.25	-	-	0.16
4.75	-	0.04	0.22
5.25	-	0.25	0.58
5.75	-	0.55	1.74
6.25	0.27	3.04	3.32
6.75 (inside)	1.10	5.18	5.58

Table 4

The nitrobenzene concentration built up with time in the inner layers, and it also appeared to diffuse steadily through the pipe wall. There was some indication that an equilibrium absorption could be being approached in the surface layer, but the results of the long term test will clarify this.

3.4 Chlorobenzoic acid

Data are presented in Table 5 and figure 4.

Distance through pipe wall mm	Concentration x 10^2 mg chlorobenzoic acid/g polymer		
	1 week	2 weeks	4 weeks
0.25 (outside)	-	-	0.04
0.75	-	-	-
1.25	-	-	-
1.75	-	-	-
2.25	-	-	-
2.75	-	-	-
3.25	-	-	-
3.75	-	-	-
4.25	-	-	-
4.75	-	-	-
5.25	-	-	-
5.75	-	-	0.14
6.25	-	0.07	0.30
6.75 (inside)	0.77	2.30	3.50

Table 5

Although relatively small amounts of chlorobenzoic acid were absorbed, the diffusion appeared to proceed steadily into the pipe wall.

3.5 Cyclohexane

The data for cyclohexane are given in Table 6 and shown in figure 5.

Distance through pipe wall mm	Concentration x 10^2 mg cyclohexane/g polymer		
	1 week	2 weeks	4 weeks
0.25 (outside)	-	-	0.62
0.75	-	-	0.52
1.25	-	-	0.20
1.75	-	-	-
2.25	-	-	-
2.75	-	-	-
3.25	-	-	-
3.75	-	-	-
4.25	-	-	-
4.75	-	-	-
5.25	-	-	-
5.75	-	-	0.21
6.25	-	0.62	0.76
6.75 (inside)	4.30	3.80	5.60

Table 6

Only small amounts of cyclohexane would seem to have been absorbed, but the diffusion appeared to proceed steadily through the pipe wall.

4. Discussion

Table 7 shows the structure, molecular mass and solubilities (in water and in polyethylene) of the organic compounds studied. The solubility data were taken from KIWA report number 87.

Compound	Structure	Molecular Mass	Solubility in Water Mg/g	Solubility in polyethylene g/g	
				LDPE	HDPE
m-cresol		110	25000	-	-
2-chloroaniline		129	10000	0.023	0.022
nitrobenzene		123	1900	0.018	0.017
3-chlorobenzoic acid		156.5	190	-	-
cyclohexane		84	55	0.132	0.079

Table 7. Data on diffusants

Consideration of the results presented in Section 3 shows that all the compounds diffused into the pipe wall to some extent, although only nitrobenzene appeared to penetrate more than 1.0mm into the material.

It can be seen from Tables 2-6 and Figures 1-5 that the amount of liquid absorbed in the first layer of the polymer - that in contact with the solution - increased in the order:

chlorobenzoic acid (~ 0.04 mg/g)
cyclohexane (~ 0.06 mg/g)
nitrobenzene (~ 0.6 mg/g)
2-chloroaniline (~ 6.8 mg/g)
m-cresol (~ 7.3 mg/g)

The m-cresol was also noticed to have a distinct softening effect on the polyethylene and to cause layers containing high levels to "explode"on oxidation.

This order shows some correlation with molecular mass, but the overriding factor would appear to be the solubility of the compound in water. (See Table 7). In the work carried out previously, phenol was found to be the only compound to diffuse into the polyethylene from aqueous solution, and it was suggested that the concentration of the solution could be of critical importance. This may well also be the case with all the present compounds.

Diffusion coefficients can be calculated from the concentration distance curves using the equation

$$D = -\frac{1}{2t}\frac{dx}{dc}\int_{c=0}^{c=c_1} x\,dc$$

where D = diffusion coefficient (cm^2/s)
t = time (s)
x = distance of penetration into pipe wall (mm)
c = concentration of diffusant (mg/g)

Approximate values of the diffusion coefficient for each compound are given in Table 8.

Compound	Diffusion Coefficient
nitrobenzene	2.5×10^{-9}
m-cresol	1.5×10^{-9}
chlorobenzoic acid	8.0×10^{-10}
chloroaniline	4.0×10^{-10}
cyclohexane	4.0×10^{-10}

Table 8: Diffusion coefficients

There is no particularly satisfactory correlation to be drawn between the diffusion coefficients and any of the parameters in Table 7, except possibly with solubility in polyethylene. No value is given for the solubility of m-cresol in polyethylene, but it might be expected to be of the same order as the solubility of phenol in MDPE (2-3 mg/g). No value is available either for chlorobenzoic acid in the polymer. However, the two compounds with the greatest diffusion coefficients have the lowest quoted solubilities in MDPE (estimated to be between values for HDPE and LDPE), whilst chloroaniline and cyclohexane, which have diffusion coefficients some five times lower than those for nitrobenzene and m-cresol, are quoted as having greater solubility in the polyethylene.

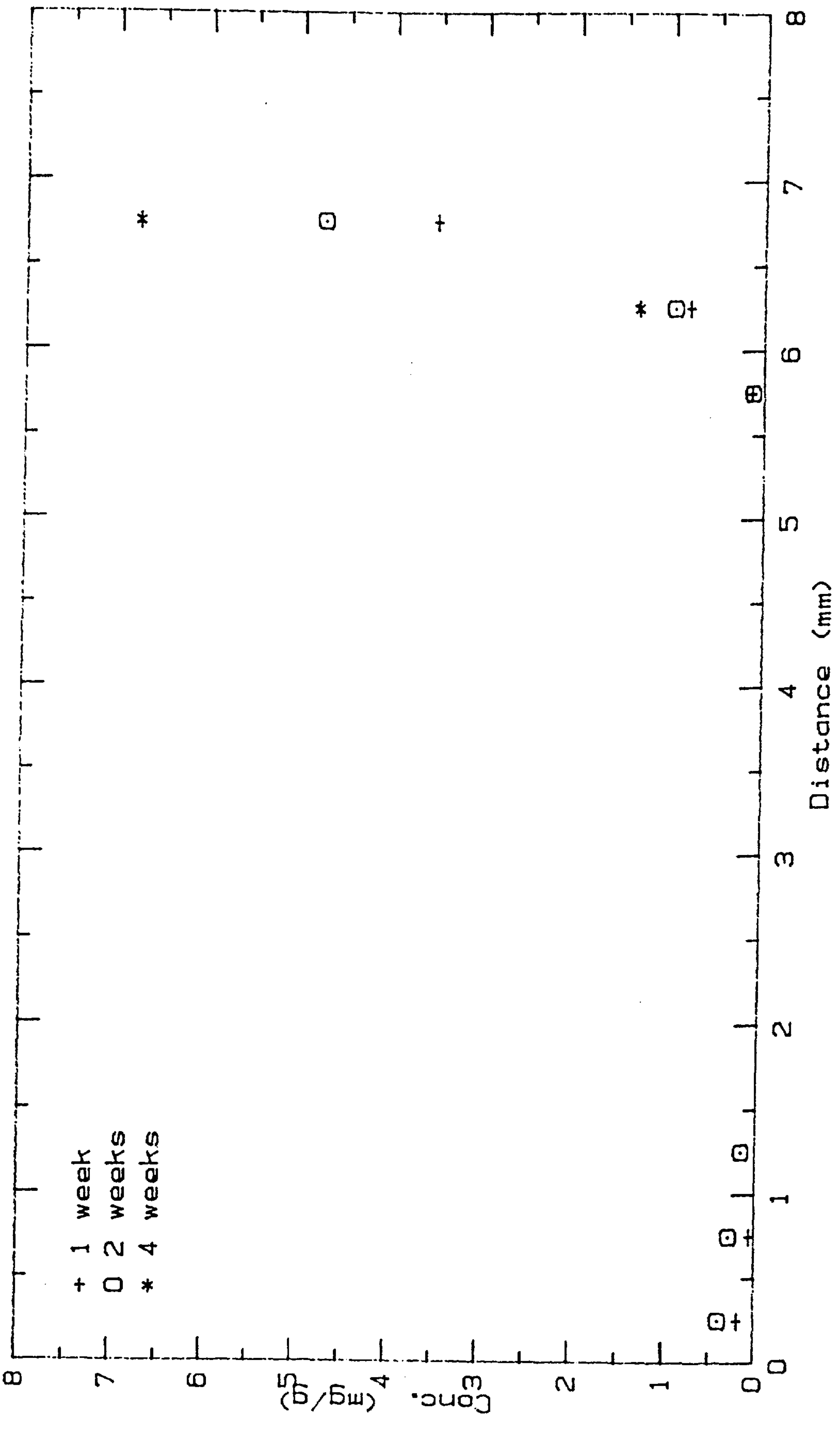
Unfortunately, the picture is far from clear, and it would probably require substantial further detailed investigation before any firm conclusions could be reached as to the reasons for the results obtained.

5. Conclusions

The solubility of the compound in water would seem to be the only property to correlate with the amount absorbed by the polyethylene, whilst a tenuous link only can be made between the solubility of the compound in the polymer and its diffusion coefficient in the material.

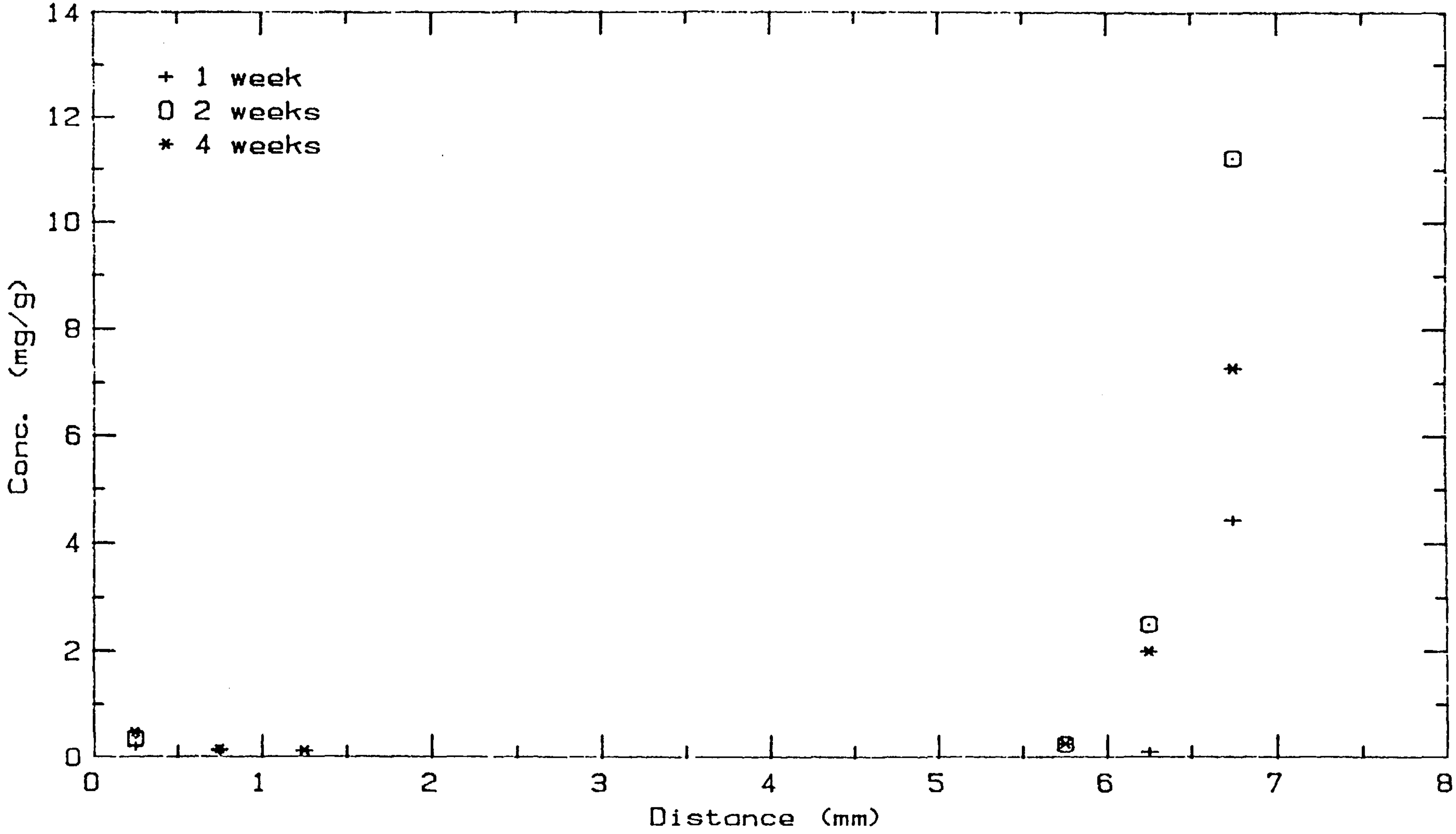
References

1. J. M. Marshall, Ph.D. Thesis "The Degradation of Polycarbonate". May, 1981.



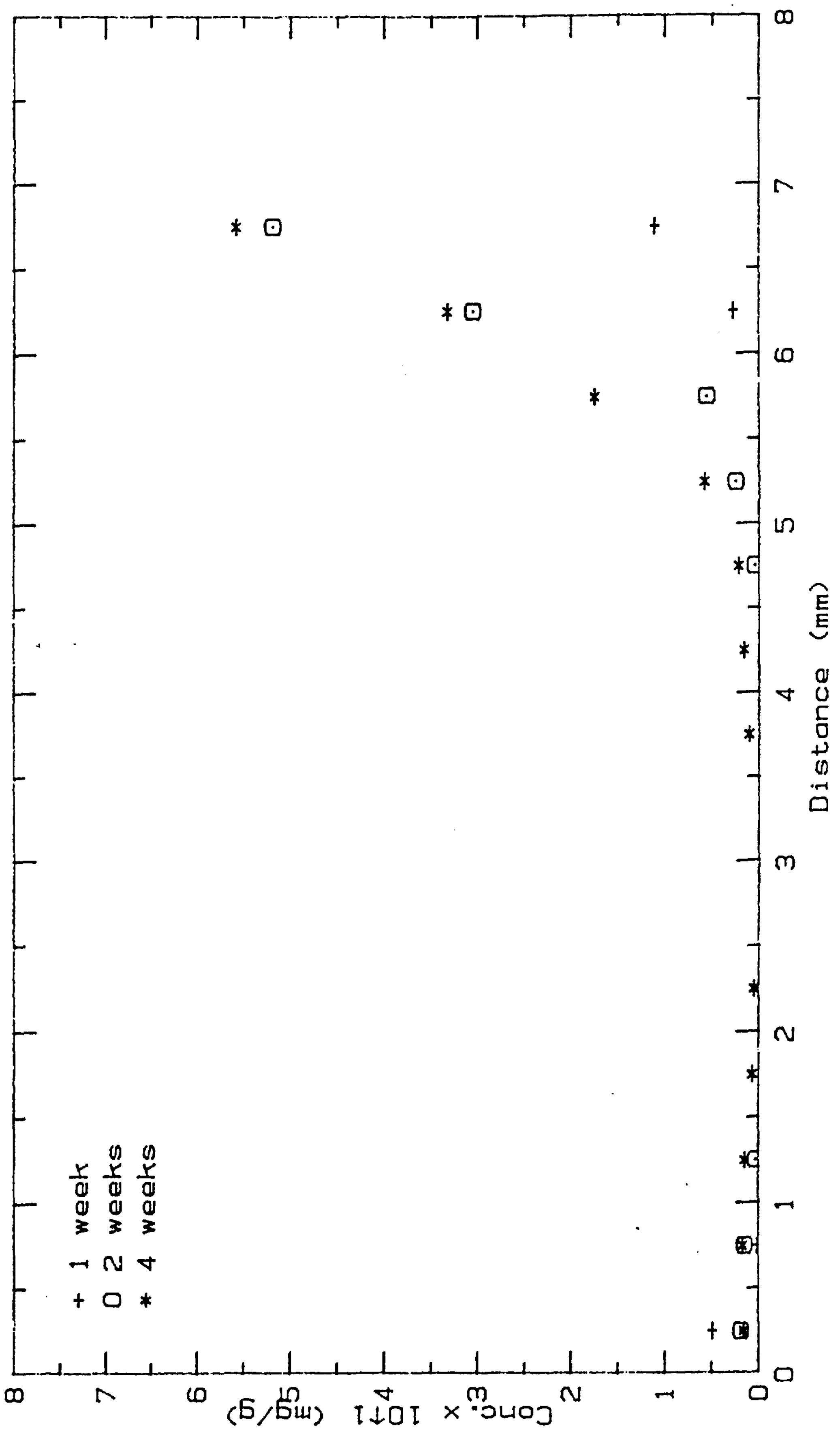
Diffusion of Chloroaniline in Blue MDPE Pipe

Fig. 1.



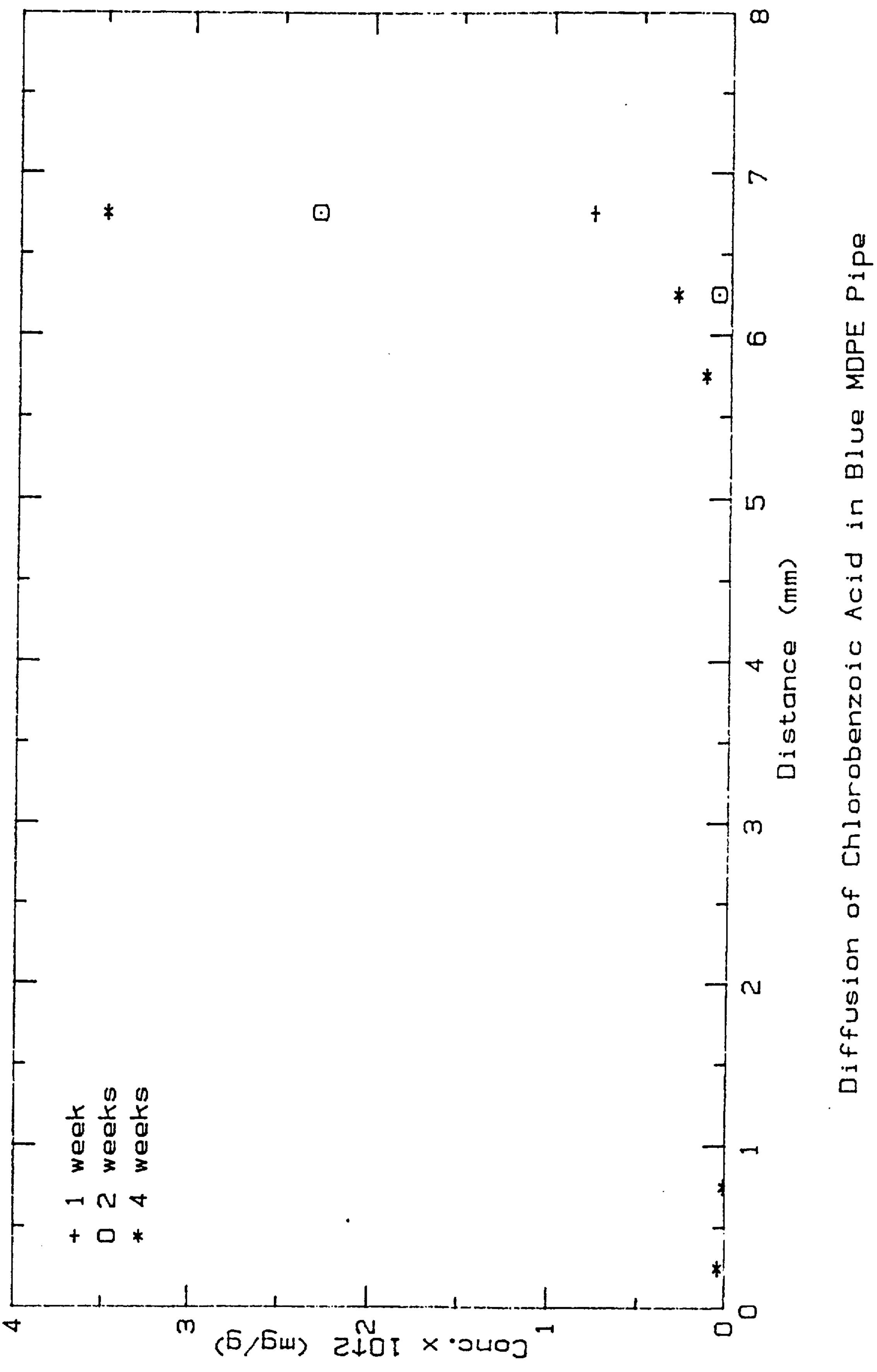
Diffusion of m-Cresol in Blue MDPE Pipe

Fig. 2



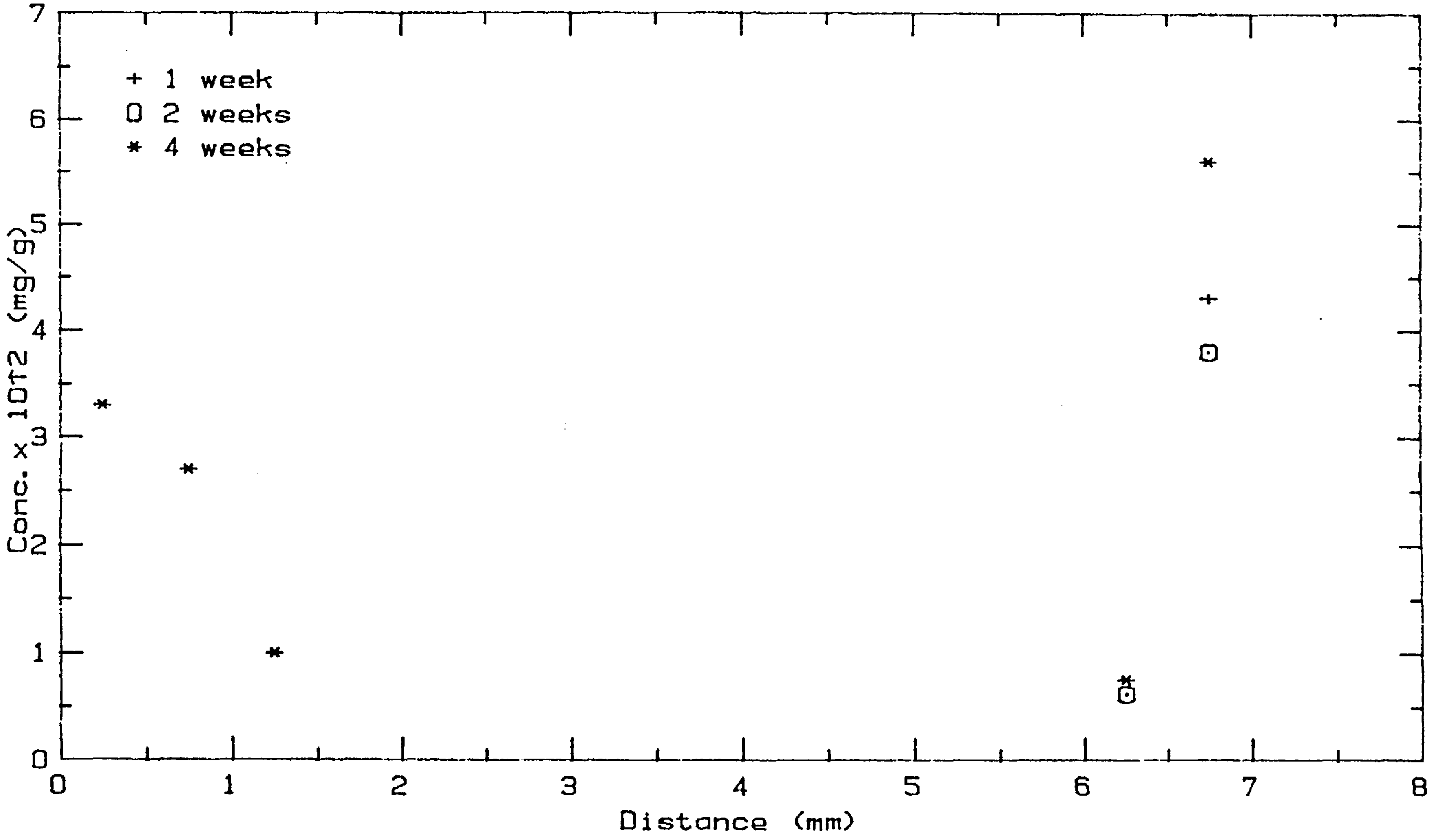
Diffusion of Nitrobenzene in Blue MDPE Pipe

Fig. 3.



Diffusion of Chlorobenzoic Acid in Blue MDPE Pipe

Fig. 4



Diffusion of Cyclohexane in Blue MDPE Pipe

Fig. 5

APPENDIX I.

Amersham International plc
White Lion Road Amersham
Buckinghamshire England HP7 9LL

Radiochemical batch analysis

2-CHLORO[U-^{14}C]ANILINE
Code CFQ.4042

Batch
analysis
Sheet C/6282

2-Chloro[U-^{14}C]aniline was prepared by reaction of [U-^{14}C]aniline with N-chlorosuccinimide. The product was purified by flash chromatography.

TECHNICAL DATA

Specific activity : 49 mCi/mmol, 1.81 GBq/mmol
: 380 µCi/mg, 14.1 MBq/mg

Molecular weight : 129 (at this specific activity)

Radiochemical purity

by thin-layer chromatography on silica gel in

(a) pentane:ether (6:1) : 95%
(b) benzene:acetone (4:1) : 98%

by gas-liquid chromatography on 8% Carbowax 20M + 2% KOH on Chromosorb W : 98.8 ± 0.4%

Chemical identity

The infra-red spectrum is consistent with that expected for 2-Chloro[U-^{14}C]aniline at this specific activity, but includes additional minor bands.

Analysed 18th December 1984

<u>Packaging and Storage</u>

2-Chloro[U-^{14}C]aniline is supplied as a liquid in a borosilicate glass ampoule, sealed under nitrogen.

An ampoule may be opened by lightly scratching the serration with the file provided, and carefully snapping off at the upper end.

Storage at -20°C is recommended for this compound.

Amersham Australia Pty Limited
P.O. Box [illegible]
[illegible]
[illegible]

Amersham Denmark ApS
[illegible]
[illegible]

Amersham Belgium SA/NV
Chaussée de Forest 171-173 Boîte 1
Vorstsesteenweg 171-173 Bus 1
1060 Bruxelles/Brussel

Amersham France SA
[illegible]
BP [illegible]
[illegible]

Amersham Buchler GmbH & Co. KG
Gieselweg 1
D-3300
Braunschweig

アマシャムジャパン株式会社
東京都中央区[illegible]
[illegible] 〒104
電話 03-543 [illegible]

Amersham Corporation
2636 S. Clearbrook Drive
Arlington Heights
Illinois 60005

Amersham Nederland BV
Burstraat 206
3572BS Utrecht

Amersham

Amersham International plc
White Lion Road Amersham
Buckinghamshire England HP7 9LL

Radiochemical batch analysis

[U-^{14}C]CYCLOHEXANE
Code CFA.275
Batch 10

Batch
analysis
sheet 19245

BATCH TECHNICAL DATA

Specific activity : 11.7 μCi/mmol
139 μCi/mg

Molecular weight : 84 (at this specific activity)

Radiochemical purity
by gas-liquid radiochromatography on
15% β,β'-oxydipropionitrile on chromosorb W : 98.5%

Chemical purity
by gas-liquid chromatography on
15% β,β'-oxydipropionitrile on chromosorb W : 99%

The infrared spectrum is consistent with that of cyclohexane.

Analysed 7th May 1976

STABILITY, AND STORAGE RECOMMENDATIONS•

[U-^{14}C]Cyclohexane is stored in our laboratories at 2°C, protected from light. Under these conditions the rate of self-decomposition is not expected to exceed 2% per annum. To ensure that this product is always of the highest standard each batch is analysed by our Quality Control Department at intervals based on our previous experience of the stability of the material.

•For further information see:

"Self-Decomposition of Radiochemicals", EVANS, E.A., Amersham International Review No. 16, 1976.

"The Self-Decomposition of Radioactively Labelled Compounds", SHEPPARD, G., Atomic Energy Review, 10(1), 1972.

Copies of these publications are available from Amersham.

Amersham Australia Pty Limited
PO Box M321
Sydney Mail Exchange
NSW 2012

Amersham France SA
2 Petite Place
BP 563

Amersham Belgium SA/NV
Chaussée de Forest 171-173 Boîte 1
Vorstsesteenweg 171-173 Bus 1
1060 Bruxelles/Brussel

アマシャム・ジャパン株式会社
東京都中央区銀座1-13-8
（第2九惠ビル）〒104

Amersham Buchler GmbH & Co. KG
Gieselweg 1
D-3300
Braunschweig

Amersham Nederland BV
Billstraat 206
3572BS Utrecht

Amersham Corporation
2636 S. Clearbrook Drive
Arlington Heights
Illinois 60005

Amersham

Radiochemical batch analysis

NITRO[U-^{14}C]BENZENE
Code CFA.134
Batch 18

Batch
analysis
sheet 26903

Nitro[U-^{14}C]benzene is prepared by the nitration of [U-^{14}C]benzene; the products of the reaction being separated by fractional evaporation under high vacuum.

BATCH TECHNICAL DATA

Specific activity : 8.48 mCi/mmol
69 µCi/mg

Molecular weight : 123 (at this specific activity)

Radiochemical purity

by gas-liquid radiochromatography on
2½% silicone E301 : 99%

Chemical purity

by gas-liquid chromatography on
5% silicone OV101 : 99%

Analysed 2nd December 1976

Packaging and Storage

Nitro[U-^{14}C]benzene is supplied in sealed borosilicate glass tubes from stocks held in our laboratories at room temperature.

To ensure that our products are always of the highest standard, each batch of this compound is analysed by our Quality Control Department at intervals based on our experience of the stability of previous batches.

The Radiochemical Centre
Amersham

Amersham International plc
Amersham Laboratories
White Lion Road Amersham
Buckinghamshire England HP7 9LL

Radiochemical batch analysis

Caution: The product is prepared for laboratory use only and not warranted for use in humans or for clinical diagnosis

3 m-CHLORO[carboxyl-^{14}C]BENZOIC ACID
Code CFQ. 2003

Batch
analysis
sheet 25861

m-Chloro[carboxyl-^{14}C]benzoic acid is prepared by the carbonation of m-chlorophenyl mangesium bromide with [^{14}C]carbon dioxide. The product is purified during the isolation procedure.

TECHNICAL DATA

Specific activity : 5.4 mCi/mmole, (199.8 MBq/mmol)
34.4 µCi/mg, (1.27 MBq/mg)

Molecular weight : 156.5 (at this specific activity)

Radiochemical purity

by thin-layer chromatography on silica gel in

(a) benzene:methanol:acetic acid (90:16:8) : > 98%
(b) benzene:dioxan:acetic acid (90:25:4) : > 98%

Chemical purity

The infra-red spectrum is consistent with that of m-Chloro[carboxyl-^{14}C]benzoic acid at this specific activity, but shows the presence of small amounts of unidentified impurities.

Melting point (Köfler block) : 155- 156°

Analysed 10th August 1978

Packaging and Storage

m-Chloro[carboxyl-^{14}C]benzoic acid is supplied as a crystalline solid in borosilicate glass vials with screw cap vials or borosilicate glass ampoules.

An ampoule may be opened by lightly scratching the serration with the file provided and carefully snapping off the upper end.

Storage at -20°C and protection from moisture and light is recommended.

Amersham International plc
White Lion Road Amersham
Buckinghamshire England HP7 9LL

Radiochemical batch analysis

Caution: The product is prepared for laboratory use only and not warranted for use in humans or for clinical diagnosis

m-[ring-U-^{14}C]CRESOL
Code CFA.685
Batch 5

Batch
analysis
sheet C/6901/1

BATCH TECHNICAL DATA

Specific activity : 56 mCi/mmol, 2.08 GBq/mmol
511 µCi/mg, 18.9 MBq/mg

Molecular weight : 110 (at this specific activity)

Radiochemical purity

by gas-liquid chromatography on 15% Carbowax 20M
on Chrom W AWDMCS : 94.6 ± 0.4%
(94.8 ± 0.5%)*

by thin-layer chromatography on silica gel in
(a) chloroform : 95%
(b) petroleum ether (40:60) ethyl acetate (4:1) : 98%

Chemical purity

by gas-liquid chromatography on 20% carbowax 20M
on Chrom Q : >95%

Analysed 29th May 1985 *Reanalysed 11th July 1985

STABILITY AND STORAGE RECOMMENDATIONS

To minimize decomposition, stocks of m-[ring-U-^{14}C]cresol should be stored in the dark at -20°C.

APPENDIX C

LONG TERM DATA FOR THE DIFFUSION OF ORGANIC COMPOUNDS INTO MDPE PIPE FROM AQUEOUS SOLUTION

Pipeline Consultant Limited

Broadway, Salford, Manchester M5 2TQ
Telephone: 061-872 5641
Telex: 665264

REPORT ON:

LONG TERM DATA FOR THE DIFFUSION OF ORGANIC COMPOUNDS INTO MDPE PIPE FROM AQUEOUS SOLUTION

by

J. M. MARSHALL

D. M. EYRE

July 1987

Registered in England No: 1638521 Directors: **G. P. Marshall** B.Sc., Ph.D., ACGI, DIC, **J. F. Mun**

1. Introduction

This report is simply an addition to the report of June 1987, and details the results of thirteen week exposure time experiments.

2. Experimental

All experimental details are the same as in the first report.

3. Results

The tables include only the long term data whilst all data have been reproduced graphically for ease of comparison.

3.1 Chloroaniline

The data are given in Table 1 and shown in Figure 1.

Distance through pipe wall mm	Concentration mg chloroaniline/g polymer 13 week exposure
0.25 (outside)	-
0.75	-
1.25	-
1.75	-
2.25	-
2.75	-
3.25	-
3.75	-
4.25	-
4.75	-
5.25	-
5.75	-
6.25	2.50
6.75 (inside)	5.35

Table 1

These results are to be compared with those given in Table 2 of the previous report. The amount of chloroaniline in the inner layer of the pipe would seem to have decreased, whilst the level of diffusant in the second layer has increased. It is felt, however, that these results indicate a levelling out of diffusant concentration rather than any significant change, and that chloroaniline is unlikely to penetrate further into the pipe wall.

3.2 m-cresol

These data are presented in Table 2 and Figure 2.

Distance through pipe wall mm	Concentration mg m-cresol/g polymer 13 week exposure
0.25 (outside)	1.00
0.75	0.16
1.25	0.11
1.75	0.66
2.25	-
2.75	-
3.25	-
3.75	0.78
4.25	1.02
4.75	0.20
5.25	2.15
5.75	1.46
6.25	3.01
6.75 (inside)	11.90

Table 2

Comparison of these data with those given in Table 3 of the first report suggests that the 4 week data were previously in error. The diffusion would seem to be progressing steadily through the pipe wall, although the amount of diffusant in the outer layers may well be tending towards equilibrium.

3.3 Nitrobenzene

The data are shown in Table 3 and Figure 3.

Distance through pipe wall mm	Concentration x 10 mg nitrobenzene/g polymer 13 weeks exposure
0.25 (outside)	-
0.75	-
1.25	-
1.75	-
2.25	-
2.75	-
3.25	-
3.75	0.11
4.25	1.24
4.75	1.26
5.25	1.24
5.75	1.30
6.25	1.40
6.75 (inside)	3.50

Table 3

These data are apparently inconsistent with the previous results (Table 4, previous report). The levels of nitrobenzene in the inner three layers of the pipe would seem to have decreased, whilst increasing in the next three layers. The diffusant did not appear to have penetrated any further into the pipe wall than previously, and there was no evidence of nitrobenzene in the outer layers. This long term exposure time will be repeated in an attempt to clarify the picture.

3.4 Chlorobenzoic acid

Data are presented in Table 4 and Figure 4.

Distance through pipe wall mm	Concentration x 10^2 mg chlorobenzoic acid/g polymer 13 weeks exposure
0.25 (outside)	-
0.75	-
1.25	-
1.75	-
2.25	-
2.75	-
3.25	-
3.75	-
4.25	-
4.75	0.08
5.25	0.15
5.75	0.70
6.25	1.70
6.75 (inside)	3.10

Table 4

These data should be compared with those given in Table 5 of the previous report. The slight decrease in amount of chlorobenzoic acid in the inner layer is not felt to be significant, and the rest of the data show a continuing penetration of the polymer by the diffusant.

3.5 Cyclohexane

The data are given in Table 5 and Figure 5.

Distance through pipe wall mm		Concentration x 10^2 mg cyclohexane/g polymer 13 weeks exposure
0.25	(outside)	1.68
0.75		-
1.25		-
1.75		-
2.25		-
2.75		-
3.25		-
3.75		0.92
4.25		1.22
4.75		2.34
5.25		4.47
5.75		4.20
6.25		7.47
6.75	(inside)	28.44

Table 5

Both the amount of cyclohexane absorbed and the depth of penetration of the diffusant have increased markedly from the 4 week exposure time. This was not unexpected, and indeed the previous data was felt to have been rather low.

4. Discussion

The new data indicated that increasing the exposure time led to an increased depth of penetration of the pipe wall by m-cresol, chlorobenzoic acid and cyclohexane. No change in penetration was observed for either chloroaniline or nitrobenzene. The amount of diffusant in the first layer of the pipe wall - that in contact with the solution, changed little for any of the diffusants with the exception of cyclohexane, where it increased significantly (section 3, tables 1-5).

Approximate diffusion coefficients were calculated for each compound from the long term data, and these are given in Table 6.

Compound	Diffusion Coefficient D $cm^2\ s^{-1}$	
	4 weeks exposure	13 weeks exposure
nitrobenzene	2.5×10^{-9}	1.3×10^{-9}
m-cresol	1.5×10^{-9} (2 week data)	1.5×10^{-9}
chlorobenzoic acid	8.0×10^{-10}	5.4×10^{-10}
chloroaniline	4.0×10^{-10}	1.6×10^{-10}
cyclohexane	4.0×10^{-10}	1.4×10^{-9}

Table 6 Diffusion coefficients

There was no change in the value of D for m-cresol, but the diffusion coefficients for nitrobenzene, chlorobenzoic acid and chloroaniline appeared to decrease. The most marked change, however, was in the diffusion coefficient for cyclohexane, which showed a significant increase.

This time dependance of the diffusion coefficient has been observed before, notably by Crank and Park (1) and Crank (2) who developed a theory to formulate this time dependance of organic vapours in polymers above their glass transition temperature. The theory is based on the idea that D depends not only on diffusant concentration but also on the time for which this concentration has existed, or on the concentration history at point in the polymer (3) A similar theory has also been postulated by Asada and Onogi (4) for water in nylon.

5. Conclusions

The long term data unfortunately did not show any better correlation with any diffusant property than did the data reported earlier.

All diffusants except m-cresol showed some time dependance in the diffusion coefficient.

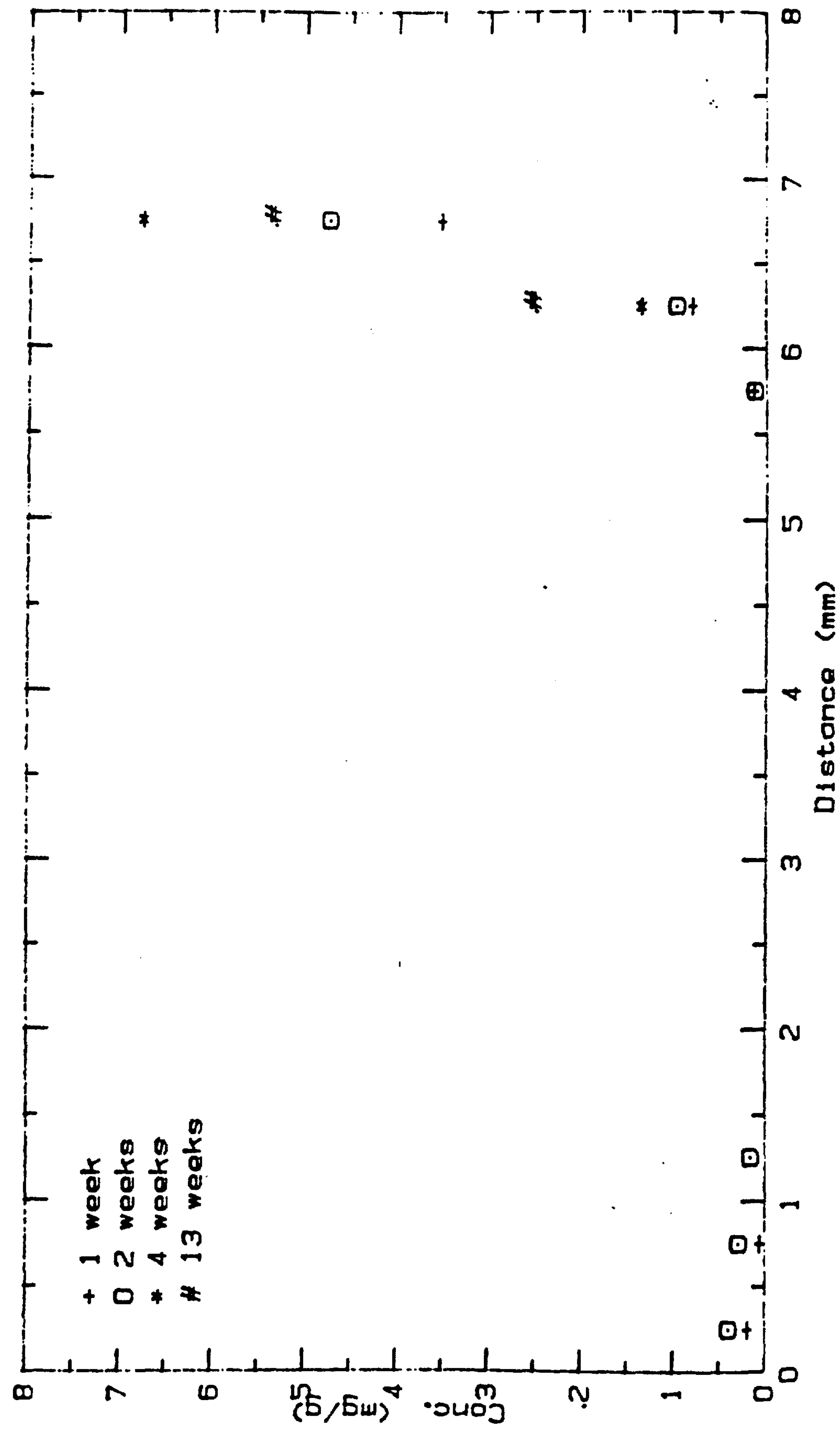
References

1. J. Crank and G.S. Park Trans. Far. Soc. 47 1072 (1951)

2. J. Crank J. Polym. Sci. 11 151 (1953)

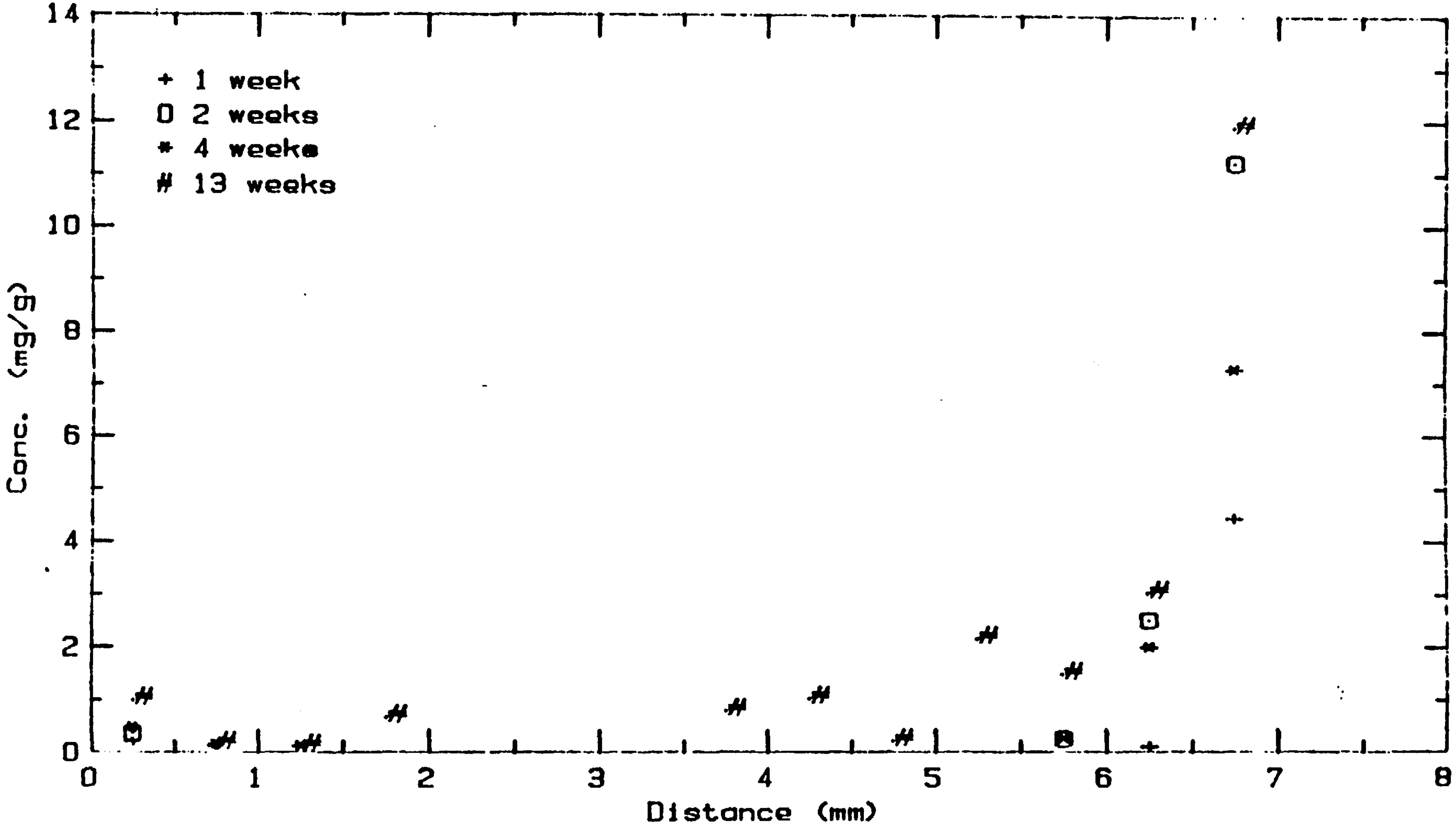
3. J. Crank and G.S. Park. Eds "Diffusion in Polymers" Academic Press 1968.

4. T. Asada and S. Onogi J. Colloid. Sci. 18 784 (1963)



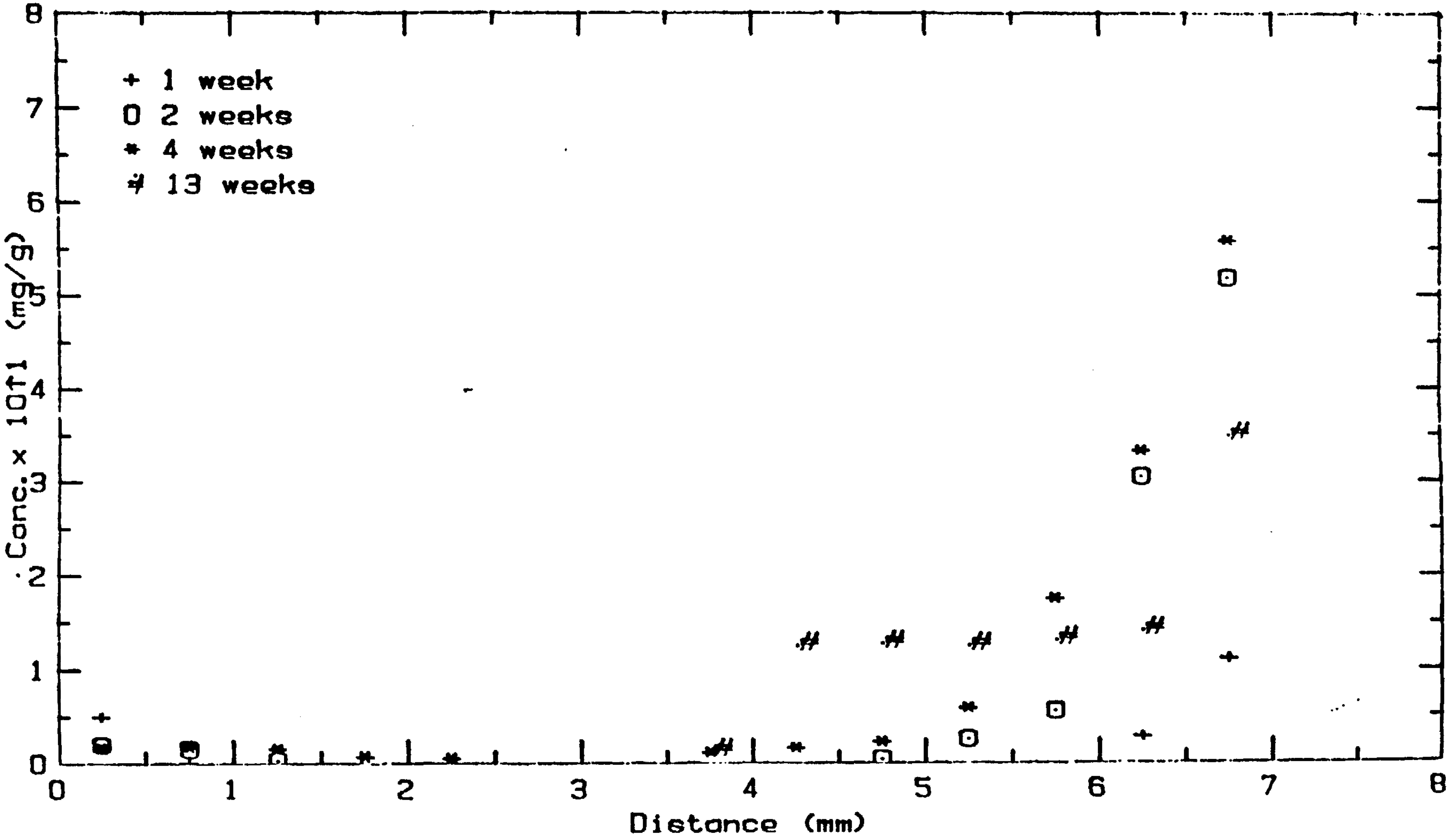
Diffusion of Chloroaniline in Blue MDPE Pipe

Figure 1



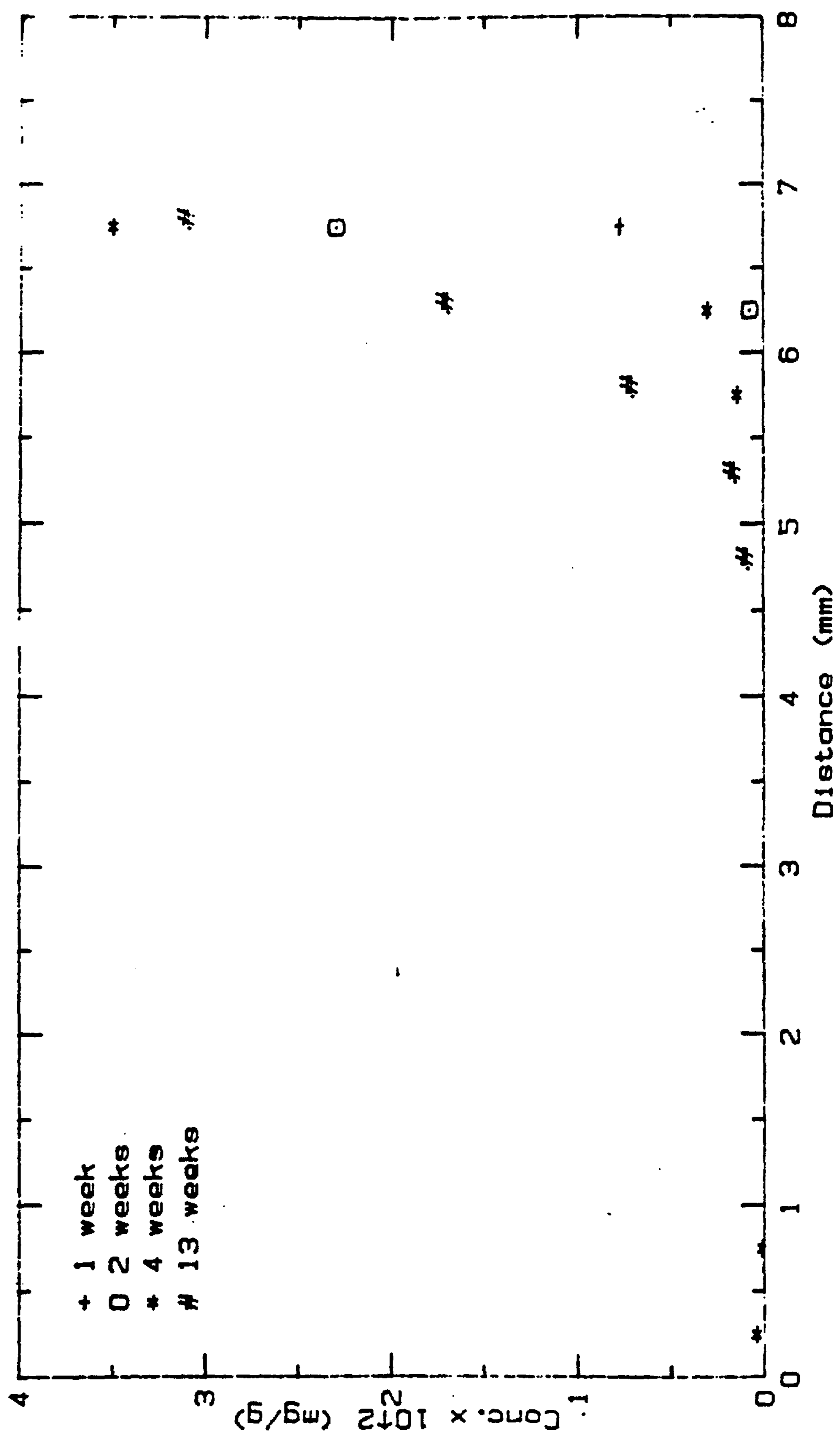
Diffusion of m-Cresol in Blue MDPE Pipe

Figure 2



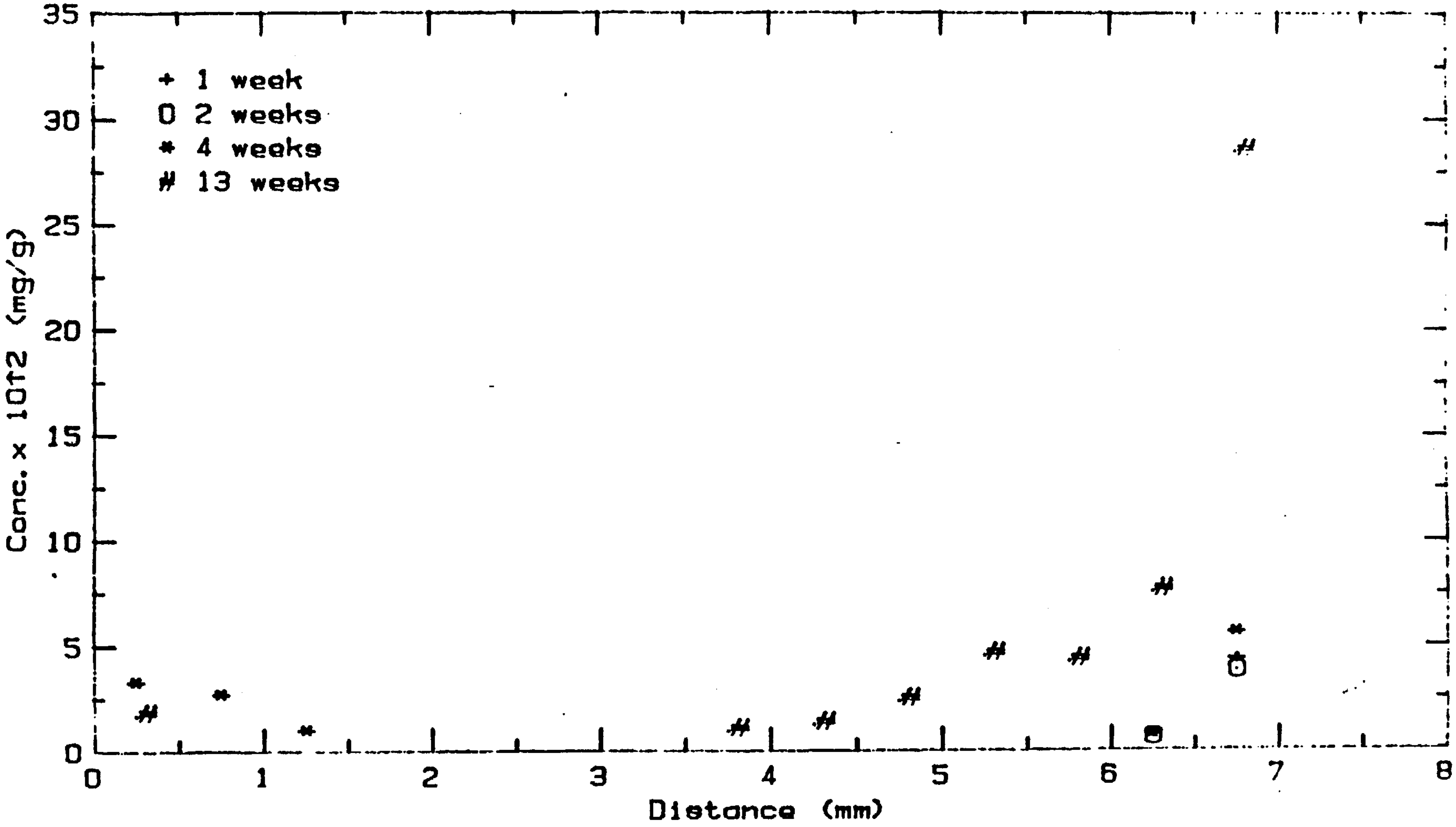
Diffusion of Nitrobenzene in Blue MDPE Pipe

Figure 3



Diffusion of Chlorobenzoic Acid in Blue MDPE Pipe

Figure 4



Diffusion of Cyclohexane in Blue MDPE Pipe

Figure 5