EFFECTS OF ORGANIC CHEMICALS IN CONTAMINATED LAND ON BURIED SERVICES (DWQ 9025)

Final Report to the Department of the Environment

DoE 2982/1

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EFFECTS OF ORGANIC CHEMICALS IN CONTAMINATED LAND ON BURIED SERVICES

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The work covered by this report was funded by the Department of the Environment (Contract PECD 7/10/253). It began 1 September 1990 and was extended on 18 June 1991. It finished on 30 November 1991.
SUMMARY

Organic chemicals in contaminated land can permeate plastic drinking water pipes and adversely affect water quality. In a report on previous WRc work under contract to DOE (ECI 9268) target organic chemicals to be monitored were recommended and analytical methods suggested for the investigation of contaminated sites (Report DoE 2222-M/1, January 1990). The objectives of the work covered by this report were, essentially, to confirm the identity of target chemicals and recommend sampling and analytical techniques for the investigation of contaminated land.

Following a literature survey and exploratory laboratory and site experimental work (which is summarised in Appendix A), an approach to the investigation of contaminated sites in relation to effects on buried services is proposed. The main conclusions are as follows:

- Two groups of volatile organic chemicals (VOCs) are proposed for monitoring contaminated land in relation to potential effects on buried water pipes. These chemicals were selected on the basis of their ability to permeate plastic pipes, occurrence in contaminated soil and their scale of use. Nine commonly used and frequently detected chemicals in Group 1 should be monitored at virtually all sites (carbon tetrachloride, trichloroethene, tetrachloroethene, chlorobenzene, benzene, toluene, and o-, m-, and p-xylene). Nine more compounds constitute Group 2 (dichloromethane, 1,2-dichloroethene, 1,1,1-trichloroethane, 1,2-dichloropropane, vinyl chloride, methyl bromide, ethyl benzene and di- and tri-chlorobenzenes); it is advisable that these should be monitored, in addition to Group 1 chemicals, at sites where contamination with unknown chemicals is suspected. Other compounds of similar nature should be investigated when the site history suggests their use.
Trigger concentrations with respect to protection of water supplies from permeation through pipe walls of buried services ('threshold' and 'action' levels) are proposed for the target chemicals selected, with appropriate values calculated for soil gas, pore water and soil samples.

The sampling and analysis of soil gas is recommended as the most appropriate approach in most circumstances (but not in water-logged ground or in the saturated zone) for predicting whether soil contaminants could permeate plastic water pipes and contaminate the drinking water supply.

Where pipes are to be laid below the water table or where the site is subject to frequent waterlogging, it is recommended that the soil pore water is sampled and analysed. Only where neither soil gas nor soil water samples can be taken, should the analysis of soil samples be employed.

A systematic approach has been proposed to the investigation of a site for possible contamination by VOCs. This approach should be adopted whenever the installation of vulnerable plastic pipes, such as polyethylene, is considered for the distribution of drinking water.

At each site, the VOCs to be determined should be chosen in accordance with information on the site history and appropriate analytical methods should be selected and validated by an experienced analyst.

In practice, contamination of water supplies by permeation into distribution pipework from redeveloped sites does not appear to pose a major problem at present. However, some compounds, such as benzene, vinyl chloride and dichloromethane, could reach unacceptable levels in drinking waters well before they would be detected by consumers as an objectionable taste or odour. Their presence would not be recognised unless appropriate monitoring was implemented.
More information on the occurrence and levels of such compounds should be gathered. To be safe, Water companies tend to use metal pipes (for both mains and service pipes) laid in clean in-fill at any site where contamination is suspected (a list of sites where such measures were undertaken is given in Appendix B). Previous WRc reports to the DOE, as well as more recent papers from the USA, concluded that taste and odour problems resulting from permeation through pipe walls were usually caused by accidental spillage of chemicals in the vicinity of the pipe.

- For the sampling of soil gas, a grab sampling technique has been recommended. Passive sampling, a technique where a sampling device is buried for an extended time under similar conditions as those for the proposed pipes, may be a useful alternative or even more appropriate than grab sampling. However, a suitable passive sampling technique needs to be developed and tested in the field.

- It is possible to determine all the target compounds using a combination of analytical methods which have adequate limits of detection. It would, however, be beneficial to assess the most suitable analytical conditions and recommend an optimised method for on-site analysis.

- Laboratory and field studies have shown that a technique employing on-site soil gas sampling followed by analysis of the gas by a portable gas chromatograph, is potentially very useful for the investigation of contaminated sites. More work is needed to evaluate this technique and, in particular, the newer instruments now commercially available.

- The same (or similar) approach to that recommended for investigating sites with respect to effects on water pipes could also be useful for general survey work on contaminated sites. For example, when assessing possible effects of contaminated sites on the quality of underlying groundwater.
OBJECTIVES

The objectives of the work covered by this report were:

- to test at contaminated land sites a range of the proposed target organic chemicals and associated analytical techniques;
- modify tests as appropriate, and then confirm the identity of suitable target chemicals;
- recommend sampling and analytical techniques for the investigation of contaminated land;
- evaluate the success of remedial measures that have already been carried out at redeveloped sites to protect buried services; and
- suggest changes to DOE policy, where appropriate, on advising on remedial measures.

1. INTRODUCTION

A variety of common industrial/commercial organic chemicals found in contaminated land can affect buried plastic pipes. Gross soil contamination by organic chemicals, such as solvents, petroleum products, phenols, etc, can affect the integrity of the material of the pipe resulting in pipe failure. The incidence of pipe failure due to contaminated land is relatively uncommon according to a survey carried out by WRC under a DoE contract (Crathorne and James 1990). Much less severe contamination by such organic chemicals, while not affecting the integrity of the pipe, can have an effect on the quality of drinking water in plastic pipes, particularly polyethylene (PE) or polybutylene (PB) pipes, due to their ability to permeate the pipe wall. Concentrations of the permeated chemicals in drinking water can reach levels causing taste and odour problems and can exceed maximum permissible concentrations specified in the Water Supply (Water Quality) Regulations 1989 or guideline values set, on the basis of toxicological assessment, by the World Health Organisation (WHO).
In order to protect water supplies to be carried in pipes laid in soil suspected to be contaminated, an investigation into the presence of contaminants with the potential to permeate should be undertaken before a decision is taken on the type of water pipes to be used.

Any potentially contaminated site where plastic pipes are to be laid should be investigated, even when drinking water supplies are not involved to identify possible gross contamination which could cause eventual pipe failure. In particular PVC, which is virtually impermeable at low soil contamination levels, will suffer from high permeation or structural failure when exposed to high levels of some organic chemicals (Crathorne et al 1987). In the United States fifteen percent of reported pipe permeation incidents occurred with PVC pipes (Holsen et al 1991) demonstrating that gross soil contamination in the area surrounding the pipe can give rise to water quality problems.

The Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRCL) of the UK has issued Guidance Notes on the assessment and redevelopment of contaminated land (1987) and landfill sites (1990) which recognise this potential problem. However, target chemicals to be measured, 'trigger' values or recommended procedures for site investigation have not yet been specified for the type of organic chemicals considered in this report.

Previous WRc reports to the Department (Crathorne and James 1990, Crathorne et al 1987) have described experimental work on permeation through different pipe material which was carried out in WRc and elsewhere, particularly at KIWA (The Netherlands Waterworks' Testing and Research Institute). As a result we now have an understanding of the type of compounds likely to permeate plastic pipes (concrete, asbestos cement and metal pipes are virtually impermeable) and the time required for such compounds to pass through the pipe wall. On the basis of these data provisional target chemicals were identified which could be monitored at contaminated sites to provide an indication of potential problems from pipe permeation. This report reconsiders the possible target chemicals, taking into account their potential to permeate PE pipes, their occurrence, and their chemical/physical properties and behaviour in soils and proposes a modified list.
One of the previous reports (Crathorne and James 1990) also provides estimated maximum acceptable soil concentrations for a range of chemicals which should not give rise to concentrations in drinking water, in the most permeable pipe (PE), which would exceed acceptable levels (based on existing drinking water quality standards or potential for causing tainting of supplies). These 'trigger' values have been updated in this report in line with the modified list of target chemicals and with the recommended procedures for site investigation.

The great majority of the proposed target chemicals are volatile organic compounds (VOCs). In soils VOCs can be adsorbed on soil, dissolved in water and, in the unsaturated zone, they can occur in the vapour phase. The advantages and disadvantages of analysing soils, soil gas and water are discussed together with the choice of appropriate sampling and analytical techniques.

Following a literature survey and exploratory laboratory and site experimental work, an approach to investigation of contaminated sites in relation to effects on buried services is proposed. (A summary of the experimental work is given in Appendix A.) It has been concluded that the recently developed techniques of soil gas measurement offer attractive methods for soil analysis but they could not be applied to all situations, e.g. where pipes would be laid in the saturated zone. Alternative techniques for analysing water and/or soil samples in situations where soil gas analysis would not be appropriate are therefore proposed.

2. SELECTION OF TARGET CHEMICALS AND CALCULATION OF TRIGGER VALUES

2.1 Type of compounds to be monitored

Many chemicals have the potential to permeate plastic pipes, polyethylene and polybutylene pipes in particular, and rubber gaskets. The history of a site's previous use needs to be taken into account before deciding which compounds to measure. From a practical point of view a previous report to the Department (Crathorne and James 1990) recommended a range of commonly-used chemicals to be
measured. The list of recommended chemicals consisted of halogenated aliphatic hydrocarbons (carbon tetrachloride, tri- and tetra- chloroethenes and methyl bromide), chlorinated aromatic hydrocarbons (mono-, di-, and tri- chlorobenzenes), aromatic hydrocarbons (benzene, toluene, xylene and trimethylbenzene), and phenols (phenol and mono-, di-, and tri- chlorophenols).

The aromatic hydrocarbons and the halogenated aliphatic hydrocarbons have the highest potential to permeate. Other chlorinated hydrocarbons with a high permeation potential, such as dichloromethane, vinyl chloride, and chlorinated ethanes and propanes, which have been detected in some countries in contaminated soil or in the underlying groundwater (Schleyer et al 1988, Ioch et al 1989) should also be included in the investigation of some sites, particularly where the site history suggests their possible presence.

It is unlikely that a single sampling/analytical procedure could be used to determine all the target chemicals with adequate accuracy. For example, when using solvent extraction the very volatile compounds such as dichloromethane or vinyl chloride would not be determined due to interferences from the solvent peak on a gas chromatogram but, on the other hand, the least volatile compounds such as trimethylbenzene or chlorophenols would not be adequately recovered in head-space analysis which is a good method for the determination of the more volatile compounds. Therefore priority has been given to selecting suitable procedures for the more volatile contaminants (VOCs) since they have a greater tendency to permeate, though the possibility of long term permeation by gross contamination with less volatile compounds should not be neglected. (High levels of a range of non-volatile organic chemicals would be detected during already established methods of site investigation, e.g. for phenols and polycyclic aromatic hydrocarbons (ICRCL 59/83, 1987)).

In the UK, little information exists on the level and extent of soil contamination with the target chemicals mentioned above. Chlorinated hydrocarbon solvents, tetrachloroethene in particular, have been identified as common contaminants in aquifers below industrial sites (Rivett et al 1990). In Germany, the Netherlands and the USA chlorinated hydrocarbons (trichloroethene, tetrachloroethene, dichloromethane, 1,1,1-trichloroethane, dichloroethenes and vinyl chloride) and volatile aromatic hydrocarbons (benzene, toluene, xylenes
and ethyl benzene) are the most frequently detected compounds (Schleyer et al 1988, Loch et al 1989) in groundwaters affected by waste sites.

Chemico/physical constants important for the behaviour in soil and an indication of permeation potential are given for some of the compounds of interest in Table 2.1.

2.2 Samples to be analysed

Most buried sources are likely to be laid at a depth of less than 2 metres in unsaturated soil. Liquid organic contaminants (which include the VOCs) in unsaturated soils are partitioned into the gas and solid phases and become dissolved in soil moisture and adsorbed onto the surfaces of soil minerals and organic matter associated with the soil. The distribution of the contaminants among these components will depend on many factors including the volatility and water solubility of the contaminants, soil moisture content, soil temperature and soil properties, particularly its organic carbon content. The dynamics of VOCs in unsaturated soils are very complex. Several dissolution, diffusion and volatilization processes affect the transport from saturated groundwater to unsaturated soils, from soils to atmosphere and from unsaturated soil to groundwater.

Permeation through plastic pipes may take place from both the liquid and gaseous phase (Veenendaal et al 1985). When the water supply pipe is located in the unsaturated zone, permeation will only take place from the vapour phase. When the pipe lies in the saturated zone or water-logged ground permeation will take place mainly from the aqueous phase.

One approach, recommended in a previous report (Crathorne and James 1990), was to determine the 'total' content of VOCs by analysing a soil sample using Soxhlet extraction or similar techniques. However, such an approach has two main disadvantages, i.e. the volatile compounds of interest could easily be lost during sampling and/or sample handling and the results for soil samples would be less relevant in estimating the amounts of contaminants available for permeation than the measurement of soil gas or water concentrations.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Water solubility (mg l⁻¹ at 20 °C)</th>
<th>Vapour pressure (mmHg at 20 °C)</th>
<th>Henry’s law constant (kPa m³ m⁻¹ cm⁻¹)</th>
<th>Permeability coefficients (LDPE) m⁻¹ day⁻¹ +</th>
<th>PVW x 10⁶</th>
<th>PW x 10⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon tetrachloride</td>
<td>800</td>
<td>91</td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>trichloroethene</td>
<td>1100</td>
<td>60</td>
<td>1.3</td>
<td></td>
<td>8.2</td>
<td>16</td>
</tr>
<tr>
<td>tetrachloroethene</td>
<td>150</td>
<td>14</td>
<td>2.3</td>
<td></td>
<td>3.5</td>
<td>7.7</td>
</tr>
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<td>dichloromethane</td>
<td>13000</td>
<td>349</td>
<td>0.26</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1,2-dichloroethane</td>
<td>8700</td>
<td>64</td>
<td>0.11</td>
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<td></td>
</tr>
<tr>
<td>1,1,1-trichloroethane</td>
<td>4400</td>
<td>100</td>
<td>2.8</td>
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<td>1,1,2-trichloroethane</td>
<td>25</td>
<td></td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2-dichloropropene</td>
<td>2700</td>
<td>42</td>
<td>0.4*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>vinyl chloride</td>
<td>1100 (25 °C) 2600 (25 °C)</td>
<td>2.4  (50)*</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>methyl bromide</td>
<td>900</td>
<td></td>
<td>0.06</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1,1-dichloroethene</td>
<td>500*</td>
<td>15*</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>1,1-dichloroethane</td>
<td>200*</td>
<td>0.6*</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>trans-1,2-dichloroethene</td>
<td>300*</td>
<td>0.6*</td>
<td></td>
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<td>cis-1,3-dichloropropene</td>
<td>40*</td>
<td>0.2*</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1,1,2,2-tetrachloroethane</td>
<td>5*</td>
<td>0.05*</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>chlorobenzene</td>
<td>500</td>
<td>9</td>
<td>0.4</td>
<td>14.0</td>
<td></td>
<td>35</td>
</tr>
<tr>
<td>dichlorobenzenes</td>
<td>69-100</td>
<td>0.6-2.0</td>
<td>0.2-0.4</td>
<td></td>
<td></td>
<td>19</td>
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<td>trichlorobenzenes</td>
<td>6-19</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>benzene</td>
<td>1800</td>
<td>76</td>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>toluene</td>
<td>520</td>
<td>28</td>
<td>0.7</td>
<td>7.6</td>
<td></td>
<td>12</td>
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<tr>
<td>xylenes</td>
<td>160-210</td>
<td>6-9</td>
<td>0.5-0.7</td>
<td>9.1 (m-isomer)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>150</td>
<td>7</td>
<td>0.8</td>
<td>8.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>propylbenzenes</td>
<td>50</td>
<td>3</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>trimethylbenzene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>phenol</td>
<td>82000</td>
<td>0.2</td>
<td></td>
<td>&lt;0.008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>chlorophenols</td>
<td>~27000</td>
<td>0.1-40 (&lt;70 °C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dichlorophenols</td>
<td>0.4</td>
<td>1 (2,4-DCP at 53 °C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>trichlorophenols</td>
<td>~1000</td>
<td>0.1-1.0 (72 °C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* from Schuring (1989)
** from Verschueren (1983)
+ from Veenendaal et al (1985) (PVW and PW permeability coefficients 'vapour-PE-water' and 'water-PE-water' respectively)
It would therefore be preferable to analyse either the vapour phase from the unsaturated zone or soil-pore water where pipes would be laid in the saturated zone. In the past such analyses were not feasible since appropriate techniques had not been established.

A literature review and experimental work (Appendix A), carried out under this contract, have shown that adequate procedures are now available. These are discussed in Section 3.

2.3 **Concentration levels of interest**

In the Netherlands, VOC concentrations in soil and groundwater samples have been determined during site assessment for new developments, and sites classified as categories A (uncontaminated), B (more extensive analytical investigation required) or C (cleaning up of soil required) in accordance with set trigger values. However the trigger values are not based on any consideration of effects on pipe materials or permeation.

More recently, trigger concentration limits related to permeation through plastic pipes have been set in the Netherlands for organic compounds in soil and groundwater for PE and PVC pipes (Table 2.2) (State Inspectorate of Public Health and Environmental Hygiene 1990). However, in the Netherlands, unlike the UK, the majority of drinking water pipes is laid in the saturated zone in contact with water and therefore concentrations in soil gas are of less concern.

In their report, Crathorne and James (1990) derived 'trigger levels' for a range of compounds which, if exceeded, indicated that further site investigation should be undertaken. The 'trigger levels' were expressed as concentrations in soil and were based on rough calculations of the lowest concentration of a chemical that is able to permeate PE pipe over a period of 8 hours which would lead, if water in the pipe were stagnant, to a concentration in the water inside the pipe exceeding the maximum 'acceptable' concentration in drinking water (taste and odour threshold values or World Health Organisation guideline or tentative values).
<table>
<thead>
<tr>
<th></th>
<th>Initially proposed trigger levels*</th>
<th>For use of polyethylene</th>
<th>Current Dutch values**</th>
<th>For use of PVC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg kg(^{-1}) dry soil</td>
<td>Groundwater µg l(^{-1})</td>
<td>Soil (dry) mg kg(^{-1})</td>
<td>Groundwater mg l(^{-1})</td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>0.15</td>
<td>20</td>
<td>1</td>
<td>none</td>
</tr>
<tr>
<td>trichloroethene</td>
<td>1.5</td>
<td>10</td>
<td>0.01</td>
<td>275</td>
</tr>
<tr>
<td>tetrachloroethene</td>
<td>0.5</td>
<td>25</td>
<td>0.1</td>
<td>40</td>
</tr>
<tr>
<td>1,2-dichloroethane</td>
<td>-</td>
<td>20</td>
<td>0.2</td>
<td>850</td>
</tr>
<tr>
<td>1,1,1-trichloroethane</td>
<td>-</td>
<td>10</td>
<td>0.5</td>
<td>1100</td>
</tr>
<tr>
<td>dichloropropane</td>
<td>-</td>
<td>20</td>
<td>0.2</td>
<td>275</td>
</tr>
<tr>
<td>methyl bromide</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>0.1</td>
<td>5</td>
<td>0.3</td>
<td>50</td>
</tr>
<tr>
<td>dichlorobenzenes</td>
<td>0.015</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>trichlorobenzenes</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>benzene</td>
<td>0.5</td>
<td>10</td>
<td>0.1</td>
<td>450</td>
</tr>
<tr>
<td>toluene</td>
<td>50</td>
<td>15</td>
<td>0.25</td>
<td>125</td>
</tr>
<tr>
<td>xylenes</td>
<td>2.5</td>
<td>10</td>
<td>0.1</td>
<td>50</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>-</td>
<td>10</td>
<td>0.5</td>
<td>40</td>
</tr>
<tr>
<td>propylbenzene</td>
<td>-</td>
<td>10</td>
<td>2</td>
<td>15</td>
</tr>
<tr>
<td>1,3,5-trimethylbenzene</td>
<td>25</td>
<td>3</td>
<td>0.1</td>
<td>5</td>
</tr>
<tr>
<td>phenol</td>
<td>5</td>
<td>23000</td>
<td>45</td>
<td>none</td>
</tr>
<tr>
<td>chlorophenols</td>
<td>1</td>
<td>4000</td>
<td>5</td>
<td>none</td>
</tr>
<tr>
<td>dichlorophenols</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>trichlorophenols</td>
<td>5</td>
<td>35</td>
<td>5</td>
<td>none</td>
</tr>
</tbody>
</table>

* From Crathorne and James (1990)
** From State Inspectorate of Public Health (1990)
The report concluded that a limit of detection of 0.1 mg kg\(^{-1}\) should be adequate for the determination of most compounds of interest. The calculated ‘trigger values’ for the target compounds under consideration are also given in Table 2.2.

2.4 Proposed target chemicals and trigger values

In view of the complexity of the permeation process, the variety of factors affecting the amount of a contaminant available for permeation and the wide range of compounds with a potential to permeate plastic pipes, the proposed trigger values have to include a number of assumptions and can only cover the compounds which are judged most likely to have effects on water quality.

It is recommended that nine compounds in common use, frequently detected in contaminated land (Eastwood et al 1991) and with high permeation potential (Group 1), i.e. carbon tetrachloride, trichloroethene, tetrachloroethene, chlorobenzene, benzene, toluene and o-, m-, and p-xylenes, should be monitored at all sites unless the history of the site precludes any organic chemical contamination by solvents, petroleum products or other oils.

It is further suggested that the presence of other volatile chlorinated solvents (dichloromethane, 1,2-dichloroethane, 1,1,1-trichloroethane and 1,2-dichloropropane), vinyl chloride, methyl bromide, di- and tri-chlorobenzenes and ethylbenzene (Group 2) should be investigated on sites where contamination with unknown complex chemicals is strongly suspected or where any of these compounds were known to have been used or manufactured.

For these two groups of compounds trigger values with respect to pipeline permeation are proposed in this report (see Table 2.3). Other compounds of similar nature should be investigated when the site history suggests their use.

The calculation of the proposed trigger values is based on the following principles, which are similar to those used by Crathorne and James (1990):
Table 2.3 Proposed ‘threshold’ and ‘action’ trigger values for target compounds which could affect water quality in plastic pipes

<table>
<thead>
<tr>
<th>Group 1 compounds:</th>
<th>Maximum 'acceptable' Concentrations in drinking water (µg l⁻¹)</th>
<th>In soil gas (µg l⁻¹)</th>
<th>In pore water (µg l⁻¹)</th>
<th>In soil (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Threshold</td>
<td>Action</td>
<td>Threshold</td>
<td>Action</td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>3 (1)</td>
<td>3</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>trichloroethene</td>
<td>30 (1)</td>
<td>30</td>
<td>300</td>
<td>150</td>
</tr>
<tr>
<td>tetrachloroethene</td>
<td>10 (1)</td>
<td>20</td>
<td>200</td>
<td>100</td>
</tr>
<tr>
<td>benzene</td>
<td>10 (2), (3)</td>
<td>10</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>toluene</td>
<td>10 (2)</td>
<td>10</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>xylene</td>
<td>10 (2)</td>
<td>10</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>20 (4)</td>
<td>10</td>
<td>100</td>
<td>50</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Group 2 compounds:</th>
<th>Maximum 'acceptable' Concentrations in drinking water (µg l⁻¹)</th>
<th>In soil gas (µg l⁻¹)</th>
<th>In pore water (µg l⁻¹)</th>
<th>In soil (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Threshold</td>
<td>Action</td>
<td>Threshold</td>
<td>Action</td>
</tr>
<tr>
<td>dichloromethane</td>
<td>20 (3)</td>
<td>20</td>
<td>200</td>
<td>100</td>
</tr>
<tr>
<td>1,2-dichloroethane</td>
<td>4 (3)</td>
<td>4</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>1,1,1-trichloroethane</td>
<td>160 (4)</td>
<td>160</td>
<td>1600</td>
<td>800</td>
</tr>
<tr>
<td>1,2-dichloropropane</td>
<td>2 (4)</td>
<td>2</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>vinyl chloride</td>
<td>2.5 (3)</td>
<td>3</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>methyl bromide</td>
<td>400 (5)</td>
<td>400</td>
<td>4000</td>
<td>2000</td>
</tr>
<tr>
<td>dichlorobenzenes</td>
<td>0.3 (4)</td>
<td>0.3*</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>trichlorobenzenes</td>
<td>5 (4)</td>
<td>10</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>10 (2)</td>
<td>10</td>
<td>100</td>
<td>50</td>
</tr>
</tbody>
</table>

* It may be difficult analytically to satisfy this requirement. Concentration techniques would be needed.
(1) Water Supply (Water Quality) Regulations 1989
(2) Water Supply (Water Quality) Regulations 1989– hydrocarbon parameter
(3) Acceptable concentrations calculated at WEC, based on recent toxicity data
(4) Concentrations based on taste and odour threshold values (lower value of report range)
The trigger value (action level) represents an approximate concentration of a contaminant in soil gas, pore water or soil which could lead to a concentration in drinking water in a polyethylene pipe exceeding its maximum 'acceptable' concentration.

The threshold trigger value is usually one tenth of the trigger level for action and represents the required limit of detection for the analytical method to be used for the initial investigation.

The maximum 'acceptable' concentration is either that given in the Water Supply (Water Quality) Regulations 1989, or a concentration which would exceed taste and odour thresholds, or values calculated at WRc, which are based on recent toxicity data.

For the target compounds, all of which readily permeate PE pipes, it has been assumed that the concentration which will pass through the pipe in 8 hours, i.e. average overnight stagnation time, (after the steady-state condition has been reached) will be 2% of the concentration in the water and 10% of the concentration in the vapour surrounding the pipe. These percentages are based on a series of laboratory investigations carried out at KIWA (Venendaal et al 1985). For compounds where experimental data were determined the measured values were used instead of the average percentages.

Trigger values calculated for pipes laid in the unsaturated zone were lower than those for water surrounding the pipe, since the same concentration in a vapour would lead to a higher concentration in the drinking water. For soils, the concentrations which could lead to concentrations in drinking water exceeding the maximum 'acceptable' value will be higher than for soil gas or water as a proportion of the contaminant most likely to be adsorbed on the solids and would not be available for permeation. This however is difficult to quantify. For practical reasons, therefore, the threshold values for soil samples were made equivalent to the action values for water samples and the action values were calculated to be in line with the current Dutch values for soil surrounding PE pipes.
The proposed trigger values are given in Table 2.3.

ICRCL has already set a tentative 'threshold trigger concentration' for phenols of 5 mg kg\(^{-1}\) of air dried soil (ICRCL Guidance Note 59/83 1987). It is reasonable to assume that the procedure based on 4-aminoantipyrine, the analytical method which is usually used for soil investigation, could detect phenolic contamination that would give rise to water quality problems in PE pipes. Also the tentative trigger concentration of 50 mg kg\(^{-1}\) set for polyaromatic hydrocarbons (as a 'marker' for coal tar) should be sufficient to detect the presence of a range of less volatile compounds which could permeate over a long period.

3. SELECTION OF SAMPLING TECHNIQUES AND ANALYTICAL METHODS

3.1 Required limits of detection

The choice of the sampling and analytical techniques for the investigation of contaminated soils will, inter alia, depend on the required limits of detection. The methods to be used should therefore be able to detect the threshold trigger values or less.

3.2 Soil gas samples

3.2.1 Scope of soil gas analysis

Soil gas monitoring has recently gained popularity for the detection of subsurface ground contamination (Marrin, Kerfoot 1988). Soil gas measurements have been primarily employed for mapping contaminant plumes. Attempts are also being made to use soil gas measurements as an indicator of groundwater contamination (Kerfoot 1987 and 1988). The main advantage is the comparatively low cost of a soil gas survey relative to drilling exploratory wells and analysing groundwater (or soil samples). The absence of non-volatile compounds in the samples reduces contamination problems during the analysis. In addition such techniques require minimal sample handling before analysis which,
particularly for soil samples, is the main cause of often significant losses of VOCs (Siegrist and Jenssen 1990).

Generally, soil gas sampling is most applicable to sites at which the unsaturated zone is characterised by dry, coarse-grained soils containing a low amount of organic matter. Fine grained soils tend to have a relatively low air-filled porosity and to trap moisture and organic material that can adsorb the VOCs. Compounds which could be determined by soil gas analysis should have a Henry’s law constant of at least 0.05 kPa m³ mol⁻¹ and a vapour pressure (at 20 °C) of 1.0 mmHg or greater (Marrin 1988). Data in Table 2.1 show that the compounds with the greatest ability to permeate plastic pipes satisfy these conditions.

Clearly soil gas samples cannot be obtained from either water-logged ground or the saturated zone. The temperature of the ground will affect the distribution of the contaminant between the soil and soil gas. The vapour pressure of organic chemicals increases with increased temperature so that at higher temperatures the concentration in soil gas will be higher and more of the contaminant will be 'available' for permeation. The variation in available concentration with temperature may vary from site to site depending on a number of factors such as the amount of soil organic matter, total concentration of the contaminant in the soil, nature of the contaminant, rate of evaporation from the ground, etc. This needs to be taken into account when evaluating the analytical results.

### 3.2.2 Sampling techniques

The sampling of soil gas requires specialised techniques which usually fall into two categories, i.e. grab sampling and passive sampling.

In grab sampling, a hollow pipe is driven into the ground to a predetermined depth and, using pumps or syringes, soil gases are pulled through the pipe and then either analysed directly when using an on-line instrument or collected in a gas tight vessel, or adsorbed in a tube containing an adsorbent such as Tenax or activated carbon. The collected samples are usually analysed at or near the
sampling location but can be taken to a laboratory for analysis provided steps are taken to prevent sample losses during transport. Each technique has to be properly validated before use. Any leakage from the sampling vessels needs to be determined and, when using adsorption tubes, the breakthrough volume during sampling (i.e. the maximum volume of sample which can be passed through the tube before the compounds starts eluting from the tube) and recoveries of the compounds of interest need to be established.

In passive sampling, an adsorbent sampler is buried in a manifold at a predetermined depth and is allowed to collect VOCs from the surrounding soil gas. After a set time (usually several days) the samplers are retrieved, sealed and sent to a laboratory for analysis.

Grab sampling permits the collection of a large number of samples and produces rapid results. Methodologies for passive sampling are evolving. This approach requires more time and is less flexible than grab sampling and is therefore less suitable for rapid surveying of contaminated sites. The measurement of 'integrated' data provided by passive sampling could be more appropriate for more detailed follow-up site investigations because, while grab samples represent VOC concentrations at particular subsurface locations at the time of sampling, the passive sampling provides an integrated measure of VOC concentrations over a period of time.

At present there is insufficient information to recommend any particular technique of passive sampling. Grab sampling has therefore been chosen for the experimental work under this contract (Appendix A) and proposed as the technique for site investigation in Section 4.

### 3.2.3 Sample preservation and transport

Wherever possible soil gas samples should be analysed directly on site. However in a number of situations samples need to be transported to a laboratory, e.g. when the identification of the contaminants by gas chromatography - mass spectrometry (GC-MS) is required or when a particular contaminant needs to be concentrated to achieve the required limit of detection.
Where on-line soil gas analysis is not feasible samples can be collected and transported to laboratory in gas-tight containers (e.g. sample bulbs (Eastwood et al 1991), canisters (Hsu et al 1991) or bags (Robbins et al 1990a and 1990b)) or the compounds of interest can be adsorbed from a known volume of sample gas onto adsorbent-filled tubes (Young and Parker 1984).

Transport and storage in sample containers could result in significant bias due to leakage of sample gas. With some containers, when carefully checked and handled, negligible losses of VOCs would occur in the interval of several hours between collection and analysis (Bishop et al 1990).

Plastic bags are the least expensive sample containers but also the least suitable as they tend to suffer from adsorption of some VOCs and cross contamination (Schuring 1989, Rudolph et al 1990). Consequently, they should not be used when quantitative results are required. Uncontaminated bags may be adequate for collecting samples with high levels of VOCs for GC-MS identification.

Gas adsorption tubes, sealed with gas-tight end-caps, can be a more reliable and convenient means of sample transport. They also allow preconcentration of the determinands, useful where the limits of detection of the analytical technique are insufficient. On the negative side specialised equipment is needed for the desorption from the tube into an analytical instrument and only one analysis can be performed on each tube.

3.2.4 Analytical methods

For each site investigation there will probably be a choice of suitable analytical techniques and methods. Many factors need to be considered when selecting the optimum method, such as:

- which contaminants are to be determined;
- how many determinands;
- the required limits of detection/threshold trigger values;
- the number of samples to be analysed;
- the expected range of concentrations;
- available instrumentation and expertise.

Not enough may be known from the site history on the identity, complexity and levels of the VOCs contaminants to assure the correct choice of the analytical method. After the preliminary site investigation the method may need to be optimized or a better method selected.

As a general guidance this section discusses the various analytical techniques which could be used and their advantages and limitations.

Most methods for the determination of VOCs are based on gas chromatography (GC). For a majority of situations, provided the limits of detection are sufficient, soil gas samples can be analysed directly without any sample treatment. For water and soil samples, even when the limits of detection would be adequate, some method of extraction is usually needed to separate the compounds of interest from the sample matrix before gas chromatographic analysis. Minimising the sample handling thus minimises losses of the determinands and makes soil gas samples particularly suitable for on-site analysis.

The selection of a detector is an important consideration. The electron capture detector (ECD) and photoionization detector (PID) are both very sensitive to some of the target compounds but not to others. The flame ionization detector (FID) does not achieve comparable sensitivity but is less selective. It is however less suitable for field operation.

A PID is well suited to field work as (unlike FID) it does not require additional gas supplies and is quickly stabilised. It is capable of detecting a range of compounds at the low microgram per litre levels. Whether a compound is detectable and how sensitive the detection is depends on the photoionization energy of the lamp in use and the ionization potential of the compound. The most frequently used lamp (photoionization energy of 10.2 eV) is sensitive to most of the target compounds (ionization potential <10.2eV) except carbon tetrachloride, dichloromethane, and dichloro- and trichloroethanes. Detectors with a 11.3 eV lamp, which are sensitive to these compounds, are available but are less robust and more prone to environmental factors such as moisture.
The electron capture detector is more sensitive to chlorinated compounds and could be an alternative to the high energy PID detector for the determination of the target compounds with high ionization potential or for the measurements of very low levels of chlorinated VOCs. It is, however insensitive to the commonly occurring target compounds benzene, toluene and xylenes.

Detectors, based on the mass spectrometer (MS), are usually used for the identification of contaminants or as a confirmation technique. Often a direct introduction of a relatively large volume of soil gas sample into a GC-MS causes technical problems. For some instruments, therefore, analysis using adsorbent tubes would be preferable.

To locate sampling areas for more specific analytical investigation non-specific organic vapour analysers (OVA) can be used in some situations. Commercially available field instruments are based on flame ionisation (FID) or, more often on photoionization (PID) detectors. Some recent instruments combine OVA with GC, where OVA has a set trigger concentration and when that is exceeded the GC is automatically started to provide information on specific compounds.

However, the usefulness of OVAs is limited to detecting ‘hot spots’ at a contaminated site. OVA cannot be relied on to provide interpretative data because its response is influenced by a number of factors (Robbins 1990a, 1990b) and should be followed by more specific investigative techniques such as portable GCs or by analysis of collected samples by laboratory GC or GC-MS. Limits of detection for PID-based analysers are usually around 1 mg l⁻¹, which is not sufficient to detect most of the target compounds even at the action trigger level. Therefore, during site investigations, when no positive response is obtained by an OVA, samples still need to be analysed by a GC technique.

Portable GCs can be equipped with various detectors. An electron capture detector (ECD) and particularly PID detectors are increasingly being used for soil gas analysis.
Portable GCs are less sophisticated than the laboratory GCs but the latest instruments have improved temperature control and use wide-bore capillary columns which have better separation power than the previously used packed columns. Valid estimates of concentrations of VOCs can be obtained rapidly when measuring only a few specific compounds known to be present at a site. For example, the target chemicals in Group 1 can all be determined in one analysis, under optimized conditions, with adequate limits of detection using a PID detector. (For all but carbon tetrachloride the more practical 10.2eV PID lamp would be sufficient; the higher energy lamp or ECD would be needed to achieve the required limit of detection for carbon tetrachloride). For unknown mixtures of contaminants confirmation by other analytical techniques is usually required.

Portable GCs could provide satisfactory data for a limited number of known contaminants if the type of detector and chromatographic conditions are selected and validated appropriately.

Laboratory grade GCs, even GCs with a mass spectrometric detector or MS-based VOC monitors can be mounted in a van or a mobile field laboratory to provide on-site results of comparable quality to laboratory results. On the other hand there are some drawbacks (Schuring 1989):

1. Delicate equipment can easily be damaged or knocked out of calibration;

2. Running all analysis in the field may tend to slow down the soil gas sampling process; and

3. Capital cost and cost to operate a mobile laboratory are relatively high.

While samples transported in sealed containers can be analysed on standard laboratory GC instruments, thermal desorption/GC equipment is necessary to analyse samples collected in adsorption tubes.

For a site of unknown contamination or where a complex mixture needs to be monitored a GC-MS technique should be involved.
3.3 Soil-pore water samples

Where pipes are to be laid in the saturated zone or when investigation is carried out in water-logged ground the analysis of soil gas is not possible. As discussed in Section 2.2 the sampling of the pore water would be preferable to sampling of soil to obtain better estimates of the amounts of contaminants available for permeation.

A soil-survey inert-suction sampler with a push-fit porous ceramic cup has been described recently (Clark et al 1991) for sampling pore water from the unsaturated zone. As the device was used only for studies on less volatile compounds (pesticides) no information is available on whether significant losses of VOCs would occur when applying the suction vacuum.

There is little practical experience with this type of sampling. In principle pressurised rather then suction samplers should be used and they should be constructed from inert materials such as stainless steel or Teflon.

Normally samples would be collected and taken to a laboratory (mobile on-site or off-site) and analysed by routine GC analytical methods for VOCs using ECD, PID, FID or MS based selective ion monitoring (SIM) detectors.

Though it is possible to use direct aqueous injection into a GC and though most of the chlorinated solvents could be detected at the threshold level with an ECD, most laboratories employ headspace techniques or solvent extraction before GC analysis to isolate and concentrate the determinands. Headspace techniques need specialised equipment but would have an advantage when determining the more volatile compounds such as dichloromethane or vinyl chloride. Solvent extraction would be preferable when the less volatile target compounds such as di- and tri-chlorobenzenes are of interest.

3.4 Soil samples

When soil gas or pore water sampling is not possible, e.g. in the unsaturated zone of compact clay, analysis of soil samples may be the only option to
investigate VOCs in contaminated land. With soil samples it is more difficult to know what the analytical results represent. How good the recovery of the VOCs adsorbed on the soil will be depends on the extraction technique used. (Crathorne and James 1990). Whether the concentration of VOCs available for permeation in soil gas or pore water of the soil sample contributes significantly to the analytical result will depend on the extent of losses during sample handling and on the character of the sample, i.e. factors such as organic matter, moisture content and porosity.

Numerous mechanisms and models have been proposed to describe the behaviour of VOCs in soil and uptake of organic vapours in the unsaturated zone have been proposed (e.g. Baehr 1987, Ong and Lion 1991, Kliest and Fast 1988). However the mechanism is complex and not yet fully understood and, at present, it seems to have little practical value to enable calculations of the amounts of VOCs available for permeation from concentrations in soil.

Analysing soil samples has the advantage in allowing the use of routine sampling techniques probably already employed in site investigation to provide samples for other determinations and standard analytical procedures, such as Soxhlet or solvent extraction followed by gas chromatographic analysis are usually used, though more specialised instruments are needed for techniques such as 'static headspace' or 'gas stripping (purge and trap)' analysis.

3.4.1 Sampling techniques

Sampling procedures could be a source of serious losses of VOCs, particularly when the sample has to be disturbed. Usually samples have to be transported to a laboratory and further processed before analysis. Soil samples often have to be further disturbed, e.g. during sub-sampling or transfer to an extraction vessel, when further losses may occur.

There is a range of methods that can be used for the sampling of soils although their suitability for specific contaminants has not been assessed (de Vera et al 1980).
3.4.2 Sample preservation and transport

Great care must be exercised when sampling soils for VOCs. Heterogeneity of the sample, sample disturbance, headspace volume or the material of the sample container can cause gross differences in analytical results. The following practices have been shown to minimise losses of VOCs:

- Collection of undisturbed samples in Teflon-sealed glass jars;
- Immediate immersion of samples in methanol or the extraction solvent;
- Refrigeration at 4 °C between sampling and analysis;
- Elimination or minimisation of sample headspace in containers;
- Analysis of as large a sample as practicable to avoid analytical bias due to sample heterogeneity;
- Analysis as soon as possible after sample collection.

3.4.3 Analytical techniques

As with water samples the extracts of soil samples can be analysed by standard GC analytical instruments with PID, ECD, FID or SIM detectors or can be submitted to GC-MS identification/confirmation.

Preparation of extracts enables repeat analysis when required or additional analysis, such as GC-MS to be carried out on the same sample. Recoveries of organic compounds in general and VOCs in particular differ depending on sample extraction procedures. Each laboratory therefore needs to validate their methods for the compounds of interest. Validation of analytical methods for soil samples is hindered by the unavailability of representative soil sample of known concentrations of the determinands.

Headspace and 'purge and trap' techniques are particularly suited to the determination of volatile compounds in water but from soil VOCs are recovered usually much less efficiently than by Soxhlet or solvent extraction (Crathorne and James 1990). Only one analysis can be performed on each sample and small samples are analysed which may not be representative of the surrounding soil due to heterogeneity.
Nevertheless a manual, static headspace method in combination with a portable GC when set up on site can be useful for quick screening to identify the extent of the contamination and to help to determine which samples should be taken to the laboratory for further analysis.

4. PROPOSED APPROACH TO SITE INVESTIGATION

4.1 General considerations

Whenever it is suspected that a site intended for development is contaminated, reliable measurement and monitoring are needed to assess the potential effects on the integrity of the material of buried services in general and on the quality of drinking water in the pipes in particular. Results of the assessment should enable suitable pipe materials to be selected or remedial measures recommended where appropriate. It is therefore important that a site being considered for development is investigated thoroughly and comprehensively.

Recommendations for the investigation of potentially contaminated land are given in the ICRCL Guidance Note 59/83 (1987) and, for specific types of sites, in other Notes in the same series (e.g. ICRCL 17/78 for landfill sites and ICRCL 18/79 for gasworks sites). A Code of Practice for the identification of potentially contaminated land and its investigation has been prepared by BSI as a Draft for Development (1988) and provides valuable guidance on the approach to preliminary investigation and site sampling. The Code of Practice also outlines the general principles of sampling and analysis of gases, liquids and soil samples but no details are specified for VOCs. The objective of the approach proposed in this report is to complement and extend the guidance given in the above documents to provide information on the best available techniques for reliable site investigation for potential effects of organic contaminants on buried services.

The proposed approach is shown diagrammatically; in Figure 4.1, which illustrates the main steps and decisions to be taken before conducting sampling and analytical investigation, and in Figure 4.2, where the process of analytical investigation is outlined.
Drinking water mains need to be laid through site

Obtain Information on site history and inspect site (DD175: 1988)

Consider migration from neighbouring sites-hydro-geological investigation

Site contamination possible?

Yes

Contaminant(s) known?

Yes

Listed target compounds?

Yes

Sampling soil gas possible?

Yes

Sampling pore water possible?

Yes

Select appropriate sampling and analytical techniques

Design sampling programme (DD175: 1988)

Conduct sampling and analytical investigations (see Figure 2)

No

Plastic pipes may be used

Possible contamination with complex chemicals?

No

Investigate target chemicals Group 1

Yes

Investigate target chemicals Groups 1 + 2

Likely to permeate?

Yes

Estimate required limit of detection

No

Soil sampling

Figure 4.1 Selection of sampling and analytical methods
Figure 4.2 Procedure for analytical site investigation for VOCs
4.2 Selection of contaminants for analysis

Preliminary site investigation should always be carried out before compounds to be monitored are specified and any sampling planned. The BSI draft Code of Practice (DD 175:1988) sets out objectives and strategy in its Section 3, and, in its Section 4, specifies two main stages of a preliminary investigation, namely the collection and examination of information on the site history and a site reconnaissance or inspection by visiting the site. Sometimes, during the inspection, obvious signs such as oil patches or smells could uncover additional contamination which was not apparent from the site history.

VOCs in Group 1 target chemicals (see Section 2) have been used widely in a range of applications, for example in petroleum products or as cleaning solvents, and should be investigated at all sites unless the site history definitely precludes their presence.

Whenever the site history suggests that the chemicals from Group 2 target chemicals (see Section 2) have been used or when site contamination with complex unspecified organic mixtures is suspected, the investigation should be extended to these compounds.

Note also that evidence of the hydrogeology of the site may indicate migration of contaminants into the site from adjacent or neighbouring contaminated land.

Other organic chemicals with a high potential to permeate plastic pipe should also be included when the investigation of site history identifies them as possible site contaminants. Before specifying sampling and analytical conditions it is, however, necessary to calculate the lowest concentrations of interest and required limits of detection from available information on their maximum acceptable concentrations in drinking water using assumptions and calculations as described in Section 2.4.

This approach is primarily concerned with sites where water supply pipes would be located. However, where plastic pipes (particularly PVC) are to be used for other purposes, any potential gross contamination by VOCs should be investigated as this could cause eventual pipe failure.
4.3 Selection of sampling techniques and analytical methods

The information from the preliminary site investigation should be used to decide whether soil gas analysis is feasible and if not, whether pore water or soil samples should be analysed.

Appropriate analytical methods should be chosen such that the method will detect all the selected contaminants to be measured with adequate limits of detection and accuracy to assure that all the contaminants would be detected, if present, at the threshold trigger concentration. On the other hand, for investigations at sites where high levels of contamination are known to be present, different analytical methods may be needed that are suitable for the expected range of concentrations.

It may be necessary to use a combination of techniques, e.g. samples may have to be analysed under two different GC conditions or two types of GC detectors (e.g. photolization and electron capture) may need to be employed or a concentration technique may be required for some of the determinands, while for the others, direct analysis would be preferable. Methods may also need to be modified, or different methods selected if the analytical results from a preliminary investigation show that the contaminants present, or their concentration levels are different, from those anticipated.

It is therefore important that suitable analytical methods to be used for site investigation should be selected by an experienced analyst. Any concentration step and analytical method to be used should be validated before taking samples from the site. If samples are to be transported off-site, any sample containers/sampling tubes will also need to be validated for the compounds to be determined to prevent unacceptable sample losses and establish safe storage times prior to instrumental analysis.

4.4 Site sampling

There is no single recommended formula for designing a sampling programme. The BSI draft Code of Practice (DD 175:1988) discusses, in its Section 5.4, the
important factors which need to be considered to obtain the optimum design. Consideration should be given to taking samples at intervals over a sufficiently long period of time, under different weather conditions, to enable reliable information to be obtained.

4.5 Investigation of sites where pipes are to be laid in an unsaturated zone

4.5.1 Sampling

Suitable equipment for sampling soil gas consists of: hollow tubes with hardened steel shaft sections, each about 1 metre long, which can be connected to reach the desired depth; a drive point and a gas sampling cap; power driven hammer drill with a masonry bit; and a retrieval jack.

The shaft sections are driven into the ground, the sampling cap is attached and a soil gas sample is withdrawn by means of either a gas tight syringe or a vacuum pump and analysed directly or collected for off-site analysis.

Clays and other fine-grained soils have little air-filled porosity. From a practical standpoint soil gas sampling should not be conducted unless a rate of at least 200 ml per minute of soil gas is obtainable at a vacuum of less than 10 inches of mercury (Schuring 1989).

Field sampling should not be undertaken during, and immediately after, heavy rainfall to avoid sampling in water-logged ground.

4.5.2 On-site analysis

In most cases, on-site analysis using a portable GC is preferable as the first stage of an analytical investigation. Usually the analytical method should be validated for the compounds selected over the concentration range expected (Sections 4.2 and 4.3) but the use of the method may serve a different purpose in different situations. On-site analysis with a portable GC may be used in the following ways:
For relatively uncontaminated sites, a well validated method should be adequate to confirm that threshold concentrations for the selected compounds have not been exceeded.

For sites where only a small number of known VOCs need to be measured, quantitative data could be obtained and used for comparison with the trigger values but representative samples still need to be taken to a laboratory for confirmation. If the presence of interferences or different compounds of interest are detected in the samples and confirmed, the analytical method should be modified, if necessary, validated and site analysis should be repeated.

For sites with unknown or complex mixtures of chemical contaminants, where samples need to be taken to a laboratory for quantitative determination, a portable GC should be used to obtain rapid estimates of the levels of contamination in order to select appropriate volumes of samples for the laboratory analysis.

For heavily contaminated sites the non-specific 'Organic Vapour Analyser' (OVA) technique could be used instead of a portable GC, or in combination with it, for rapid identification of contaminated areas or to locate 'hot spots'.

Good analytical quality control is essential. The instruments should be calibrated in the laboratory and a working concentration range should be established for each determinand. During site investigation, frequent checks should be included to assure the stability of the calibration and retention times of the determinands and that cross-contamination does not occur.

4.5.3 Sample collection and transfer

Glass bulbs or metal canisters could be used when a small number of samples is being collected or when techniques for the desorption of gas adsorption tubes are not available. Direct gas analysis require only small volumes of sample gas (<1 ml), but to minimise possible errors due to leaking seals, sample volumes of several hundreds millilitres are usually collected. Adequate
flushing between samples must be ensured to prevent cross-contamination. Samples have to be analysed within an established period of stability (usually only a few hours) and each container should be checked whether it is gas tight (Bishop et al 1990).

When transferring larger numbers of samples or for GC-MS identification, adsorption of the VOCs on an adsorbent (usually Tenax) is preferable. To collect a sample, a known volume of the soil gas is passed through a tube filled with the adsorbent and the tube capped. The actual volume is governed by the target compounds to be measured and the performance of the selected analytical method, as assessed initially in the laboratory. When the level of contamination is not known it may be necessary to sample several tubes with different volumes of sample gas to assure that a sample within the working range of the analytical method is collected. Alternately, the level of contamination could be estimated on-site, as described above (Section 4.5.2). Adsorbed samples can be stored longer than gas samples, particularly when stored in a refrigerator or a freezer. Before sampling, the tubes should be purified by heating and capped to prevent analytical interferences from contaminants in the surrounding atmosphere.

For the determination of known compounds, the recovery from the adsorbent should be determined for each compound and breakthrough volumes of samples should be established. For soil samples containing an unknown mixture of VOCs for GC-MS identification, conditions of sample collection and desorption should be selected such that the widest possible range of compounds could be detected.

4.5.4 Laboratory analysis

Laboratory analysis may be required in the following situations:

- when concentration of the sample is necessary to achieve the required limit of detection;

- to confirm the analytical results obtained on-site, using either a laboratory GC operated under different GC conditions or by GC-MS;

- to identify unknown compounds in samples by GC-MS.
Most or all of the analytical instruments for the above analysis could also be operated on site in a mobile laboratory.

4.5.5 Confirmation analysis

Unless there is no concern about either the identity of the determinand or determinands or the possibility of interferences from other compounds can be excluded, 'confirmation analysis' should always be carried out to obtain a positive identification of the detected substance.

How many samples from a site should be taken for confirmation should be an informed judgement. For example, from a relatively small area where a consistent pattern of results has been observed, a few samples should suffice; more samples should be taken from larger sites, when the pattern of results is inconsistent or where quality control checks indicate instability in the GC system.

Where other compounds, apart from the selected determinands, are detected, samples should also be taken for GC-MS analysis to identify the unknowns.

4.6 Sites where pipes are to be laid in the saturated zone or water-logged ground

4.6.1 Sampling

Sampling of groundwaters for the determination of VOCs and other organic chemicals is well established and is used routinely. Any of the sampling techniques found suitable could also be used for site investigation (Hatayama 1986, van Oosterom et al 1988, Rivett et al 1990, Schalla et al 1988).
4.6.2 On-site analysis

When rapid results are needed during a preliminary investigation to locate contaminated areas of a particular site and to estimate levels of contamination, water samples could be analysed on-site by a field headspace technique combined with a portable GC or the samples could be extracted with a small volume of organic solvent and the extract analysed by a portable GC. However such analyses are more time consuming and the results are likely to be less accurate than those from on-line analysis of soil gas samples, because of the necessity to include a separation technique. Samples for headspace analysis have to be stabilised at a certain temperature before a portion of the vapour is analysed. In field conditions, accurate temperature control is difficult.

4.6.3 Sample collection and transport

A glass sampling vessel should be filled completely with the sample, leaving no headspace, and sealed with a glass stopper or a PTFE-lined screw cap. The actual volume is governed by the target compounds to be measured and the performance of the selected analytical method, as assessed initially in the laboratory. Usually sample volumes of 25 - 100 ml should be sufficient to detect the proposed threshold trigger concentrations for all the target compounds.

Samples should be kept cool, preferably refrigerated at 4 °C (in a fridge free of organic solvents) and analysed the same or, at the latest, the following day.

Compared to soil gas analysis, laboratory quantitative analysis of water samples is generally preferable to on-site analysis because it is easier to prevent significant losses of the determinands during transport and storage, the results should be more accurate and the overall analytical time is probably shorter in the laboratory particularly when employing automated instruments.
4.6.4 Analysis

Any analytical method set up in a laboratory for the determination of VOCs could be used provided it has been validated for the compounds to be measured at the site and is suitable for the concentration range expected to be found in the pore water samples. Many routine methods for the determination of chlorinated solvents in drinking water or groundwater may have to be modified (e.g. reduced sample volumes or concentration factors) because they are normally set up to determine concentrations well below the proposed threshold concentrations.

4.6.5 Confirmation analysis

Confirmation of the results by re-analysing the samples under different GC conditions or by GC-MS should also follow, as for soil gas samples.

4.7 Site investigation using the analysis of soil samples

4.7.1 Sampling

The analysis of soil samples is usually the least suitable method for estimating the concentration of VOCs 'available' for permeation of buried plastic pipes. However soil samples may be analysed in the following situations:

- when pipes are to be laid in the unsaturated zone of fine grained soil such as clays, where sampling soil gas or pore water is not feasible;

- at sites where pipes are to be laid in the saturated zone or water-logged ground the analysis of soil samples would be a suitable alternative to water analysis for the mapping of areas of contamination;
at sites where plastic pipes are to be laid (but not for the
distribution of drinking water) to detect any gross contamination
which could affect the integrity of the pipe material; such
contamination would usually be detected equally well by analysing
either soil gas, water or soil.

A number of established soil sampling techniques could be used provided that
the precautions listed in Section 3.4.2 are adhered to.

4.7.2 Analysis

As for water samples, when rapid results during a preliminary investigation are
needed to locate contaminated areas or to estimate levels of the contaminants,
a static headspace technique or a simple solvent extraction should be used on
site and the vapours or the extract analysed by portable GC.

When conducting a full site investigation to obtain quantitative data, soil
samples should be taken to a laboratory to be analysed by more reliable
methods.

Confirmation analysis, as well as GC-MS identification of any other compounds
detected in the samples and which would be likely to permeate plastic pipes,
should be carried out as for soil gas and water samples.

4.8 Interpretation of the results

The measured concentration of the contaminants detected at the site should be
compared with the proposed trigger values.

For heavily contaminated sites, where the action trigger values are frequently
exceeded, results from the preliminary investigation may provide sufficient
evidence to decide what action, e.g. remedial measures, should be taken.
After a full investigation, various patterns of results could be obtained which would require different decisions. The following steps should be considered according to the outcome of the investigation:

<table>
<thead>
<tr>
<th>Outcome of investigation</th>
<th>Steps to be taken</th>
</tr>
</thead>
<tbody>
<tr>
<td>o No compounds likely to permeate were detected above threshold trigger values</td>
<td>Plastic pipes from any material suitable for contact with drinking water can be used - any contamination present is unlikely to affect drinking water quality.</td>
</tr>
<tr>
<td>o Concentrations of one or more compounds exceeded threshold trigger values but all were below the action values.</td>
<td>PVC pipes can be used. Before PE or other permeable pipes could be considered at least one of the following should be performed:</td>
</tr>
<tr>
<td></td>
<td>(i) the contaminated areas should be monitored over a period of time to determine any significant variations in the concentrations with temperature and to detect any decreasing or increasing trends, or (ii) a trial pipe should be buried in the contaminated area, filled periodically with water and the water should be monitored for permeation of the contaminants, or (iii) appropriate remedial measures should be taken, especially if time is important.</td>
</tr>
<tr>
<td>o Concentrations in most of the samples were below the action trigger value but in a few samples one or more compounds exceeded action values.</td>
<td>More samples should be taken in the vicinity of the contaminated sampling point and analysed to locate the area where remedial measures should be taken.</td>
</tr>
<tr>
<td>o Concentrations of one or more compounds frequently exceeded the action trigger values.</td>
<td>Plastic pipes should not be used unless appropriate remedial measures are taken.</td>
</tr>
</tbody>
</table>

The safest way to protect drinking water services at sites where VOCs have been detected is to use pipes from impervious material such as metals or cementitious materials (provided that other forms of contamination do not rule this out). Usually, PVC pipes can be safely used in trenches infilled with clean backfill. When plastic pipes are still to be used after remedial measures have been implemented, follow up sampling and analysis of the area should be undertaken to monitor the success of the measures.
5. DISCUSSION

5.1 Scope and limitations of the proposed procedures

The aim of the proposed approach is to assess the degree of contamination at a site with respect to the potential for adversely affecting drinking water quality if plastic pipes were used for drinking water distribution. The possibility of using mathematical models has been considered, in order to be able to make decisions more appropriate to each particular situation; such as for different plastic materials, for specific pipe dimensions, for individual contaminants and specific levels of contamination, or for a range of soil conditions. However, at present, the relationships between the many factors involved and their possible effects are still not sufficiently understood to allow reliable predictions. A more pragmatic approach has therefore been adopted, which is based on three important factors:

- the use of threshold and action trigger values;
- analytical methods validated for contaminants selected on the basis of information on the site history; and
- the estimation of the concentration of the contaminants which is available for permeation.

These are discussed in more detail in the following sub-sections.

5.1.1 Trigger values

In theory many compounds could permeate plastic pipes laid in contaminated soil, but only volatile, relatively non-polar compounds are likely to pose problems in practice. Even so, the number of compounds with a high potential to permeate is extensive. For practical reasons, trigger values were therefore calculated only for those compounds which have previously been detected in contaminated land or in the underlying groundwater and which are either widely used (Group 1 target compounds) or which are used more locally but in
relatively high quantities (Group 2 target compounds). Nevertheless, according to the proposed approach, maximum acceptable concentrations in drinking water should be established and trigger values calculated for other, similar, compounds whenever the site history or any analytical investigations undertaken indicate their presence.

The calculations used to arrive at proposed trigger values assumes more or less the 'worst case' conditions for most of the factors affecting the possible concentration of the contaminant in drinking water, i.e. a readily permeable material (PE), a narrow pipe, full immersion of the pipe in the vapour or water phases (from which the permeation takes place), and an eight-hour stagnation time for water in the pipe. Such a worst-case calculation should give a safety factor which will allow for variations due to inaccuracies in the estimation of the permeation potential, analytical errors and temporal variations in contaminant concentrations.

5.1.2 Analytical methods

Rather then to propose a list of VOCs which should be investigated at all sites, the approach recommended is based on using analytical methods validated for compounds selected at each site in accordance with information available on the site history. Only when there is insufficient information on the identity of the compounds likely to be present, should analytical methods capable of detecting all the target compounds be used (either Group 1 compounds alone or together with Group 2 compounds).

In practice, in many cases, there may not be much difference between the methods for the determination of site-related VOCs and those for the set determinands (e.g. Groups 1 and 2). However, the more flexible approach allows the use of simpler and quicker methods where only one or a small number of contaminants is thought to be present. At the same time the approach covers the investigation, where appropriate, of contaminants for which special analytical methods have to be used and includes unsuspected contaminants with high permeation potential.
The proposed approach cannot guarantee the detection of all significant VOCs at all sites. For example, when a compound requiring special analytical conditions (e.g. vinyl chloride) is present where only Group 1 target compounds would be monitored. It should, however, cover most situations at a reasonable cost and effort.

5.1.3 Contaminants 'available' for permeation

Permeation takes place from a liquid or a vapour phase in contact with the surface of the plastic pipe. Since, in most cases, pipes will be in contact with the vapour phase of the unsaturated zone the primary proposed method of site investigation is the direct measurement of soil gas concentration. The concentration determined should then be a reasonable estimate of the concentration available for permeation. The validity of this assumption will depend on how representative the sample analysed is of the concentration in the surrounding area over an extended period. Compared to other sampling techniques, soil gas sampling is rapid and inexpensive and when combined with an on-line portable GC, more measurements can be obtained from a larger number of sampling points and from more than one depth.

An alternative approach would be to utilise the potential advantage of passive sampling which provides an integrated measure of VOCs over a period of time. However the practical aspects of routine passive sampling still need development and the relationship between the concentrations measured and the potential for permeation have not yet been established.

When pipes are to be laid in the saturated zone, we propose sampling the pore water. While for sampling soil gas relatively simple equipment is available, equipment for groundwater sampling is fairly complex and expensive because it has been developed for sampling at much greater depths than is required for investigations relating to buried services. Simpler equipment, which would be sufficient for sampling in this context, needs to be developed specifically for this purpose.
The concentration of a contaminant determined in a soil sample is not a direct measurement of the amount available for permeation, as different proportions of the contaminant will be bound to the solids, adsorbed by the organic matter and dissolved in the liquid phase, i.e. the associated moisture. How much of the total will be available for permeation will depend on many factors such as the type of the soil, the presence of natural organic material, soil temperature etc. Moreover, the concentration measured may not represent the total concentration in the soil because many separation techniques recover only part of the VOCs and it is difficult to establish what the recoveries are. Soil samples should therefore be used only when direct measurement in soil gas or pore water is not possible or, when it is convenient for practical purposes, to locate areas of contamination.

5.2 Remedial measures to protect buried services

Suitable remedial measures to protect buried services were assessed by WRC under a previous DOE contract (ER 319E 1988). The outcome of a questionnaire sent to water undertakers was summarised by Crathorne and James (1990) and a report was prepared (ER 319E 1988) which outlined several options for pipeline installations in contaminated land.

A follow-up investigation has been conducted under this contract to find out what remedial/protection measures are used in practice, how such decisions are made and whether the measures adopted are successful. The Water companies which indicated in the previous questionnaire that they were planning to lay pipes at redeveloped sites were contacted.

Of the 16 Water companies contacted, 15 have been installing pipes in redeveloped sites of different types (disused gas or chemical works, landfills, mine workings, etc). The source of information on previous use of a particular site was usually 'local knowledge' or the developer or the local planning authority. The site survey for soil contaminants was generally carried out by independent consultants on behalf of the developer, and in some cases the results were passed to the water undertaker and Environmental Health Office for comment.
As far as we could find out, the presence of VOCs was not investigated at any of the sites. In most cases metal pipes have been used both for mains and service pipes (ductile iron mains and copper service pipes). It would therefore appear that protective measures against permeation are being implemented even when there are no analytical results to indicate that permeation would be likely to occur.

Metal pipe protection against corrosion consisted of loose PE sleeving for the mains and shrink wrapped PE for copper pipes, with taped joint and service connections. The pipes were laid in trenches infilled with clean backfill. In addition some water undertakers lined the trench with PE sheeting and installed drainage.

After completion none of the water undertakers monitored either water quality in the pipes (except as part of the normal routine random sampling) or inspected the pipe material. It is not considered likely that, where several levels of protective measures have been taken, any effects on water quality or material integrity would be observed, at least in a short term.

PVC pipes have been used for mains installations on several occasions, noticeably at disused gas works where metal pipes failed due to corrosion.

PE pipes, usually service pipes, have been laid at only three sites, which were not expected to be polluted by compounds able to permeate PE. Nevertheless, from the information available it is not clear whether the possibility of such contamination could be excluded. No taste and odour problems in the drinking water have been reported but the water is not monitored to ensure that no VOCs would be present at concentrations above maximum acceptable levels. It is important to note that some VOCs such as benzene or dichloromethane, could exceed acceptable levels but not be detectable by taste and odour of the drinking water.

Several guidelines for pipe installation in contaminated land were used. The most common source of information was from pipe manufacturers, followed by the ICRCL Guidance Notes, WRC Reports and ‘in house’ knowledge.
PVC is relatively impervious to permeation. Placing the pipes in a clean in-fill would avoid contact with any gross contamination (except where subsequent accidental spillages would occur) which could cause swelling, increase permeation and, eventually, pipe failure. In practice, incidents involving PVC, where drinking water taste and odour problems or pipe failure are caused by organic contaminants in soil do happen (Crathorne and James 1990). In a recent paper from the USA (Holsen et al 1991) PVC pipes were implicated in 15% of the reported incidents. However, all of the incidents were associated with gross contamination in the area surrounding the pipe, which was caused primarily by accidental spills.

When PE pipes are to be used, appropriate site investigation should be conducted even if the possibility of contamination by VOCs is not obvious.

A list of sites where remedial measures have been undertaken to protect buried services is given in Appendix B.

5.3 Future work

The work on this contract has revealed several areas where more information is required or where improvements would have long term benefits, in particular the following:

- Vinyl chloride and dichloromethane have been included in Group 2 of the target compounds because, in other countries, they were amongst compounds frequently detected in groundwaters below contaminated sites. In California both have to be monitored at landfill sites (Kirshen and Almasi 1991). We are not aware of any investigation of their occurrence in the UK. Using routine methods for monitoring volatile chlorinated compounds in groundwaters would probably not detect either vinyl chloride or dichloromethane (except, possibly, at high concentrations), because of their rapid elution from GC columns and because both ECD and PID are relatively insensitive to both compounds. They can, however, be determined with modified analytical methods.
Both compounds are expected to permeate PE easily and acceptable concentrations in drinking water, based on recent toxicity data, are well below their taste and odour threshold values. Vinyl chloride (a suspected carcinogen) and dichloromethane are also reported to be breakdown products of the commonly occurring tetra- and trichloroethenes, respectively. More information is therefore needed on their occurrence so that consideration can be given as to whether they should be included in Group 1 target compounds.

Passive sampling appears to be a promising approach to obtain reliable estimates of the amounts of VOCs available for permeation. In this technique, a manifold containing an adsorbent sampler is buried in the ground, then recovered after a period of time and the adsorbed VOCs determined. This gives an integrated measure of the contamination over a period of time in very similar conditions to those which a pipe would experience. However, before such a technique could be recommended a suitable manifold and a sampler need to be developed and validated. In addition, the relationship would have to be established between the amount of the contaminant adsorbed, its potential to permeate plastic pipes and the resultant concentration in drinking water inside the pipe.

A simple device for sampling 25 to 100 ml of water for the determination of VOCs in the saturated zone or water-logged ground at a depth of about two meters should be developed and validated to allow rapid investigation at sites where pipe surface would be mainly in contact with water.

It is relatively simple to determine, with the required sensitivity, the target compounds from the proposed Group 1. However, to include also all the target compounds from Group 2 may pose considerable analytical, technical or financial difficulties to some laboratories. Assessment and testing of suitable analytical conditions would, therefore, be desirable to be able to recommend an optimal analytical method, particularly for on-site determinations.
A technique for the on-site investigation of contaminated land, involving soil gas sampling and analysis by portable GC, has been investigated and has shown considerable potential (see Appendix A for details). Further work is needed to fully evaluate this technique and, in particular, assess the usefulness of the newer instruments now available.

Assessment of the techniques recommended in this report in relation to investigating potential effects of soil contaminants on groundwater quality would be worthwhile.

6. CONCLUSIONS AND RECOMMENDATIONS

1. Two groups of volatile organic chemicals are proposed for monitoring contaminated land in relation to potential effects on buried water pipes. These chemicals were selected on the basis of their ability to permeate plastic pipes, occurrence in contaminated soil and their scale of use.

2. Trigger concentrations with respect to protection of water supplies from permeation through pipe walls of buried services ('threshold' and 'action' levels) are proposed for the target chemicals selected, with appropriate values calculated for soil gas, pore water and soil samples.

3. The sampling and analysis of soil gas is recommended as the most appropriate approach in most circumstances (but not in water-logged ground or in saturated zone) for predicting whether soil contaminants could permeate plastic water pipes and contaminate the drinking water supply.

4. Where pipes are to be laid below the water table or where the site is subject to frequent waterlogging, it is recommended that the soil pore water is sampled and analysed. Only where neither soil gas nor soil water samples can be taken, should the analysis of soil samples be employed.
5. A systematic approach has been proposed to the investigation of a site for possible contamination by VOCs. This approach should be adopted whenever the installation of vulnerable plastic pipes, such as polyethylene, is considered for the distribution of drinking water.

6. At each site the VOCs to be determined should be chosen in accordance with information on the site history and appropriate analytical methods should be selected and validated by an experienced analyst.

7. In practice, contamination of water supplies by permeation into distribution pipework from redeveloped sites does not appear to pose a major problem at present. To be on the safe side Water companies tend to use metal pipes (for both mains and service pipes) laid in clean in-fill at any site where contamination is suspected. Previous WRC reports to the DOE, as well as more recent papers from the USA, concluded that taste and odour problems resulting from permeation through pipe walls were usually caused by accidental spillage of chemicals in the vicinity of the pipe.

8. Some compounds, such as benzene, vinyl chloride and dichloromethane, could reach unacceptable levels in drinking waters well before they would be detected by taste and odour. Their presence would not be recognised unless appropriate monitoring was implemented. More information on the occurrence and levels of such compounds should be gathered.

9. For the sampling of soil gas, a grab sampling technique has been recommended. Passive sampling, a technique where a sampling device is buried for an extended time under similar conditions as those for the proposed pipes, may be a useful alternative or even more appropriate than grab sampling. A suitable passive sampling technique needs to be developed and tested in the field.

10. It is possible to determine all the target compounds using a combination of analytical methods which have adequate limits of detection. It would, however, be beneficial to assess the most suitable analytical
conditions and recommend an optimised method for on-site analysis. Soil gas sampling and analysis by a portable GC has shown promise in this context (see Appendix A). It is recommended that further work is carried out to evaluate this technique for the investigation of contaminated land.

11. The same (or similar) approach to that recommended for investigating sites with respect to effects on water pipes could also be useful for general survey work on contaminated sites. For example, when assessing possible effects of contaminated sites on the quality of underlying groundwater.
REFERENCES


APPENDIX A - STUDIES OF AN ON-SITE TECHNIQUE FOR ANALYSIS OF SOIL GAS AND SOIL ANALYSIS

A1. INTRODUCTION

Until recently, the analysis of soil or water samples were considered to be the principal means for the investigation of contaminated soil in relation to permeation of plastic pipes by VOCs into water supplies, because suitable techniques for soil gas analysis were not available (Veenendaal et al 1986, Crathorne and James 1990). A literature review, undertaken under this contract, revealed however, that equipment and procedures for soil gas measurement were being developed, particularly in the USA, primarily to map areas of land contaminated with volatile chemicals, and to use results as indicators of potential groundwater pollution.

It was therefore decided to test equipment for soil gas sampling and analysis in the laboratory and under field conditions, to assess its scope and limitations. It was originally intended to carry out tests at a number of contaminated sites and to set up field experiments providing data from which to study the relationship between the measured concentration in soil gas and permeation through PE pipes into water. However, finding suitable sites where such tests could be undertaken proved difficult, and it was possible to visit only two contaminated sites.

For both, the laboratory and field work, a portable gas chromatograph (GC), specifically designed for soil gas and air analysis for volatile organic compounds, was hired. The model used was one of the instruments routinely used in the USA for the investigation of contaminated land.

For comparison with the results from soil gas analysis, a few soil samples were collected at the two sites, taken to the laboratory, extracted with an organic solvent and analysed by GC-MS, in accordance with the previously recommended procedure (Crathorne and James 1990).

The following sections describe the compounds investigated, the equipment used and analytical conditions employed, the conditions at the test sites and the results obtained.
A2. LABORATORY TESTS

A2.1 Compounds investigated

All of the proposed target chemicals in Group 1, except p-xylene, were analysed by a portable GC in the laboratory. In addition, two proposed target chemicals from Group 2 were included. Therefore the following chemicals were investigated:

Benzene
Toluene
m- and o-Xylene
Chlorobenzene (ClBz)
Dichloromethane (DCM) - Group 2
Carbon tetrachloride (CCl4)
1,1,1-Trichloroethane (1,1,1-TCEA) - Group 2
Trichloroethene (TCE)
Tetrachloroethene (PCE)

Chlorobenzene and trichloroethene, two compounds which were found on the contaminated sites visited, were investigated in more detail.

A2.2 The portable GC and analytical conditions used

The GC was small and, consequently, readily portable. For on-site operation a small external battery pack provided power for the column heater. Chromatography was performed on a wide-bore CPSil™5CB\(^1\) capillary column (10 m x 0.53 mm i.d.) in a precolumn/backflush configuration with 1 m precolumn and 9 m analytical column. The column is encapsulated in epoxy resin to provide good thermal conduction and protection during transportation. Three settings are available on the column heater, providing temperatures of 30 ± 1 °C (used for our experiments) with 40 and 50 °C also available for the determination of less volatile compounds.

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1. CPSil™5CB is Trademark of Chrompack
The GC was fitted with solenoid valves to control the flow of gas through the sample loop, pre-column and analytical column in accordance with a program entered into a memory via keyboard.

In standby mode, carrier gas enters the system at a 'tee' between the analytical column and pre-column. The gas flows through the analytical column and backflushes the pre-column. At the start of an analysis a built-in pump draws sample gas into a sample loop (1000 μl) via a sample probe. The time the pump operates can be adjusted to allow for different sampling times. When the pump is switched off, carrier gas flushes the contents of the sample loop into the pre-column and carrier gas flow to the 'tee' between the columns is stopped. The volume of carrier gas flushing the sample loop is controlled through the solenoid valves so that only a desired portion of the sample loop volume enters the pre-column, after which, carrier gas by-passes the sample loop and flows through the pre-column onto the analytical column. In this way the actual volume of sample gas entering the analytical column can be controlled. The pre-column affords a preliminary separation of the sample such that the more volatile chemicals are generally the first to pass onto the analytical column. After a predetermined time, when all the compounds of interest have eluted from the pre-column, the carrier gas is switched to flow back into the 'tee' backflushing remaining compounds out of the pre-column. This procedure reduces the time required for analysis since less volatile compounds not of interest, are not transferred to the analytical column.

The GC was fitted with a photoionization detector (PID) operating at 10.6 eV. Carrier gas (nitrogen) was contained in a small pressurised cylinder within the GC. The cylinder contained sufficient gas for one day's work before needing to be refilled. Flow rates between 5 and 10 ml min⁻¹ were used for the analyses.

Chromatograms of separated compounds with retention times and peak areas are presented on a paper strip from the built-in printer. Identification of the peaks and determination of concentrations can be obtained when calibration values are entered into a built-in microprocessor, either manually or during a calibration run. The times the solenoid valves are actuated are controlled through the microprocessor and are determined by the operator. The GC also has the facility for manual injections using a gas tight syringe.
A2.3 Separation

On the column tested, it was possible to separate 7 of the 10 compounds investigated. Benzene could not be separated from carbon tetrachloride nor trichloroethene from 1,1,1-trichloroethane. Dichloromethane was retained very little under these conditions and therefore it would be difficult to distinguish DCM from other non-retained volatile substances. Relative retention times for the compounds of interest are given in Table A1. A typical chromatogram is shown in Figure A1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>RT*</th>
<th>Limit of detection µg l⁻¹</th>
<th>Ionization potential eV</th>
<th>Relative response to benzene (peak heights)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichloromethane</td>
<td>0.1</td>
<td>&lt;100</td>
<td>11.35</td>
<td>0.1</td>
</tr>
<tr>
<td>Benzene</td>
<td>1</td>
<td>&lt;5</td>
<td>9.25</td>
<td>1</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
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<td>&lt;500</td>
<td>11.28</td>
<td>0.01</td>
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<td>Trichloroethene</td>
<td>1.4</td>
<td>&lt;5</td>
<td>9.45</td>
<td>1</td>
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<tr>
<td>1,1,1-Trichloroethane</td>
<td>1.4</td>
<td>&lt;500</td>
<td>11.25</td>
<td>0.03</td>
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<td>Toluene</td>
<td>2.4</td>
<td>&lt;5</td>
<td>8.82</td>
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<td>6.9</td>
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</table>

* RT retention time relative to that for benzene (2.1 min at 30 °C, flow rate of 5 ml min⁻¹ of nitrogen)

A2.4 Calibration

The built-in calibration method of the instrument tested was based on one-point calibration. Detector response to the two compounds analysed over a wide range of concentrations (chlorobenzene and trichloroethene) was reasonably linear, provided that the sensitivity of the instrument was adjusted, so that the peak of interest was within the scale of the printer. Peak areas calculated by the microprocessor for off-scale peaks were found to give large errors.
Calibration samples were prepared by injecting calculated amounts of the determinands into 1-litre and 5-litre sealed glass bottles. Initially the samples were prepared in laboratory air but that was found to contain some impurities giving rise to high baseline levels. Since sufficiently purified air was not readily available, the calibration standards were then prepared in nitrogen containing less than 0.1 ppm hydrocarbons. The standards were prepared fresh on each day of analysis.

Three calibration standards were prepared containing 20, 10 and 5 µg l\(^{-1}\) of benzene, toluene, o-xylene, ClBz, TCE and PCE and 100, 50 and 25 µg l\(^{-1}\) DCM, respectively. These standards were analysed to estimate the limits of detection. Distinct peaks of benzene, toluene, ClBz, TCE and PCE were detected in the most diluted (5 µg l\(^{-1}\)) standard. A visible peak of DCM was obtained for the standard containing 100 µg l\(^{-1}\).

For other compounds the limit of detection was estimated from the response relative to that of benzene. The estimated limits of detection and the relative response values are given in Table A1.

The manufacturer recommends as the carrier gas, zero grade air rather than nitrogen or helium, the preferred gases for standard laboratory GC instruments. Nitrogen containing less than 0.1 ppm hydrocarbons was used for all our experimental work because zero grade air was not readily available. However this caused some difficulties when analysing large samples of air (up to 1000 µl) as the baseline was disturbed where the air gas was introduced into the nitrogen carrier gas, resulting in incorrect assignment of peak areas by the microprocessor at high sensitivity. It was, therefore, often necessary to measure peak heights manually.

A3. **FIELD TESTS**

A3.1 **Test sites**

Two contaminated sites suitable for the evaluation of assessment techniques were found. These were an industrial site and a gravel pit infilled with domestic and industrial waste.
Site W

The industrial site was used for plastics research and development for over 50 years. Prior to the work carried out in this contract, a survey of an adjacent site had showed the presence of chlorinated hydrocarbons in the groundwater. Further investigations, carried out to determine the source and extent of the groundwater contamination showed that both sites were contaminated with chlorinated hydrocarbons and an area of the industrial site was also found to be heavily contaminated with chlorobenzene.

The site had been cleared of buildings and rubble, and consisted of open waste ground overgrown with grass and weeds. The foundations of some buildings could still be seen. The area had about 10 metres depth of made ground and gravel on chalk; the level of ground water was at a depth of about 25 metres. Access to the site was permitted before the site was 'cleaned-up' prior to redevelopment. Information about the site, including locations of trial boreholes and pits and concentrations of chemicals found was provided by the owners.

Site D

The second site was a former gravel pit, infilled with industrial and domestic waste of unknown origin. A survey of the site showed the presence of boron, phenols and toluene extractables (possibly hydrocarbons from diesel or oil). The site was overgrown with vegetation and saplings. The site included a small pond, a gravelled car park and a small stream flowed along the boundary on one site. Below the level of the infill there was gravel over chalk with the water table at a depth of, typically about 0.6 metres. However, at the time of sampling it was significantly lower.

A3.2 Soil gas samples

For field studies, the portable GC described in Section A2 was used. The GC in combination with a commercially available soil gas sampler enabled soil gas analysis to be carried out on site.
Using an electric rotary hammer drill (powered by a portable 110V petrol generator) a pilot hole, diameter 25 mm and about 400 mm deep, was drilled into the soil. Into the pilot hole was inserted a gas sample probe (slotted well screen), to which was attached a hollow rod (diameter 15 mm, length 1000 mm). Using the electric drill the rod was driven into the soil to the required depth. If sampling was required at a greater depth a second rod was attached. Inert teflon tubing connected the exposed end of the rod to the portable GC. The soil gas was collected using the sampling pump built into the GC. The length of time required to purge the rods and so obtain a representative soil gas sample was determined during the laboratory experiments.

At Site W samples were analysed on 5 September 1991. Four test holes were drilled and concentrations measured at two depths in each hole, ie, at 0.8 and 1.4 m (one rod and two rods). Two test holes (1 and 2) were drilled within the zone recognised to be contaminated with chlorobenzene, the third (test hole 3) was just outside the zone and the fourth (test hole 4) was outside the site, approximately 20 m away from the recognised contaminated zone.

At test hole 1 only one distinct peak was detected, the retention time of which corresponded to that of ClBz. In test hole 2, a second, earlier eluting peak was detected, which was identified, from its retention time, as TCE (see Figure A2). Surprisingly, samples from the third and even the fourth test hole also contained both ClBz and TCE. To check that significant carry over of the determinands did not occur from sample to sample, samples of air were taken through the sampling rod in between sampling from test holes. A small background concentration of ClBz was detected in the 'blank' samples; this was then subtracted from the concentrations found in the test holes. A non-retained peak, detected in some of the samples, was thought to be DCM but it could be another highly volatile compound. The location of the test holes and concentrations of ClBz and TCE measured during the visit are shown in Figure A3.

During the second sampling visit to Site W, in October, the GC was contaminated by very high levels of ClBz present in the first soil gas sample and it was not possible to purge the instrument sufficiently during the visit to allow any further measurements. In addition, this visit took place during wet weather, and consequently sampling of soil gas was difficult due to water-logged ground.
Site D was visited once (9 October 1991) when two test holes were drilled for soil gas measurements at two depths in each hole. Both test holes were located approximately 6 m away from the stream, one near the pond and the other close to the car park.

At both test holes a non-retained, early eluting peak (possibly DCM) and one retained peak were detected on the chromatograms. From its retention time the retained peak was identified as TCE. In the test hole 1 the estimated concentration of TCE was 0.4 mg l\(^{-1}\) at a depth of 0.8 m, and approximately 0.1 mg l\(^{-1}\) at a depth of 1.4 m. In the second test hole no TCE was detected (< 0.05 mg l\(^{-1}\)) at the 0.8 m depth but a concentration of 0.1 mg l\(^{-1}\) was measured at the greater depth of 1.4 m.

A3.3 Soil samples

Soil samples were obtained using a soil sampler. The gas sample probe was replaced with a reamer which was driven into the gas sampling hole (to enlarge the diameter of the hole) to the required depth. The reamer was replaced with the soil sampler, a hollow tube into which was inserted a PETG copolyester liner, which was pushed into the soil to the reamed depth. Pushing the sampler further resulted in collecting a soil sample in the PETG tube. The sampler was withdrawn from the hole and the PETG tube removed and capped. Coloured caps were used to indicate the top and bottom of the collected sample. The capped PETG tubes were stored in a cool box on site until returned to the laboratory and stored in a freezer. Before extraction a weighed portion (~20 g) of the soil sample was dried by mixing with an equal portion of anhydrous sodium sulphate. The mixed material was transferred to a prewashed Soxhlet thimble and extracted in a Soxhlet apparatus for about 3 hours with pentane (100 ml). To the cooled extract was added deuterated internal standards (used for providing quantitative information) and the extract concentrated in a Junk vessel, fitted with a micro Snyder column, to a final volume of about 3 ml. The extracts were further concentrated to 100 µl and examined by gas chromatography-mass spectrometry (GC-MS). Analysis of 1 µl of the extract should provide a limit of detection of around 50 µg kg\(^{-1}\).
GC-MS conditions:

- column: 60 m DB-1
- detector: VG 7070 mass spectrometer operated in electron impact mode and linked to a VG11-259 J data system
- injector: on-column injector SGE OCI-2
- injector temp.: 20 °C
- carrier gas: helium, flow rate 1 ml min⁻¹
- column programme: initial 30 °C held for 4 minutes, 8 °C/min to final temperature 300 °C

Samples were initially examined by GC-FID under very similar chromatographic conditions to determine which should be analysed by GC-MS. Two representative samples from Site W (corresponding to test holes 1 and 2 for soil gas samples, taken at a depth of approximately 1.5 m) and one from Site D (test hole 2, depth 0.9 m) were then submitted for GC-MS analysis.

Sample W test hole 1 was found to contain chlorobenzene but Sample W test hole 2 and the sample from Site D did not. No TCE was identified in any of the samples, but small concentrations of toluene and relatively larger concentrations of benzene and cyclohexane were detected in all three samples. The estimated concentrations (approximate) are given in Table A2.

<table>
<thead>
<tr>
<th>Table A2</th>
<th>Concentrations of VOCs in soil samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
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</tr>
<tr>
<td>W</td>
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</tr>
<tr>
<td>W</td>
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</tr>
<tr>
<td>n</td>
<td>2</td>
</tr>
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</table>
A4. DISCUSSION

The GC instrument hired for the tests was specifically designed for field
determination of volatile compounds in gas samples (soil gas or air). Other
similar portable instruments are now also commercially available. Most of them
also utilise a column back-flushing system and are equipped with a
photoionization detector and dedicated data handling. They, however, vary in
the way the back-flushing system is set up and operated; some can accommodate
other detectors and the data handling systems offer different degrees of
sophistication. Consequently, some of the problems encountered with the tested
instrument may not occur when using some of the others GCs, in particular the
contamination of the instrument by samples with high concentration of the
determinands or problems with peak quantification when using nitrogen as a
carrier gas.

With the column provided, it was possible to separate most of the proposed
Group 1 target chemicals, except benzene and CCl4, which coeluted. However, it
may be difficult to find operational conditions for portable GCs under which
all the target compounds from Groups 1 and 2 could be separated, though it may
be possible using a column of different polarity and more flexible temperature
control, available with some of the more recent models.

The estimated limits of detection for the Group 1 compounds, except CCl4, were
adequate to detect the presence or absence of the compounds at the proposed
threshold trigger levels. Compounds with a high ionization potential (above
that of the photoionization detector used; 10.6 eV), such as DCM, CCl4 and
1,1,1TCE could be detected but only at concentrations above 100 µg l⁻¹. A
detector with higher ionisation potential (which is, however reported to be
less robust under field conditions) or an electron capture detector, would have
to be used to detect these compounds at concentrations corresponding to the
proposed ‘trigger’ values.

From a practical point of view the equipment, including a generator and a jack
to remove the sampling rods from the ground is simple to transport and can be
fitted in the back of an estate car.
Apart from the previously mentioned instrument contamination, the main practical problems were calibration and sampling in wet conditions. The source of the persistent contamination was found to be the plastic solenoid valves, which adsorbed a portion of the volatiles from the high-level samples and were releasing them gradually into the carrier gas over a long period of time. It was even necessary to change some of the valves, as it was not possible to remove the traces by flushing. The current models of the portable GC now have stainless steel valves which should not cause similar problems.

Daily preparation of calibration samples was time consuming and cumbersome. Certified calibration gases or gas mixtures supplied in pressurized canisters are commercially available for the common gases and solvents. These can be connected directly to the GC inlet port and would provide a rapid and convenient method for calibration, however the preparation of specific mixtures to order could be expensive.

Soil gas sampling is not possible in conditions where the ground is water logged. Field sampling in wet weather should therefore be avoided, although it may be possible to obtain soil gas samples at greater depths or, alternatively, water samples could be collected and analysed. Schuring (1989) recommends that soil gas sampling should not be conducted in any soil that does not yield soil gas at a rate of at least 200 ml per minute at a vacuum of less than 10 inches of mercury.

As the soil samples were collected during the second visit to Site W, when no results of soil gas analysis were obtained, no direct comparison between results of soil gas and soil samples analysis could be made for that site. However, there was a general agreement with the results of soil gas analysis from the first visit, in that, that the levels of CIBz were at least an order of magnitude higher in TH1 than in TH2. On the other hand, the GC-MS analysis did not confirm the presence of TCE, but identified benzene, cyclohexane and toluene. Similarly, for Site D, where soil samples were taken on the day of soil gas analysis, the presence of TCE, identified by soil gas analysis was not confirmed by GC-MS and benzene, toluene and cyclohexane were detected only in the soil extract.
There could be several reasons for the discrepancies, in particular the following:

1. TCE, which elutes close to benzene, was misidentified in the soil gas, because of insufficient control of retention times;

2. TCE could have been lost from the soil sample during sample preparation; and

3. benzene, toluene and cyclohexane could have been impurities from the extraction solvent.

It was not possible to carry out further experiments to find out the real reason. However the results illustrate the need to take samples for confirmation of identity. It would have been preferable to take soil gas samples for GC-MS analysis (using adsorbent cartridges), however this technique was not available at the time.

A5. CONCLUSIONS

1. Field analysis of soil gas using portable GC is a convenient and rapid method of investigation of contaminated land, but cannot be used in all situations.

2. The standard 10.6 eV photoionization detector provides adequate sensitivity for most proposed target compounds of Group 1, except carbon tetrachloride, (and for many compounds of Group 2) to detect the exceedance of proposed ‘trigger’ values. Other detectors would need to be used for carbon tetrachloride and other VOCs with ionization potential above 10.6 eV.

3. GC separation using a portable instrument is adequate but more work is needed to develop a method for separating all Group 1 and 2 compounds.
4. Thorough validation and calibration of the GC/soil gas sampling techniques is necessary for each system to obtain reliable results.

5. GC-MS confirmation of the identity of the compounds detected during field analysis should be carried out. Soil samples may be used for the purpose, but the procedure is time consuming, suffers from interferences from extraction solvents and does not provide reliable quantitative data. GC-MS analysis of soil gas, using cartridge adsorption sampling techniques may, therefore, be preferable.

6. It is recommended that further work is carried out to evaluate the newer instruments now available.

7. Sampling of soil gas should not be attempted when the site is water-logged.

8. Experiments carried out confirmed the soil gas sampling/portable GC analysis to be a potentially very useful technique for investigating contaminated sites. More sites should be investigated to assess the full scope and application of the techniques.
1. dichloromethane
2. carbon tetrachloride
3. trichloroethylene
4. toluene

5. chlorobenzene
6. m - xylene
7. o - xylene

Figure A1 GC Separation
Figure A2 Chromatograms of soil gas analysis at site W
Figure A3 Soil Gas Measurement at site W

Key:

CB = Chlorobenzene (mg l⁻¹)
TCE = trichloroethylene (mg l⁻¹)
● = Test Hole

- 0.8m 0.5 CB/0.5 TCE
  - ● 4
- 0.8m 0.5 CB/1 TCE
  - ● 3
- 1.4m 0.5 CB/0.5 TCE
- 0.8m 0.2 CB/7 TCE
  - ● 2
- 1.4m 0.1 CB/5 TCE
- 0.8m 2 CB/<0.05 TCE
  - ● 1
- 1.4m 2 CB/<0.05 TCE

- 5m
APPENDIX B

A LIST OF SITES WHERE REMEDIAL MEASURES HAVE BEEN TAKEN
TO PROTECT BURIED SERVICES
<table>
<thead>
<tr>
<th>WATER UNDERTAKING</th>
<th>SITE</th>
<th>SOURCE OF INFORMATION</th>
<th>SURVEYED BY</th>
<th>CONSUMED</th>
<th>PROTECTION</th>
<th>PIPE TYPE</th>
<th>COATING</th>
<th>PROTECTED FITTINGS</th>
<th>NON-RETURN VALVE FITTED</th>
<th>CLEAN BACKFILL</th>
<th>PIPE</th>
<th>WATER</th>
<th>DATE</th>
<th>GUIDELINES</th>
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<tbody>
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<td>2</td>
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<td>?</td>
<td>?</td>
<td>HEAVY METALS (Fe, Hg, Cu, Zn) OIL</td>
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<td>TAPE</td>
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<td>Y</td>
<td>Y</td>
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<td>N</td>
<td>pre 1987</td>
<td>A, B, C, D, I</td>
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Guideline

B. Appendix 3 from GLC Guidelines for Contaminated Soils
D. Assorted papers and letters
E. Local knowledge
F. Liaison with local Environmental Health Department
G. Land Reclamation in Cities HMSO
I. AERE Report R-10366 1981 (Rawell Document)
J. Building Research Establishment (DoE), concrete in sulphate bearing soils and ground waters, BRE Digest 250, June 1981
K. No guidelines used
L. Manual for the design, installation and operation of MDE pipe systems for water supply distribution. WRC Eng., June 1986 and WRC in general
M. Pipe manufacturers, direct consultation and literature
N. AW Manual of Water Supply and Distribution. Lay metallic pipes where hydrocarbon pollution is known to have occurred
O. Correspondence with NWC 1980
P. In-house knowledge
Q. Central Directorate on Environmental Pollution DoE