Factors causing off-taste in waters, and methods and practices for the removal of off-taste and its causes

Final Report to the Department of the Environment, Transport and the Regions

DETR/DWI 5008/1
NOVEMBER 2001

FACTORS CAUSING OFF-TASTE IN WATERS, AND METHODS AND PRACTICES FOR THE REMOVAL OF OFF-TASTE AND ITS CAUSES

Final Report to the Department of the Environment, Transport and the Regions

Report No: DETR/DWI 5008/1

November 2001

Authors: H R Rogers

Contract Manager: P Jackson

Contract No: 11841-1

DETR Reference No: DWI 43/2/121 Part II

Contract Duration: 26 March 2001 to 30 June 2001

This report has the following distribution:

External: DWI Nominated Officer
Internal: Author

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

WRc plc, Henley Road, Medmenham, Marlow, Buckinghamshire SL7 2HD.
Telephone: + 44 (0) 1491 636500 Fax: + 44 (0) 1491 636501

FACTORS CAUSING OFF-TASTE IN WATERS, AND METHODS AND PRACTICES FOR THE REMOVAL OF OFF-TASTE AND ITS CAUSES

EXECUTIVE SUMMARY

OBJECTIVES

To provide an overview of the issues relating to taste and odour problems in drinking water with particular regard to the consumer perception of off-taste episodes, their causes and methods for detection and control.

REASONS

Tastes and odours are major factors influencing the consumers' perception of drinking water quality. Consumers generally believe that if their drinking water tastes or smells 'off ', then it is probably not safe to drink. This is because unfamiliar or unpleasant tastes or odours and appearance represent the only tangible and instant means for consumers to gauge the quality of drinking water.

Consumer complaints relating to off-tastes in drinking water are a significant concern for water supply companies, particularly in terms of their public image. Although drinking water quality in the U.K. as measured against health based parameters is very high, the recognition of objectionable odours or flavours in drinking waters undermines consumer confidence and raises often unfounded concerns about the safety of water supplies. The widespread usage of point of use devices (PoUs) in households to remove residues from drinking water is a largely a consequence of this consumer concern.

CONCLUSIONS

Objectionable tastes and odours in drinking water originate from a wide variety of potential sources. However detecting the specific causes of what are often ephemeral taste and odour episodes poses particular technical challenges to water companies. The isolation and identification of chemicals responsible for off taste problems is often hindered by the fact that some residues have very low taste and odour thresholds down to ng l^{-1} .

Assessments of consumer survey data following serious taste and odour incidents confirm that the reporting of symptoms or health problems can in some cases be related to psychological factors or anxiety caused by an incident rather than to any actual toxic effects from the contamination. Attempts by water supply companies to reassure consumers are often unsuccessful because of difficulty in identifying specific causes of taste and odour problems, which may be short lived and may be caused by chemicals present at very low concentrations.

Significant discrepancies between the taste and odour descriptors used by consumers and those provided by trained taste and odour panellists can result in misleading data on which to base taste and odour investigations. A recent French study has indicated that about 90% of consumer complaints were identified by expert panellists as being caused by tastes or odours other than chlorine. Consumers' may recognise and report unpleasant off-flavours, but may not provide accurate or consistent taste descriptors. A combination of the use of trained panellists and rapid analytical screening methods provides a more effective means of taste and odour identification.

The development of strategies or ‘tool-kits’ for water companies to enable better prevention, identification and optimised treatment of taste and odour problems could result in swifter resolution of taste and odour incidents and maintain better public relations. ‘Tool-kits’ could include operational monitoring or screening methods for taste and odour chemicals, micro-organisms identification methods, optimisation of removal techniques, and intake protection methods. The use of ‘surrogate’ chemical indicators for identification of causative organisms may also be applicable.

More rapid sample screening and identification of the extent and causes of taste and odour problems would be achieved by the use of integrating sample preconcentration techniques such as solid phase extraction (SPE). Solid phase micro-extraction (SPME-GCMS) merits further assessment as a rapid 'emergency' screening tool for taste and odour and other drinking water pollution incidents. There is considerable scope for assessing the utility of different SPME microextraction fibres for target suites of taste and odour compounds from both natural and anthropogenic sources.

The recent implementation of the Water Industry Approved Plumbers’ Scheme (WIAPS) may improve plumbing practices in domestic premises and avoid some taste and odour problems which occur within consumers’ premises such as from drinking water pipes being warmed by close proximity to hot pipes and lack of thermal insulation. However, it is likely that the main improvements from the introduction of these measures will occur in new premises or installations. The number of customer complaints relating to taste and flavour of drinking water which can be directly attributed to problems with washing machine supply hoses is significant and these problems would be reduced by restricting the use of non-metallic products to only those which meet the requirements of BS6920 and by better use of check valves.

Manufacturers normally test the efficiency with which point of use devices (PoUs) remove taste and odour problems from drinking water by carrying out chlorine reduction tests. Although it is generally assumed that PoUs based on activated carbon will remove many organic chemicals responsible for taste or odour problems from challenge waters no data was available from manufacturers to confirm this. The removal of some of the highly polar organic chemicals that may cause taste and odour problems by activated carbon may be less effective than for more hydrophobic chemicals. Further investigations would be required to determine the efficiency of activated carbon removal of taste and odour chemicals with a range of physicochemical properties.

Consumers’ perceptions of health risks posed by taste and odour problems in drinking water and their desire for choice, their willingness to pay for ‘quality’ and their perception that food and drink products should satisfy their own view of what constitutes ‘wholesome’ or ‘safe’ will ensure that the use of PoUs for the treatment of drinking water and consumption of bottled waters will continue to be significant.

CONTENTS Page

Page

LIST OF TABLES

LIST OF FIGURES

1. PUBLIC PERCEPTION OF WATER QUALITY

Tastes and odours in drinking water can be caused by a wide range of factors including:

- Natural products in water used for abstraction
- Chemicals formed during water treatment, storage or distribution
- Ingress of materials into distribution systems that either react with compounds in the water or cause tastes or odours themselves

The detection of off-taste and odour in drinking water is one of the principal causes of complaints from consumers to water companies. Some chemical contaminants have very low taste and odour thresholds and can be detected by consumers at very low concentrations (ng to $\mu g\ l^{-1}$ levels; Young et. al. 1996). However, although the actual health risks associated with many taste and odour incidents may be insignificant, the recognition of an off-taste or odour can simply be perceived by consumers as representing a toxicity problem (McGuire 1995). Because the taste, odour and appearance of drinking water is really the only tangible means for consumers to judge water quality it is reasonable to expect that unfamiliar or unpleasant taste or odours create a perception of health risk. Unfortunately, the reported responses of water utilities to public concerns following taste or odour episodes often do not provide assurances to consumers (Table 1.1).

Table 1.1 Interpretation of reported responses from water utilities in the USA and Canada to consumers complaints following taste and odour episodes (from McGuire 1995 and Jardine et al. 1999)

Utility response	Interpretation of consumer reaction to utility response
"… something that happens at least every winter"	They expected it, but they haven't done anything about it.
"But it won't make you sick.. "	.. even though it tastes disgusting and I am still concerned that there is a health problem.
".. the problem should be solved by tomorrow"	They want me to put up with it and it will eventually go away (they hope).
"We don't know what is causing the odour, but we know the water is safe" @	Rational consumers are not likely to be reassured

@ Canadian water utility spokesperson statement to public following an odour episode (Jardine et al. 1999)

The first and fourth utility responses in Table 1.1 appear to reflect the difficulties associated with identifying the causes of taste and odour problem episodes and taking measures to avoiding their recurrence.

Statistical analysis of survey data of consumer symptoms following some drinking water contamination incidents have provided evidence to support the observation that consumers often link the recognition of a taste or odour with adverse health effects. The ‘Wem incident’ of April 1994 involved the contamination of influent water abstracted from the River Severn to Barbourne water treatment works with two little-known solvents. The solvent contamination resulted in a serious taste and odour problem with the water supply to about 100,000 consumers in Worcester. Young et al (1995) examined the consumer survey data from the study and control areas, and concluded that the reporting of ‘soft’ symptoms (e.g. nausea, headaches) was associated with the recognition and perception of contamination and not with the contamination itself. It was suggested that in this case the higher rates of reported symptoms could be attributed to the consumers’ ability to detect an unusual taste or smell, rather than to a toxic effect of the chemical contamination. These findings indicate that the reporting of symptoms can in some cases be related to psychological factors or anxiety caused by an incident rather than to actual toxic effects.

Whilst water quality as measured by the parametric standards defined in the Water Supply (Water Quality) Regulations 1989 and 2000 are largely met by water undertakers in the U.K. the consumer will generally judge the acceptability and safety of drinking water purely on the basis of the aesthetic quality of what is drawn from the tap. Conversely, the absence of a detectable taste or odour in drinking water does not necessarily indicate that consumers are not exposed to undesirable contaminants in drinking water. Familiarity with tastes or odours can have a significant bearing on the confidence of consumers in the quality of their drinking water. Often one exposure to a problem taste or odour can be sufficient to generate a serious consumer concern which can result in a conviction that the water supplied is not safe (Canter et al. 1992-93).

There are various factors which may contribute to influence consumers’ perception of risk regarding their drinking water:

- Increasing consumer demands for ‘quality’ and ‘choice’ when selecting goods, services, food and drink
- Consumers’ willingness to pay for ‘quality’ and ‘safe’ products
- Effectiveness of representation (or misrepresentation) of the nature of risks by the water utility or the media
- Frequency of/proximity to/or familiarity with taste and odour problems
- Advent of more stringent drinking water standards
- Stricter enforcement of the Water Regulations by the Drinking Water Inspectorate (DWI)

- Media attention regarding prosecutions taken against Water Companies by DWI

- Other water quality incidents (e.g. cryptosporidium)

The recent popularity of household appliances designed to remove ‘harmful’ or odorous residues from drinking water (point of use devices or PoUs) have found favour mainly as a result of the greater environmental awareness of consumers and careful presentation of product benefits by manufacturers. It is interesting to note that the levels of some residues specified as being removed by many PoU devices (e.g. pesticides) are already very effectively controlled by water supply companies during water treatment using granular activated carbon (GAC) and it likely that many other organic residues that can cause tastes or odours may also be removed from influent water by this treatment method (Farrimond 1995).

2. CLASSIFICATION OF TASTE AND ODOURS

The classification of tastes and odours recognised in drinking waters by category in a flavour wheel was proposed in 1986 by the Taste and Odour Committee of the International Association on Water Pollution Research and Control (IAWPRC; Mallevialle and Suffet 1987). It was intended to provide a consistent terminology for the description of taste odours. There are four gustatory taste sensations, namely sour, salty, sweet and bitter. All the other apparent tastes or flavours described result from the fact that the consumer usually smells anything that is tasted. Figure 2.1 shows the primary taste and odour categories and some of the chemicals that have been associated with these specific tastes and odours are shown in Table 2.1. Similar taste and odour descriptors are included in the SCA 'Blue Book Method'.

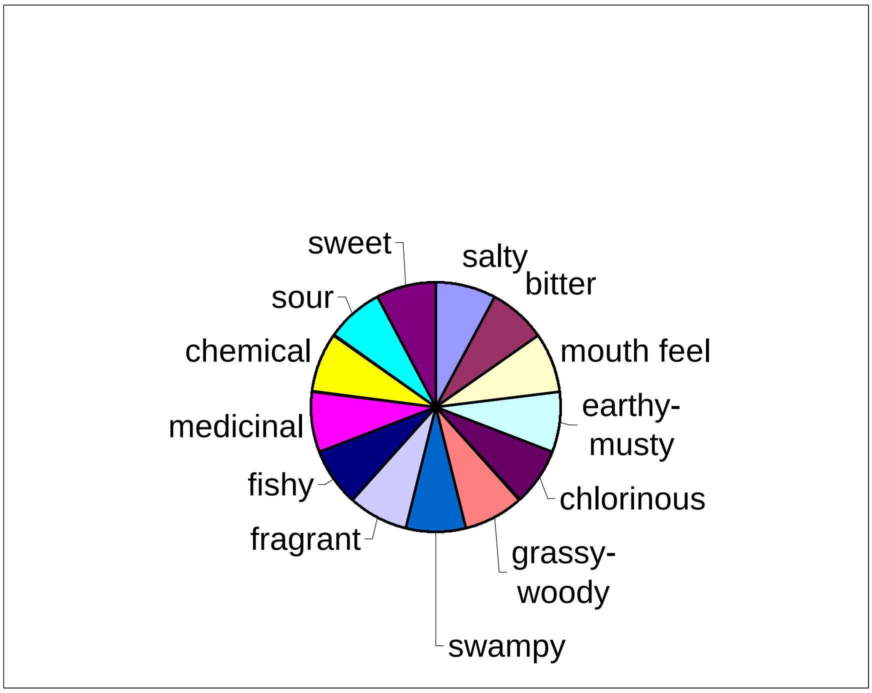

Figure 2.1 Drinking water flavour wheel (adapted from Mallevialle and Suffet 1987)

Table 2.1 Chemicals identified as causing specific tastes and odours in water (from Suffet et al. 1999)

Descriptor and chemical responsible	Source	Odour
Earthy/musty/mouldy		
Geosmin	actinomycetes, cyanobacteria	Earthy
2-methyl isoborneol	actinomycetes, cyanobacteria	Musty
isopropyl methoxypyrazine	actinomycetes	Potato-bin, musty
cadinene-ol	actinomycetes	Woody/earthy
2,4,6-trichloroanisole	biochemical methylation of chlorophenol	musty
Fragrant/vegetable/fruity/flowery		
Trans,cis-2,6-nonadienal	Algae	Cucumber
Aldehydes (higher molecular weight)	ozonation	Fruity/fragrant
Grassy/Hay/Straw/Woody		
Cis-hexenyl-1-ol acetate	Leaching of chemicals from grass	Sweet grassy
Cis-hexen-1-ol	Leaching of chemicals from grass	Grassy
β-cyclocitral	Cyanobacteria in water supply.	Tobacco-like
	Microcystis cyanobacteria culture.	1) Sweet-pipe tobacco 2) grassy/fruity
	Algal bloom in lake water and drinking water	1) fresh grass, <1µg l^{-1} 2) hay/woody, 2-20µg l^{-1} 3) tobacco-like, >10µg l^{-1}

Descriptor and chemical responsible	Source	Odour
Fishy		
n-hexanal and n-heptanal	Flagellate algae, diatoms	Fishy
trans, cis-2,4-decadienal	Flagellate algae	Cod liver oil
2-trans,4-cis,7-cis-decatrienal	Algae-*Synura petersenii* and *Dinobryon cylindricum* cultures.	Fishy/cod liver oil
hepta- and deca-dienals	*Dinobryon* algae	Fishy
trans,trans-2,4-heptadienal	Drinking water supplies	Fishy/swampy
trans,4-heptenal	Drinking water supplies	Fishy
1-penten-3-one (tentative)	Drinking water supplies	Fishy/swampy
Swampy/sulphurous/decaying vegetation/septic		
Mercaptans	Decomposed or living blue-green algae	Odorous sulphur
Dimethyl polysulphides	Bacteria	Swampy fish
Hydrogen sulphide	Anaerobic bacteria (reduce SO_4^{2-} to S^{2-})	Rotten egg
Dimethyl disulphide, dimethyl trisulphide, 2-isobutyl-3-methoxypyrazine and 2-isopropyl-3-methoxypyrazine	Biochemical decay of grass, drinking water supplies	Decaying vegetation
Dimethyl trisulphide and indole	Biochemical decay of grass, drinking water supplies	Septic
Aldehydes (low Mol. Wt.)	Chlorination of amino acids	Swampy/swimming pool
Medicinal		
Chlorophenols, 2-CP, 4-CP, 2,4-DCP, 2,6-DCP, 2,4,6-TCP)	Phenol chlorination/chloramination	Medicinal

Descriptor and chemical responsible	Source	Odour
Bromophenols	Phenol chlorination/presence of bromide ions	Medicinal
Iodinated THMs (iodoforms)	chloramination	medicinal
Chemical/hydrocarbons/miscellaneous		
Phenolic oxidants	Polyethylene pipes	Plastic/burnt plastic
2-EDD	Mixing-waste-aldehyde and glycol	Sweet(tutti-fruity)
2-EMD	Mixing-waste-aldehyde and glycol	Sweet (medicinal)
methyl t-butyl ether (MTBE)	Unleaded fuel oxygenate	Turpentine (hydrocarbon)
dicyclopentadienes	Industrial chemical	
Chlorinous/ozonous		
Chlorine (free)	Disinfection of water	Chlorinous
Monochloramine	Disinfection of water	Chlorinous
Dichloramine	Disinfection of water	Swimming pool
ozonous	Disinfection of water	ozonous

3. FACTORS CAUSING OFF-TASTES AND ODOURS IN DRINKING WATER

Taste and odour problems in drinking water can be caused by contamination of the water supplies with anthropogenic (man-made) chemicals or with chemicals from natural sources or by chemicals used to disinfect the water supply. Chemicals produced during microbial growth and from water treatment processes or mains cleaning or lining activities can also result in off-tastes and odours.

The receipt of customer complaints about their tap water is often the primary indication of a taste and odour problem. Such complaints can result from intentional changes made in the source, treatment or distribution of drinking water which may include:

- mixing of waters in distribution from different sources (e.g. groundwater and surface water)
- water treatment processes, and in particular the amount of chlorine residual
- seasonal or weather related effects, which affect stratification in reservoirs, run-off into reservoirs and rivers, particularly after long periods of dry weather
- the nature of the distribution system, residence times and materials used in the distributions system and in plumbing after the point of supply

Extremely low levels of many organic compounds can be detected by drinking water consumers due to their taste and/or odour. Some of these compounds may be produced during water treatment, due to reaction of organic chemicals in raw waters with the disinfectant used, and are therefore not detectable in the source waters. Others may contaminate drinking water due to problems in water distribution systems. For example, some organic compounds in contaminated soil can permeate plastic water mains, although this risk can be minimised or controlled by the use of pipes with laminated metallic barrier layers.

It is reasonable to assume that most taste and odour problems associated with source waters originate from surface water sources. However, the petroleum oxygenate methyl t-butyl ether (MTBE), which has a low taste threshold, and its leakage in petrol from underground storage tanks has recently raised concerns about the potential for the contamination of groundwater sources in the USA. Ether oxygenates are persistent in the subsurface and plumes of contamination from leaking underground storage tanks have become a major issue in the U.S.A., resulting in moves to reduce or remove them from motor fuel. The obvious solution to reducing the sources of MTBE contamination is to reduce leakage from storage tanks. However, there are significant differences in volumes of fuel that is handled, priced and taxed between the U.S.A. and the U.K. which have a bearing on the extent of groundwater contamination. Fuel prices are higher in the U.K. and in the U.S.A. tax is added to the cost of the petrol as it is dispensed from the pump, not as it leaves the refinery as in the U.K. As a consequence leaking fuel in the U.S.A. has not incurred tax and there is less incentive to address leakage problems.

Other factors also contribute to greater risks of groundwater contamination with petroleum hydrocarbons in California. There are significant differences in rates of recharge of catchments in California and the U.K. because of the higher rainfall in U.K. The high water demand and heavily depressed water tables in California result in abstraction of shallow urban groundwater which is more at risk from petroleum hydrocarbon spills from petrol stations. In contrast the U.K. has relatively small numbers of high yield deep public supply boreholes which are less vulnerable to contamination because they are more protected by consolidated less permeable strata. Although the Californian state government is currently considering adopting a drinking water standard on the basis of its organoleptic properties (Stocking et al 2001), there is currently no evidence that MTBE poses a similar threat to public water supplies abstracted from boreholes in the U.K. (Dottridge et al. 2000).

Mains relining operations may result in leaching of components present in the coating materials, and are generally detected due to complaints regarding taste and odour, caused either by the leached compounds or of their reaction products with chlorine, and detected at the consumers' taps (Gardner et al. 1995).

Taste and odour thresholds can vary over several orders of magnitude depending on the nature of the chemical and an extensive study of these using trained panellists has been published by Young et al (1996; summary of data presented in Annex A). The recognition of a specific chemical's taste and odour can also vary between different individuals and from day to day. In addition some individuals are particularly sensitive to certain chemicals and consequently the level and quality of taste and odour that is regarded as acceptable can vary considerably.

3.1 Tastes and odours produced during water treatment

Chemical residues present in influent water to drinking water treatment plants can undergo reactions as a result of coagulation, oxidation and sorption processes. Of these, the most important process related to taste and odour problems is oxidation as a result of chlorination or ozonation (Mallevialle 1987).

Biological activity can occur during the storage of raw water, sand filtration and granular activated carbon filtration and may result in the biodegradation of organic substrates present in influent waters and some chemical degradation products can cause taste and odour problems. The formation of chloroanisoles has been identified as the likely cause of a musty taste and odour problem following the slow-sand filtration of clarified influent water from the River Seine (Mallevialle 1987). This has since been attributed to the methylation of chlorophenols to chloroanisoles which are detectable by consumers' at very low concentrations in drinking water (threshold odour threshold for 2,4,6-trichloroanisole is ~0.1 ng l^{-1} Young et al. 1996). Nystrom et al. (1992) have identified fungi and actinomycete bacteria in the drinking water which are capable of microbial methylation of 2,4,6-trichlorophenol which is formed during the chlorine disinfection of drinking water.

The removal of musty and muddy odours caused by naturally occurring compounds such as geosmin, 2-methylisoborneol and trichloroanisole in aerated sand filters has been shown to be an effective method depending on the degree of aeration (Lundgren et al. 1988). However, although treatment with ozone was more effective in removing the same odorous chemicals, it was found to produce other fruity odours and sweet tastes caused by the formation of mainly aldehydic compounds such as heptanal, octanal, nonanal, decanal, benzaldehyde, phenyl acetaldehyde and 3-methoxysalicylaldehyde (vanillin) and other unidentified chemicals (Thorell et al. 1992; Anselme et al. 1988). The production of such fruity taste and odours in an operational ozonation plant was identified by Anselme et al. 1985.

Chlorination of water supplies has long been recognised as an indirect cause of taste and odour in drinking water. Taste and odour are produced by the reaction of chlorine with trace organic compounds present in the water. Probably the most common trace organic chemical which reacts with chlorine to cause distinctive taste and odour problems is phenol and its homologues. Chlorine reacts with trace organic chemicals in two ways; firstly, oxidation by accepting electrons from the organic substrate; secondly, by substitution into the molecule. Substitution only occurs when there is an activated carbon atom within the molecule and only a small percentage of chlorine consumed actually substitutes onto organic compounds, the majority being simply reduced to chloride (Johnson and Jensen 1986).

However, although the chlorine species present in drinking water are detectable to consumers an important concern has been the formation of chlorinated reaction products with trace organic compounds in water some of which can impart taste or odour.

In water supplies with source water that contains traces of bromide and iodide at concentrations of about 0.1 mg l-1, chlorine can oxidise the bromide and iodide to bromine and iodine which then react with organic residues to form brominated and iodinated trihalomethanes. These chemicals can be responsible for ‘medicinal’ tastes and odours at very low concentrations (Mallevialle and Suffet 1987).

3.2 Microbially mediated taste and odour and aesthetic problems

Surface water may contain a variety of bacteria, micro-fungi and yeasts indigenous to its source and the soil and vegetation in the catchment. Taste and odour chemicals can originate as either metabolites, as a result of lysis of dead algal cells or when the dead cell biomass supports bacterial growth.

Actinomycete bacteria and cyanobacteria have long been associated with the production of earthy or musty odours and Gerber and Lechevalier (1965) and Safferman et al (1967) isolated and identified two chemical metabolites, namely geosmin and 2-methylisoborneol as the chemical compounds responsible. However, confirmation that these compounds could cause taste and odour problems in drinking water at very low concentrations was not technically possible until the advent of GC-MS analysis. Several instances of drinking water quality off-taste problems resulting from the presence of these chemical residues at trace (ng l^{-1}) concentrations have since been reported (Izaguirre and Taylor, 1995; Wnorowski and Scott, 1992; Berglind et al. 1983; Yagi et al. 1983; Hayes and Burch 1989). These chemical metabolites can be produced in source waters and pass through treatment processes into water for supply, or may originate from biofilm growth on the walls of pipes or on sediments or other deposits within the distribution system. Other metabolites from actinomycetes which result in woody-earthy and musty-mouldy potato odours include cadin-4-ene-1-ol and 2-isopropyl-3-methoxypyrazine (Suffet et al. 1999).

The decomposition of cyanobacterial algal cells following a bloom can result in the release of significant amounts of mercaptans, dimethyl sulphide and polysulphides and other volatile sulphur compounds which can produce fishy, swampy or septic odours (Environment Agency 1998). However, ascribing the cause of a microbially mediated taste and odour problems to a particular species is difficult as the problem may be detected some distance from the source. Some of the main microbially mediated sources of tastes and odours are summarised in Table 3.1.

Table 3.1 Summary of some of the main microbially mediated taste and odour sources

Source	Taste and odour descriptor	Compound
Actinomycetes, cyanobacteria	Earthy	Geosmin
Actinomycetes, cyanobacteria	Musty	2-methylisoborneol
Actinomycetes	Mouldy, musty	2-isopropyl-3-methoxypyrazine
Actinomycetes	Woody, earthy	Cadin-4-ene-1-ol
Green algae	Cucumber	Trans-2 and cis-6-nonadienal
Pseudomonas sp.	Swampy, fishy	Dimethyl polysulphides (dimethyl trisulphide)
Sulphate reducing bacteria (Clostridia)	Rotten eggs	Hydrogen sulphide

Long residence times within the distribution system can extend the period of microbial growth, allow residual disinfectant to dissipate and lead to build up of loose deposits. During warm weather some supplies can approach ambient temperatures and with long residence times this can promote the growth of micro-organisms Evins et al. 1990). Some measures which can reduce the residence time effects are:

- avoidance of ‘over-design’ for expected flows
- usage of the minimum storage volume necessary in reservoirs
- avoidance of dead ends in the distribution system

Temperature influences the action of disinfectants and also the growth of micro-organisms in the distribution system. In general microbial growth rates increase with temperature, and whilst disinfectants act more rapidly at higher temperatures they are also dissipated more quickly. Applying disinfectant chlorine residual within the distribution system is an effective means of maintaining biostability. However, because free chlorine is rapidly dissipated, large doses would be required in many systems, which would cause unacceptable taste and odour problems for consumers near to the treatment works. Maintenance of a chlorine residual is most likely to be successful if chlorine demand is limited by using improvements in coagulation, filtration, booster disinfection and mains cleaning operations

Chloramines, whilst being less potent oxidising agents than chlorine, are more stable and are used to provide a combined chlorine residue to the ends of distributions systems (Evins et al. 1990).

3.3 Materials in contact with drinking water in distribution systems and domestic plumbing

A significant number of taste and odour problems appear to arise in the distribution system and some of the cause include:

- substances released from pipe materials or produced as a result of reaction with them
- substances permeating through the walls of pipes
- chemical reactions in the aqueous phase, including the continuation of reactions occurring during treatment
- biological processes, particularly on surface deposits or loose sediments

Materials and products intended for use in contact with drinking water for public supply are subject to the requirements of the Water Supply Water Quality Regulations. Products with significant surface area contact with water for public supply need to be considered for approval by the DWI Committee on Products and Processes for Use in contact with water for public supply (CPP). This expert group assesses the chemical formulation of products such as pipes, coatings, membranes and filtration systems to determine whether they may adversely affect the quality of water. Smaller surface area fittings are also tested and assessed under the requirements of BS6920 and are approved by the Water Regulations Advisory Scheme (WRAS). The BS6920 testing protocol includes screening products for potential odour and flavour effects. A range of organic materials used in plumbing systems as jointing materials, pipes, washers and lubricants could potentially support microbial growth and so contribute to taste and odour problems. Such problems are most likely to occur in systems with a low turn over of water; in systems incorporating storage tanks; where localised warming of cold water pipes occurs; or in large buildings or apartments.

However, water contact products which comply with BS6920 should not taint the water supply or encourage microbial growth.

Corrosion of pipes or fittings containing zinc or copper can give rise to significant concentrations of these metals in water which imparts an astringent taste. Taste threshold concentrations for copper are about 7 mg l^{-1} (mean) and 3 mg l^{-1} for the most sensitive 5% of the population. The thresholds for zinc are 20 mg l^{-1} (mean) and 5 mg l^{-1} (most sensitive 5%). Iron, which can be present as a result of corrosion of iron mains, as residual coagulant or from the raw water can also impart an unpleasant taste to water. The mean taste threshold concentration is about 3 mg l^{-1} and about 40 µg l^{-1} for the most sensitive 5% of the population (Evins 1990). Diffusion of fuel or other chemicals through plastic pipes buried in contaminated ground can also give rise to tainting, as can contamination from other products in buildings such as floor sealing materials.

Domestic consumers receiving drinking water from rising mains through short pipe lengths, insulated from external sources of heat and jointed with suitable materials are normally unlikely to experience material-related microbial growth problems. However, Colbourne (1985) identified occasional problems from plumbed in domestic appliances such dishwashers and washing machines which were connected directly to the mains supply upstream of kitchen taps by unsuitable flexible rubber or plastic hoses. The number of customer complaints relating to taste and flavour of drinking water which can be directly attributed to washing machine supply hoses has recently been reported to be about 62 per week (Taylor 2000). These complaints have been attributed to the reaction between non-metallic materials in the hose assembly with chlorine or chloramine and diffusion back or draw back through venturi effect (Taylor 2000). Fitting backflow prevention devices upstream of appliances reduces the occurrence of this source of such contamination (WRAS 2000) as does restriction of the use of hose products to only those which meet the requirements of BS6920. Backflow protection is normally built into domestic type appliances but if this is inadequate additional external protection should be provided. Air gaps are also required for certain systems (e.g. bidets, WCs). The type of backflow prevention device required depends on the fluid risk categories downstream of the device (e.g. baths, bidets, WCs). Back contamination actually occurs by either backsiphonage or backpressure, depending on whether the system is at atmospheric pressure and the difference in pressure upstream and downstream of the pipe at the same elevation.

The temperature of water delivered by water distribution systems can vary from 4^{o}C in winter to 25^{o}C during periods of hot weather. WRAS recommendations on water system design and installation state that as far as is reasonably practicable the temperature of water within domestic cold water pipes should not exceed 20^{o}C and adequate measures are taken to ensure that this temperature is not exceeded. However, the temperature of water delivered from the mains can be up to 25^{o}C and significantly warmer during storage. Whilst these recommendations mainly arise because of concerns over proliferation of *Legionella* in water systems at elevated temperatures, the same precautions also reduce the risks of growth of non-pathogenic microbes which can be responsible for taste and odour problems.

WRAS also recommends that pipework supplying cold water taps should be as short as possible and any length of pipe serving single cold water taps should be insulated to prevent heat gain from adjacent hot water pipes or other heat sources. The relative positions of cold water pipes to hot water pipes should be such that the cold water pipes are not warmed. Wherever possible horizontal cold and hot water pipes should be fixed so that the hot water pipe is a higher elevation than the cold water pipe. Cold water pipes supplying water which may be drunk should be insulated so as not to be warmed from the ambience.

Much of the WRAS recommendations relate to good plumbing practice during pipe and appliance installation in domestic premises. However, except for new installations, these activities are effectively outside the direct control of water companies. The Water Industry Approved Plumbers' Scheme (WIAPS) has recently been introduced with the aim of identifying competent plumbers, promoting good practice and providing information on developing issues. This may improve plumbing practices in domestic premises and avoid some taste and odour problems which occur within consumers' premises. However, it is likely that such improvements will be most likely to occur in new premises or installations.

Whilst assessments of products by CPP and/or WRAS provides a means of excluding unsuitable products from use in contact with public water supplies and on domestic premises this does not remove the possibility of contamination of water supplies if products are misapplied or if instructions for use or specific guidance and codes of practice are not adhered to. The application of epoxy resin based coatings to water mains is widespread and water undertakers are required to ensure that lining procedures are carried out in accordance with guidance given in the 'Operational Guidelines and Code of Practice' (Warren 1989). However, there do not appear to be any published reports of specific taste and odour problems resulting from the misapplication of epoxy resin linings. The most likely causes of taste and odour problems resulting from the application of epoxy resin lining in water mains include:

- inadequate curing of resins leading to leaching of chemical residues (either because of incomplete mixing of resin and hardener, incorrect mixing ratios or inadequate control of cure temperature or period)
- ineffective flushing of mains prior to during recommissioning leading to a first pass slug of leachant

The practice of mains relining activities is such that if taste and odour incidents occur then the effects are most likely to be restricted to small groups of consumers in limited areas. It should be noted that the consumers' attitude to the quality of water received after the disruption of supply caused by lining operations may also have an influence on taste and odour recognition and complaints. Examples of off-taste problems caused by misapplication of products are shown on Table 3.2.

Table 3.2 Examples of off-taste problems caused by misapplication of products in distribution systems

Off-Taste problem	Source	Organoleptic chemical	Reference
“acidic and resinous” taste in drinking water	Fibre glass reinforced polyester resin in water tower	Styrene	Rigal and Danjou (1997)
“medicinal” taste in drinking water	Use of unapproved PVC reinforcement netting in approved cementitious reservoir repair material	Chlorophenols formed from lime-hydrolysed triphenylphosphate in presence of chlorine	Rigal and Danjou (1997)

4. DETECTION AND IDENTIFICATION OF CHEMICALS CAUSING TASTE AND ODOUR PROBLEMS

River catchments and water treatment works abstracting water from points on rivers can be particularly vulnerable to sudden or short-lived changes in water quality. Such ephemeral contamination can result in serious effects on both river water quality and on water abstracted for public water suppliers. Events such as the River Severn pollution incident of April 1994, which caused a major taste and odour problem in Worcester's drinking water supply, and recent incidents in Wales in 2001 have highlighted weaknesses associated with monitoring and detection of non-regulated contaminants, particularly organic contaminants present in water at low concentrations (Ives et al 1994). In the case of the Worcester incident significant problems were encountered because the causative agent was present at sub $\mu g\ l^{-1}$ levels in drinking water, had a very low taste and odour threshold and posed particular analytical problems because of it's high solubility. These factors in combination resulted in a delay in identifying the cause and source of the taste and odour incident and the potential health significance to consumers.

The following section considers the operational problems associated with determining the causes of taste and odour incidents, although the same principles apply to other water pollution incidents.

The identification of contaminants responsible for pollution incidents or taste and odour problems can pose special difficulties for the following reasons:

1. There are many thousands of organic chemicals that could have potential for causing a pollution incident should they enter a river, and presumably some proportion of these could be responsible for taste and or odour problems in drinking waters. For example, there are over 1000 high production volume chemicals that are produced in the EC in quantities of over 1000 tonnes per annum (EC 1993) and more than 60,000 chemicals listed in the European Inventory of Existing Substances (EINECS).

2. Pollution events are often ephemeral or short lived, and the concentration of the causative substance may have declined to low levels after the incident-making the analytical identification of the source difficult.

3. In some cases, taste and odour incidents can be caused by very low concentrations of chemical residues (some organic chemicals can cause taste and odour problems at concentrations $<1\ \mu g\ l^{-1}$).

4. Inappropriate or ill-timed sampling may hinder identification of pollution sources.

5. Insufficient information may be available on ‘normal’ background contaminant levels so that it may be difficult to assign the pollution incident to a specific trace contaminant.

6. Considerable resources are required to investigate the precise cause of taste and odour problems.

Water treatment works abstracting from rivers can be vulnerable to sudden, episodic contamination from industrial discharges and pollution incidents. Inherent difficulties associated with the detection and monitoring of organic contaminants include the large number and variety of types of organic chemicals that could have potential for causing a pollution incident and the fact that pollution events are often short lived. The latter means that the concentration of the causative substance may have declined to low levels by the time of any response to the incident, making it difficult to identify the cause and source of the problem. This issue is particularly important in the case of a substance that can cause taste and odour problems at concentrations that are low in relation to analytical capabilities. These substances include a range of highly soluble, polar compounds that currently present difficulties in sampling, sample preconcentration and analytical determination (Gardner et al. 2000).

Recent pollution incidents in the U.K., U.S.A. and Spain (Preti et al. 1993; Ventura et al. 1998) have illustrated these problems. In these cases contamination of source water with relatively soluble polar substances such as 2-ethyl-5,5'-dimethyl-1,3-dioxane (EDD), 2-butoxyethanol, and 2,2-dimethyl-1,3-propane-diol led to contamination of public water supplies and taste and odour problems. Furthermore, considerable difficulty was experienced by the relevant authorities in identifying the substances responsible and the source of the pollution.

Sampling is the first and often the most neglected aspect of a monitoring strategy to the determine the water quality of rivers or other waters. Also, in many situations it is the sampling stage that forms the weakest link in the process of determining the concentrations of trace residues in water samples. The problems associated with obtaining representative water samples have been reviewed by Hunt and Wilson (1988), however, two general types of sampling programme can be identified:

- **Quality assurance** – where the instantaneous concentration of determinands is needed e.g. for assessment of compliance with a standard such as an Environmental Quality Standard (EQS) or Prescribed Concentration of Value (PCV).

- **Quality characterisation** – where the quality of the water needs to be monitored over a period of time in order to assess loads of specific substances or to detect intermittent pollution.

In order to carry out the latter type of sampling programme it is usually necessary to carry out regular, and preferably continuous sampling over a period of time. However, for many determinands, and in particular organic contaminants, it is not practicable and/or extremely expensive to perform such surveys. Spot sampling is often adopted as a compromise position and this has several drawbacks:

1. Spot sampling only provides 'snap-shots' of water quality. Consequently, short term fluctuations in contaminant concentrations may not be observed unless sampling frequency is increased.

2. Frequent spot sampling and analysis for organic contaminants is prohibitively expensive (particularly for many organic residues identified as causing taste and odour problems at low concentrations)

3. Ephemeral pollution events may not be detected within the frequency of the spot sampling regime.

In order to obviate these disadvantages continuous ‘on-line’ monitoring devices have been applied to measure specific contaminants in water. These have included continuous monitors for measuring phenols on the River Dee (Rennie 1987); phenols, ammonia, trace metals and hydrocarbons on the River Seine (Cognet et al. 1986 and et al. 1987) and volatile organic chemicals using membrane inlet mass spectrometry (Harland et al. 1987; LaPack and Tou 1991).

The use of integrating sampling techniques or continuous systems of monitoring has been proposed in order to allow continuous or sequential batch analyses on intake water. Suitable approaches usually incorporate some form of sample preconcentration to allow detection of contaminants at the low concentrations of interest. Among the most important properties of the organic chemicals of potential interest in water are:

- Molecular weight- from about 30 to 1200 atomic mass units
- Molecular size from 5 to >100A diameter
- Water solubility from 1 x 10^{-6} to 1000 mg l^{-1}
- concentration range of interest from 1 x 10^{-6} to 1000 mg l^{-1}
- polarity from cationic through essentially non-polar to anionic
- water/sorbent partition coefficients (log K_{ow} – octanol-water partition coefficients) from 2 to >6.
- Vapour pressure (volatility) from volatile solvents (e.g. acetone) to involatile solutes – indicated by the Henry’s Law constant

Whilst no single extraction/preconcentration technique can accommodate chemicals with such large disparity of properties, it is important to recognise the need for monitoring techniques with an exceptionally wide scope of application. Gardner et al (2000) considered a range of procedures including:

- Equilibrium dialysis
- Continuous liquid-liquid extraction
- Fluidised bed sorption
- Sorption of contaminants on polyurethane foams
- Solid phase extraction (SPE)
- Solid phase microextraction (SPME)

Of the above techniques the most promising are SPE and SPME. The reasons for this are discussed below.

4.1 Requirements for integrating sample preconcentration techniques

The following characteristics for integrating are recognised as being of prime importance to water company end users:

1. Ability to provide sample extracts/concentrates that will provide information on water quality with adequate accuracy and minimal cost.
2. Provision of sample extracts/concentrates representative of intake water.
3. Integrating sampling devices should not affect the concentrations of determinands at the sampling point.
4. Integrating sampling devices should be designed and constructed in such a way that the concentrations of determinands entering it are the same as those in the water-body at the time and point of sampling.
5. Integrating sampling devices should not affect the concentrations of determinands in the water once it has entered the device.
6. Provision of sample concentrates that will remain stable over the period that could elapse between sampling and analysis.
7. Provide sufficient sample extract/concentrate to enable a detailed retrospective and preferably quantitative assessment of water quality following a pollution incident. (Whilst quantitative monitoring data is most useful, qualitative methods could also be of use in certain applications, particularly for general survey screening).
8. Compatibility of extraction technique with existing 'off-the shelf' abstraction or sampling equipment currently used by regulators and water undertakers.
9. Robustness and utility for end-use *'in-situ'* or in the field
10. Techniques should be capable of detecting an intermittent pulse of contamination

The options for monitoring contaminants in river catchments and water inlets are shown in Table 4.1. The use of continuous-on-site contaminant isolation or preconcentration techniques were considered by Gardner et al (2000), Rogers and Comber (1998) and Rogers (1997). These approaches to water quality monitoring avoid the disadvantages associated with spot sampling and continuous on-line monitoring, providing a series of time-specific or time-integrated extracts or concentrates that could be analysed for specific contaminants should the water quality be affected by a pollution incident.

Table 4.1 Options for monitoring water quality in river catchments and water inlets

Monitoring option 1	Spot sampling	Disadvantages⇒	1. Costs of frequent sampling prohibitive
		Advantages⇒	1. Ease of operation/flexible 2. Low capital investment
Monitoring option 2	Continuous 'on-line' monitoring	Disadvantages⇒	1. Costs prohibitive 2. Limited determinand suites 3. Expert maintenance required
		Advantages⇒	1. Provides detailed information on levels of priority determinands for specific time periods
Monitoring option 3	Continuous 'on-line' sample extraction	Disadvantages⇒	1. Some equipment maintenance likely 2. May be requirement for more than one technique
		Advantages⇒	1. Provision of extracts over a long time period 2. Option for retrospective chemical analysis of time specific sample concentrates (e.g. GCMS) following detection of pollution incident using non-specific techniques 3. Relatively cheap option 4. More likely to identify source of pollution

The use of 'on-line' continuous sample extraction /preconcentration in monitoring is outlined in Figure 4.1. Such an approach may aid the assessment of the situation with regard to unknown or unsuspected pollutants, such a biological metabolites or chemical reaction products, produced either in the environment or during treatment processes.

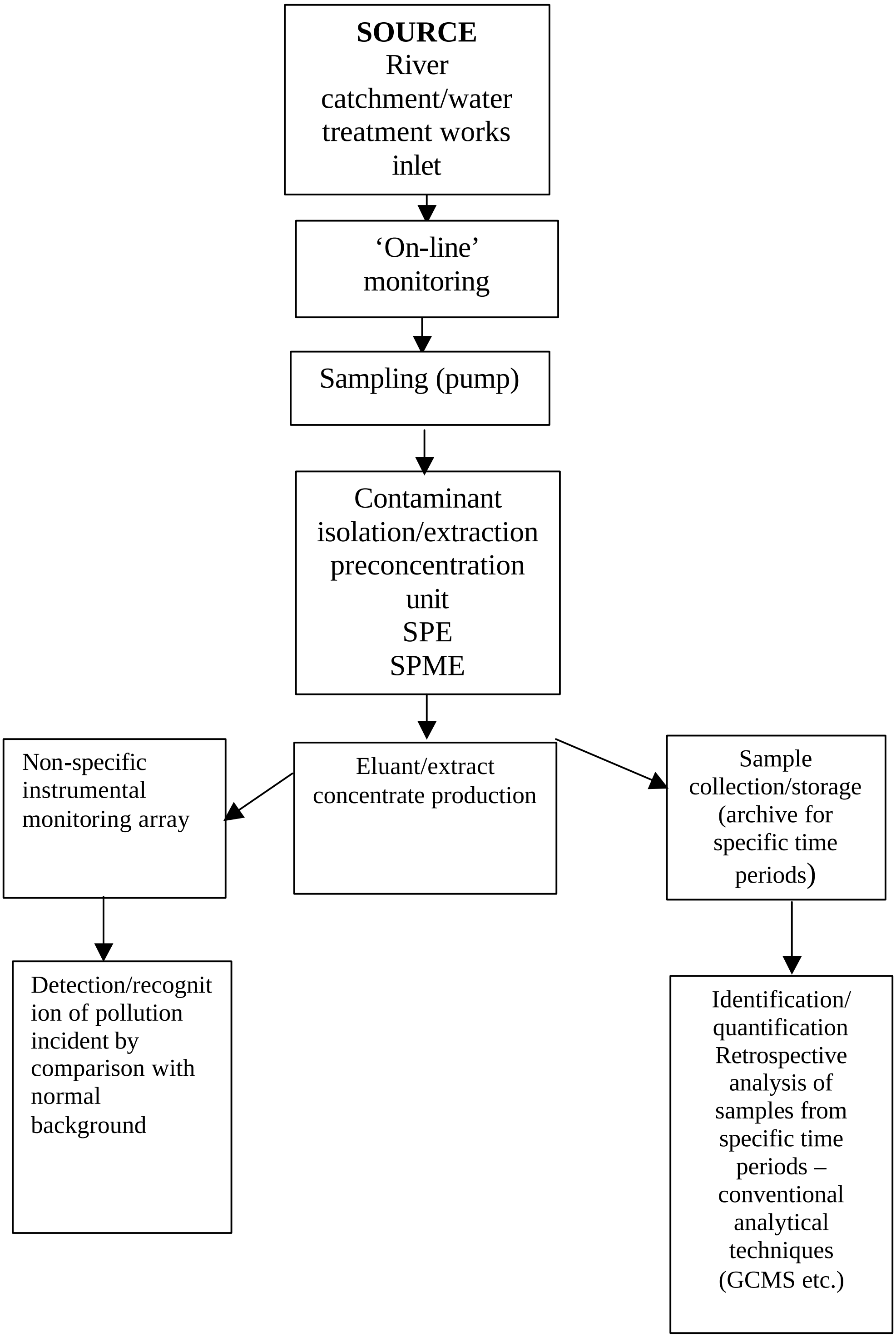

Figure 4.1 **'On-line'continuous sample extraction /preconcentration techniques in monitoring**

4.2 Criteria for the assessment of integrating sample concentration techniques

The following assessment criteria have been used to assess the ability of specific techniques to satisfy the requirements detailed previously:

- **Specificity/selectivity**
  Some techniques are capable of preconcentrating residues of a particular chemical type, or may exclude residues with certain physicochemical properties

- **Quantitative extraction**
  Some techniques have greater extraction efficiencies for specific chemical groups with differing solubilities or hydrophobicities

- **Response time**
  Techniques differ in their ability to register ephemeral changes in water quality. Factors such as diffusion, partition coefficient and kinetics of preconcentration process can control the minimum response time to a passing peak in contaminant levels.

- **Concentrate stability**
  Sample concentrate stability will largely be determined by the physical form of the samples. Concentrates or extracts in solid form should generally be more stable and for longer periods than solvent extracts which are more susceptible to photolytic effects.

- **Robustness**
  Physical or mechanical strength can be an important consideration for sampling equipment which would be in contact with flowing water or pumped water and exposed to potential fouling by suspended solids for significant periods. Susceptibility to microbial or algal fouling is another important factor.

- **Operational compatibility/serviceability**
  Compatibility with, and ease of application to existing sampling regimes and minimal servicing requirements are important factors that affect the operational utility of specific techniques.

- **Cost effectiveness**
  'On-site' integrating sampling techniques range from relatively simple passive through to active devices which may include scope for automated pumping devices and samplers. Such equipment will vary considerably in terms of capital and operating and maintenance costs. Decisions regarding the cost effectiveness of specific techniques will be determined largely by the sensitivity of the point of deployment and consideration of the extent of risks of pollution.

4.3 Review of techniques

Whilst no single extraction/concentration technique can accommodate chemicals with such a large disparity of properties, it is important to recognise the need for monitoring techniques with an exceptionally wide scope of application. Some specific examples of substances of interest, including some of marked taste and odour, are listed in Table 4.2, with their respective physicochemical characteristics.

Table 4.2 Examples of potential contaminants of interest

Substance	Reason for concern	$\log_{10} K_{ow}$ (1)	solubility g/100ml	taste/ odour threshold ng l^{-1} *	Henry's Law Constant atm m^{-3} $mole^{-1}$ +
Geosmin	taste/odour - naturally occurring	3.57	0.015	10	$3.1\ 10^{-6}$
2-Methyl-isoborneol	taste/odour - naturally occurring	3.27	0.032	29	$8.9\ 10^{-6}$
2-Isopropyl-3-methoxypyrazine	taste/odour - naturally occurring	2.37	0.069	2	$3.1\ 10^{-6}$
2,3,6-Trichloroisoanisole	taste/odour –	4.01	0.003	7	$1.3\ 10^{-4}$
2-ethyl-5,5'-dimethyl-1,3-dioxane	Chemical industry by-product	1.96	0.17	<10	$9\ 10^{-5}$
2-butoxyethanol	as above	0.57	6.4	<10	$9.8\ 10^{-8}$
2,2-dimethyl-1,3-propane-diol	as above	0.16	8.2	<10	$3.1\ 10^{-7}$
1,4-dioxane	solvent / taste	-0.32	20		$5.9\ 10^{-6}$
p-xylene	Solvent/taste	3.09	0.02		$6.5\ 10^{-3}$
trichlorobenzene	taste	3.93	0.001		$2.2\ 10^{-3}$
phenol	taste	1.51	2.6	<2000	$5.5\ 10^{-7}$
cresol	taste	2.06	0.89		$6.2\ 10^{-7}$

Substance	Reason for concern	$\log_{10} K_{ow}$ (1)	solubility g/100ml	taste/ odour threshold ng l^{-1} *	Henry's Law Constant atm m^{-3} $mole^{-1}$ +
naphthalene	odour	3.17	0.01	25000	$5.3\ 10^{-4}$
atrazine	herbicide	2.82	0.02	20000	$4.5\ 10^{-9}$
malathion	insecticide	2.29	0.007		$8.4\ 10^{-10}$

* from Keith, L.H., Advances in the Identification of Organic Pollutants in Water 1981; Ann Arbour Science, Michigan, pp1169. ISBN 0-250-403968-6

\+ from Meylan,W and Howard, P.H. 1991;Bond contribution method for estimating Henry's Law Constants. Environ. Toxicol. Chem. 10: 1283-93.

Gardner et al (2000), Rogers (1997) and Rogers and Comber (1998) carried out preliminary evaluations of a number of potentially useful techniques, including solid-phase extraction (SPE) and solid phase micro-extraction (SPME). The last two techniques appeared be the most promising. A summary of the preliminary evaluation of these two potentially useful techniques for application in monitoring water quality at treatment works intakes is given below. Semi-permeable membrane devices (SPMDs) are not likely to be generally useful for use in water treatment works intake monitoring and have mainly been used as surrogates for 'sentinel organisms'.

4.4 Solid phase microextraction (SPME) for rapid screening at the time of pollution incidents

SPME is a rapid, relatively inexpensive, solvent-free extraction method for the isolation of organic contaminants from aqueous solutions at sub-μg l^{-1} concentration levels. It has been identified as a simple alternative to purge and trap methods used for analysing volatile organic compounds in water samples (Shirey 1994; Shirey et al 1995; Whang and Pawliszyn 1998; Zhang Z and Pawliszyn 1993). The technique involves the sorption of organic residues from a water sample onto an optical fibre coated with poly(dimethylsiloxane) polymer. The fibre is immersed in, or held above the aqueous sample, then removed, and the organic compounds thermally desorbed into the injection port of a gas chromatograph. Selectivity can be controlled by using different phase coating or thicknesses. In contrast with SPE, sample conditioning is not required to ensure maximum extraction efficiency. The technique has been used successfully for the determination of volatile organic compounds such as benzene, toluene, ethylbenzene and xylenes and for the less volatile polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and the more polar and water soluble phenols. Since SPME can be used to preconcentrate determinands over a wide range of concentrations from μg l^{-1} to mgl^{-1} levels, it may be adapted for rapid screening of samples. Watson et al (1999) have recently successfully applied SPME fibres for the rapid screening of surface waters for unsaturated aldehydes (heptadienal, nonadienal and related compounds) which are responsible for off-flavours following release during algal blooms. They achieved detection limits of 1-2 μg l^{-1} for the target compounds using a polydimethylsiloxane/divinylbenzene extraction fibre and GCMS. There is considerable scope for assessing the utility of different SPME microextraction fibres for target suites of taste and odour compounds from both natural and anthropogenic sources.

Rogers and Comber (1998) tested two types of solid-phase micro-extraction fibres (Supelco, Poole, UK) each with a different fibre-coating sorptive phase. Polydimethylsiloxane (PDMS) coated fibres are recommended for extraction of non-polar determinands. Polyacrylate (PA) coated fibres are suitable for the extraction of more polar determinands. Fibres are installed in a fibre assembly and preconditioned by heating in a GC detector after which they are ready to be used for extraction purposes.

The rate of SPME fibre equilibration was investigated for a selection of priority contaminants. Fibres were exposed for periods of up to 1.5 hours in separate stirred spiked River Thames water samples spiked with 1,2-dimethylnaphthalene (DMN), phenol, atrazine, 1,2,4-trichlorobenzene (TCB) and trichloroethene (TCE) at concentrations of 1mg l^{-1}. Equilibration was substantially complete within approximately 30 minutes Figure 4.2.

However, adjustment of sorption periods to provide swifter extraction and analysis is possible provided corresponding limits of detection are determined.

Replicate SPME sorption tests indicated that a relative standard deviation of sorption of between 5 and 15% could be achieved for concentrations at the relatively elevated concentration of 1 mg l^{-1} (Gardner et al. 2000). Levels of DOC had little effect on sorption. The length of time elapsed prior to analysis of sorbed residues was found to be an important factor as response for volatile contaminants (e.g. trichloroethylene) declined rapidly within an hour of exposure. This is a potentially serious drawback; it means that sample preconcentrates on fibres should be desorbed and analysed within a few minutes after sample exposure.

Units of response are arbitrary (Peak area)

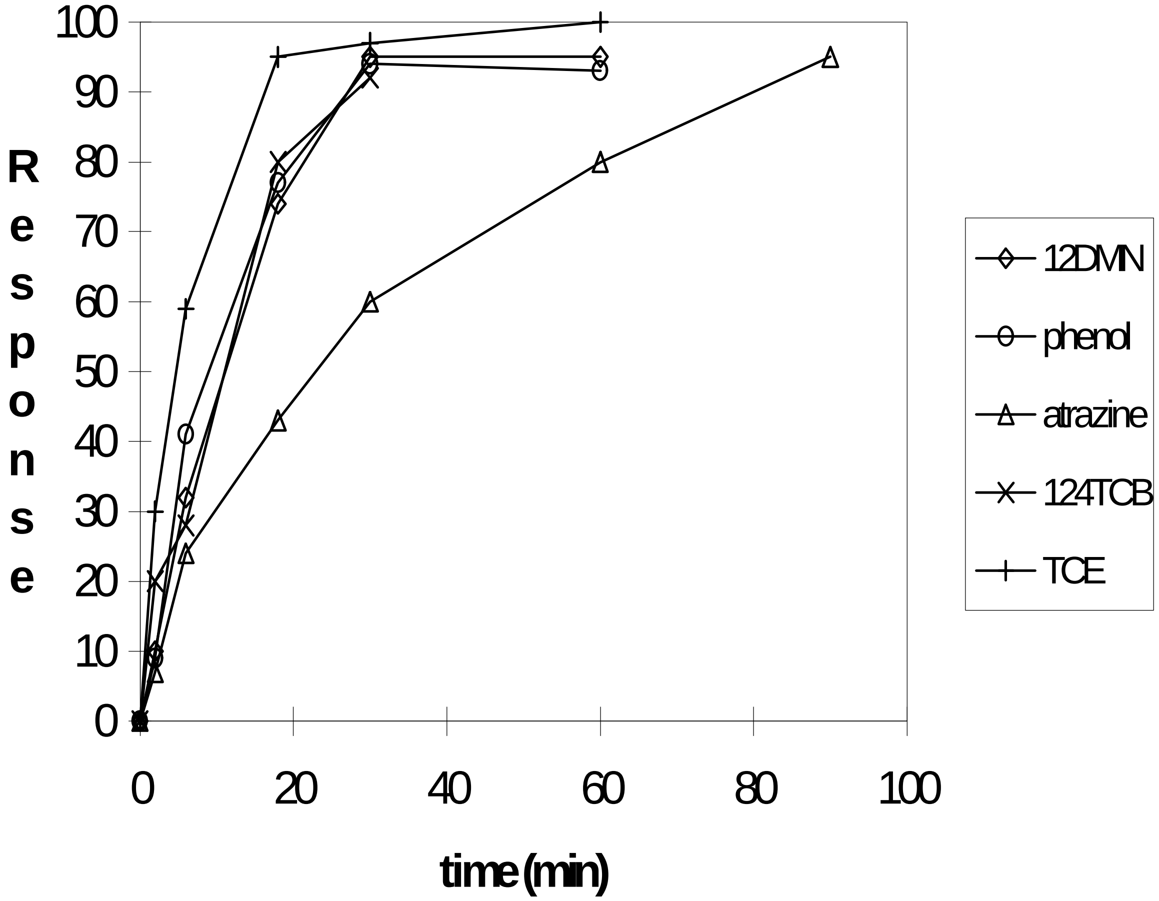

Figure 4.2 SPME Response v equilibration time for continuous exposure

SPME fibres were assessed for potential use as integrating sampling devices in a simple flow-through system. SPME fibres were inserted below the water surface in a 100 ml cell through which a spiked filtered Thames water sample was introduced at rate of 1 ml min^{-1} via a peristaltic pump. The cell contents were continually stirred and fibres were analysed following the introduction of short lived pulse of contaminant (of concentration 1-4 mg l^{-1}), followed by a return to unspiked ‘background’ levels for a period of 16 hours. Results showed that although the fibres responded to the initial contaminant plume, levels detected on the fibres declined to low or undetectable levels after the exposure to the background sample. The results suggest that desorption of determinands is occurring when contaminant levels in the passing influent sample decline to background levels. For this reason SPME fibres appear to have limited utility as 'on-line' sentinel monitoring devices. Data in Table

4.3 illustrate that the use of two different types of SPME fibre can help to address the determination of substances of different types.

Table 4.3 Theoretical and measured partitioning data for SPME fibres (Gardner et al. 2000)

Compound	Log K_{ow}	measured Log K_d	Solubility (mg l^{-1})
Phenol	1.5	2.4 (PA)	87 000
Atrazine	2.3	3.1 (PA)	28
1,2,4-Trichlorobenzene	4.0	3.4 (PDMS)	38
1,2-Dimethylnaphthalene	4.3	3.0 (PDMS)	15
Tetrachloroethylene	2.9	2.6 (PDMS)	150

K_d= fibre/water partn. coefficient = $\dfrac{\text{concentration of compound on fibre (mg kg}^{-1}\text{*)}}{\text{concentration of compound in water (mg l}^{-1}\text{)}}$

*N.B. mass of fibre coating estimated from coating thickness (µm), length/volume of fibre and assuming nominal density of 1 g cm^{-3}

Solubility data predicted using structure activity data (6)

It was concluded that:

- SPME fibres appear to have potential for rapid general survey screening for a wide range of organic contaminants that could cause a pollution incident.
- recoveries of determinands using PA and PDMS fibres show a correlation with hydrophobicity (log K_{ow}).
- SPME fibres can detect a range of contaminants with different physicochemical properties and structures. Recent work has indicated that limits of detection in the µg l^{-1} range is achievable for odorous aldehydes produced during algal blooms in surface waters. However, limits of detection need to be determined for a range of taste and odour chemicals with different physicochemical properties
- results from SPME flow-through tests suggest that considerable desorption of determinands occurs when contaminant levels in a sample stream declines to background levels after a pulse at elevated concentration. Hence, SPME fibres may have limited utility as sentinel monitoring devices. However, SPME could certainly be adopted as a relatively cheap sample screening tool for use in emergencies, provided samples are provided in batch form.

4.5 Solid phase extraction (SPE) cartridges for contaminant screening

SPE has been used widely for many years as a means of extracting organic determinands such as pesticides, PAHs and other priority pollutants from water samples **(**Walker et al. 1993; Barcelo 1993; Font (1993).

SPE cartridges have been proposed as suitable for the preconcentration of both polar or soluble determinands such as phenols and non-polar determinands. The type ENV+ Isolute extraction cartridges (Jones Chromatography, Hengoed,UK) was identified as a potentially useful sampling tool for providing quantitative information for a relatively wide range of chemical contaminants (Gardner et al 2000). ENV+ is a highly cross-linked polystyrene divinylbenzene polymer with a high surface area (~1100 m^2 g^{-1}), narrow particle size distribution and low fines content. Gardner et al (2000) carried out tests to assess the utility of these cartridges for general sample screening/preconcentration under non-optimised conditions. Experimental details: Cartridge Type: Isolute ENV+ 200 mg resin/6 ml reservoir capacity; solvation: 5 ml methanol, 5 ml deionised water; sample application: 60 ml h^{-1}; determinand elution: 5 ml 50:50 hexane/acetone.

The use of SPE cartridges for preconcentration of a range of contaminants has been investigated by Gardner et al (2000). Borehole water and sewage effluent samples (1 litre) were spiked with a range of potential contaminants at a level of ~50 µg l^{-1}. Triplicate samples were passed through separate ENV+SPE cartridges at a flow rate of 60 ml hr^{-1}. Samples were pumped both in and out of the cartridges to avoid overflow using a peristaltic pump and PVC and silicone pump tubes and connectors. No sample preconditioning, pH adjustment or 'salting-out' was carried out prior to preconcentration. Solvent eluates were subsequently dried by freezing out residual water and were then submitted for GC-MS analysis. Pesticides were analysed by negative chemical ionisation mass spectrometry and other determinands by positive ion electron impact mass spectrometry. Quantification was achieved using a range of deutero-labelled internal standards including: d_3 -1,1,1-trichloroethane, d_6 - benzene, d_5-phenol, d_{11} - hexanoic acid, d_5 - chlorobenzene, d_{10} - p-xylene, d_{34} - hexadecane, d_{10} -phenanthrene, d_5 - atrazine, d_{10} - malathion. The results for the mean recoveries of contaminants from spiked sewage effluents are shown with corresponding data for liquid/liquid extraction in Figure 4.3.

It is emphasised that the experimental conditions that were used - for column pretreatment, elution solvent etc. - could be optimised to give better recovery for some determinands, but possibly at the expense of poorer performance for others. The aim was to assess performance for screening purposes, for a range of different types of determinands with differing physicochemical properties using a single preconcentrations technique. It was concluded that:

- preconcentration efficiency does not appear to be simply related to the hydrophobicity of the contaminant residue. Comparison of log K_{ow} values with preconcentration efficiency reveals no obvious relationship.
- the preconcentration method has potential for screening for highly soluble contaminants such as phenols and cresols and atrazine, as well as for other more hydrophobic residues. This is a useful characteristic for the qualitative or semi-quantitative screening of samples.

- the approach was not particularly effective for the cyclic ether 1,4-dioxane. This contaminant was chosen to represents a class of high taste/odour substances that pose particularly difficult analytical problems because of their high water and low log K_{ow} (for 1,4 dioxane: water solubility at 25 °C = 214 g l^{-1}; log K_{ow} = -0.32 ; [from structure activity relationships, Sablic 1984]) which influence extraction efficiencies. Similarly, poor extraction efficiencies were found for 1,4-dioxane using liquid-liquid extraction, though recoveries might be improved somewhat using 'salting out' techniques.

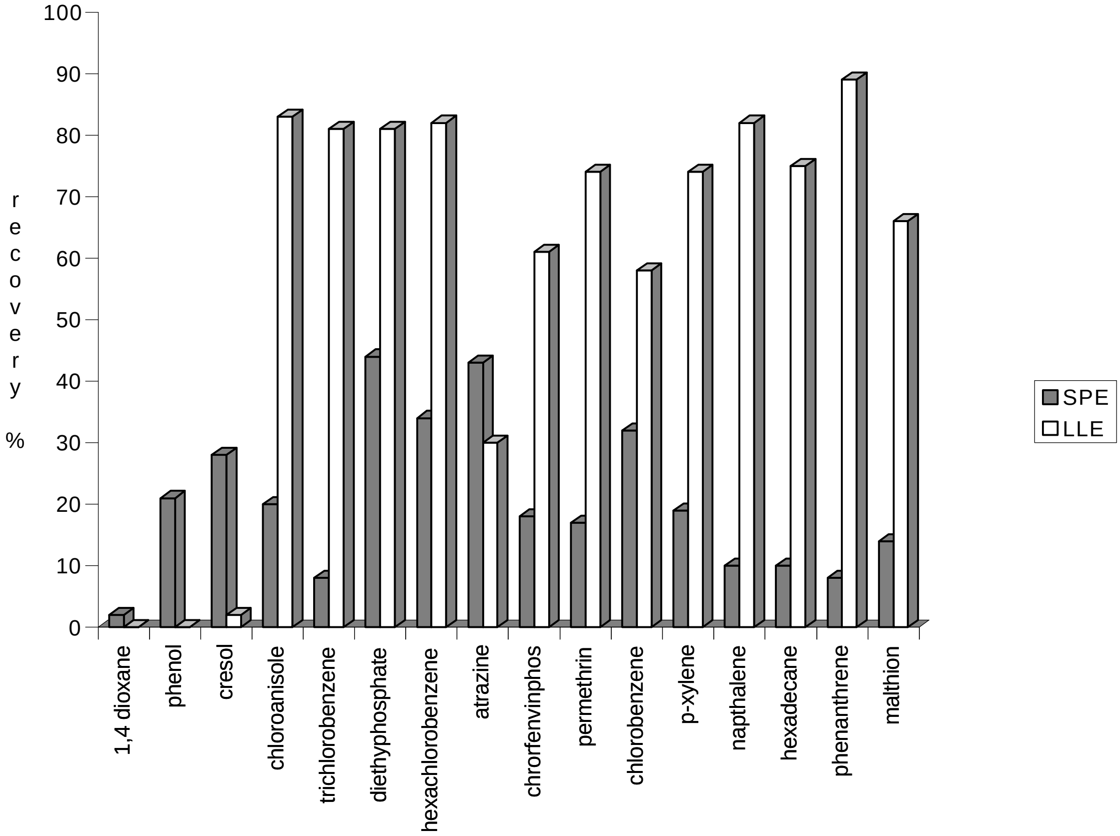

Figure 4.3 **SPE Recovery Data Compared with Liquid/Liquid Extraction (LLE). Recoveries are from a Sewage Effluent Sample Spiked with 50mg l^{-1} of each Contaminant**

4.6 Conclusions

SPE, used in a batch mode, offers a potentially powerful tool as a routine screening method. Two distinct modes of use are possible. In the first, cartridges might be eluted for analysis on a regular routine basis as a means of actively monitoring for potential contaminants. In the second, cartridges might be used to collect samples on a regular basis, stored under refrigeration and analysed only if pollution is indicated/suspected. SPME is probably more useful as a technique to be deployed rapidly in an emergency, particularly when GCMS general survey screening is to be used.

For both techniques, it is important that the "background" profiles of contaminants in any given source of raw water should be obtained at the outset of monitoring and on a regular basis, subsequently. This is essential if the introduction of new contaminants is to be identified. Support information should also include mass spectral data and limits of detection achieved by the monitoring system for specific contaminants (including those identified on the basis of local information as posing a high risk of pollution).

4.6.1 Operational applicability

Results from the laboratory testing confirmed that a 'universal' preconcentration technique that was suitable for all organic contaminants that could cause a potential pollution incident was not available. Nevertheless, three techniques were identified as being able to provide a basis for more effective monitoring. Adoption of these techniques could improve the users capability to detect and identify pollutant residues if used in combination, with each having particular benefits in terms of cost and technical performance. These techniques were solid-phase extraction (SPE), semi-permeable membrane devices (SPMDs) and solid-phase microextraction (SPME). The pros and cons for these three techniques are summarised in Figures 4.4 to 4.6.

4.6.2 Operational cost estimates

Estimates of the costs associated with applying specific preconcentration techniques operationally are summarised in Table 4.4. The estimated installation costs would be small compared to costs associated with installation of continuous 'on-line' GCMS monitoring equipment. Also, the techniques would provide additional pollutant source and identification capability without excessive operating costs.

SOLID PHASE EXTRACTION (SPE)

Pros

- quantitative
- qualitative
- continuous or intermittent sampling
- active
- soluble or hydrophobic contaminants preconcentration possible (e.g. phenol, permethrin)
- co-interferent oils/DOC/detergents not serious problem
- routinely used by analytical labs
- contamination free (if preconditioned)
- low capital cost
- new cartridge resins under development (increase determinand range/scope for specificity)

Cons

- prefiltration required in turbid waters
- pump system/rig and power required
- cartridges require preconditioning in laboratory
- cartridge exchange ≤24 hours depending on sampling regime
- maintenance of pump/cartridge required - possibly weekly if automated

Figure 4.4 Summary of pros and cons of specific preconcentration methods

SEMI-PERMEABLE MEMBRANE DEVICES (SPMDs)

Pros	Cons
♦ qualitative	♦ not applicable to ionics/polar contaminants
♦ semi-quantitative if =bration/exposure period known (unlikely) could be quantitative	♦ triolein-filled SPMDs require specialised preparation facilities (unless purchased from US supplier)
♦ suspended solids not a problem under normal conditions	♦ triolein dialysate sample work-up required after collection
♦ medium to high hydrophobicity range	♦ field/river deployment housing ~£500
♦ applicable to field or treatment works site	
♦ simple and robust (layflat PE)	
♦ deployment period of up to weeks	
♦ low maintenance once deployed	

Figure 4.5 Summary of pros and cons of specific preconcentration methods

SOLID PHASE MICROEXTRACTION (SPME)

Pros	Cons
♦ ideal for rapid ‘pollution event’ batch sample screening	♦ potential for passive sampling on-line requires further assessment
♦ rapid extraction of contaminants (~15 mins) with wide range of physicochemical properties	♦ fibres require careful handling/ not suited to use in field
♦ not affected by suspended solids under normal conditions	♦ partitioning of contaminants from aqueous solutions is limited by diffusion and is governed by the partition coefficients for each determinand. Consequently internal standard calibration is required to enable quantitative analysis.
♦ swift concentrate transfer to GCMS	
♦ cheap (and reusable) fibres and holders	

Figure 4.6 Summary of pros and cons of specific preconcentration methods

Table 4.4 Estimates of materials and maintenance costs for specific techniques

Technique	Sampling frequency	Unit costs	Approximate costs per annum	Other materials costs	Approximate man-time/maintenance (travel time excluded)	Approximate analytical man-time
SPE	Daily cartridge exchange (automated)	£1-3 each (various stationary phases available)	£400-1500 p.a. (including control sample cartridges)	Special assembly including relays, valves, batteries approx. £2500 (assembly and testing costs not inc.) or modified proprietary batch/composite system ~£2200 **plus** optional inlet filtration device dependent on location	~1-2 hours per week	Cartridge elution and eluate evaporation time ~ 2 hours per weekly batch GCMS analysis~ 1 hour per sample (plus variable spectral interpretation time for unknowns)

Table 4.4. Continued

Technique	Sampling frequency	Unit costs	Approximate costs per annum	Other materials costs	Approximate man-time/maintenance (travel time excluded)	Approximate analytical man-time
SPME	Dependent on frequency of spot sampling or screening of known polluted samples	~£40 per 30 samples	Assuming daily samples ~ £500 p.a. (not including GCMS analysis and spectrum interpretation costs)	Fibre assembly holders ~£150 each (2 per annum)	sampling & analysis ~1-2 hours per sample including GCMS analysis(i.e. rapid)	(time included in adjacent column)

N.B. all figures are approximate and relate to use of device at a single site

4.7 RECOMMENDATIONS

On site/field application

There is a need to apply, adapt and test preconcentration devices before they can be introduced as routine operational monitoring tools. The practical ‘*in situ*’ assessment of preconcentration devices in parallel, or in conjunction with automated sampling equipment currently used by the water industry or regulators would enable users to select the most effective system for contaminant detection whilst taking into account both cost and technical limitations. Such an integrated approach should maximise the use and application of existing equipment and so minimise investment costs.

The field testing of ‘*in situ*’ preconcentration devices will provide end-users with information on their operational practicality and will identify specific strengths and weaknesses of the different approaches. Areas requiring additional technical refinement or development will also be identified.

Benefits of the development of an operational system will be:

i) facilitation of more rapid and effective river water quality monitoring

ii) detection of fluctuations from ‘normal’ background contaminant levels (pre-emptive recognition of pollutants)

iii) provision of more effective means for protecting public water supplies and rivers

iv) improve compliance with possible future requirements of regulatory bodies (DWI etc)

Preconcentration techniques such as solid phase extraction (SPE) should be considered for the ‘*in situ*’/field assessment, and solid phase microextraction (SPME) merits further assessments as an 'emergency' screening tool, particularly as a tool for identification of chemicals causing taste and odour incidents.

Statistical, analytical and practical approach to the application, testing and development of an operational system for ‘*in situ*’ sample preconcentration

‘*In situ*’ sampling tests should be carried out with both ‘spot batch sampling’ and preconcentration devices in parallel in order to investigate any differences in data obtained for trace organic contaminants at a water inlet. Particular emphasis should be given to the development of a system capable of providing data representative of typical background contaminant concentrations and the differentiation of this from short lived pollution events. Particular regard would be given to the statistical design of the monitoring and assessment programme to determine whether fluctuations are attributable to real changes in water quality rather than system variability. Consideration will be given to the quality of data produced from the sample preconcentration system and an analytical quality control (AQC) scheme should be incorporated into the testing regime so that performance could be determined on a continuous operating basis.

The testing phase should involve the field testing of the proposed system with preconcentrates and batch water samples being screened in parallel using GCMS analysis. Recommendations will be made regarding the utility of specific methods including assessments of monitoring data obtained using different techniques. Areas where particular techniques would find operational application will be identified and technical limitations specified. Practical field testing will enable the investment and running costs for specific techniques to be more accurately estimated.

Sample screening techniques for pollution incidents

There is scope for a detailed performance assessment of specific solid phase microextraction (SPME) fibres for use in routine or emergency screening of water samples using GCMS. Such an assessment should give special attention to highly polar solvents including those that were identified during the Wem incident and other potential pollutants such as high production volume chemicals (HPVCs). SPME fibre performance data, mass spectral data and limits of detection for specific contaminants should be obtained for future reference and used in the event of an incident.

5. CONTROL AND REMOVAL OF TASTE AND ODOUR PROBLEMS

If tastes and odours cannot be controlled at source then water treatment can be altered to remove causative agents. Conventional sand filtration can aid in taste and odour removal as it encourages biochemical oxidation and coagulation and sedimentation have also been reported as having some utility. However, oxidative methods and adsorption using activated carbon are the most widely used techniques for odour and taste control. Adsorption with activated carbon has been shown to be more generally effective at removing a wider range of odours than oxidative techniques (Evins et al. 1990).

A recent overview of water treatment processes and their efficacy for removing taste and odour problems has been produced by McGuire (1999). The following treatment technologies were considered:

- adsorption
- oxidation
- membrane technology
- biological treatment

Oxidation has traditionally been used as a method for solving taste and odour problems in water treatment plants. Whilst chlorine or other oxidants are primarily applied for the purposes of disinfection, they can also be used for oxidation of residues responsible for taste and odour. However, it is well known that oxidants, particularly free halogens that are used as water disinfectants can produce undesirable tastes and odours in water. The taste (often now referred to as flavour in standard panellist tests) and odour thresholds for some chlorine species and chloramines are shown in Table 5.1. .

Table 5.1 Detection thresholds for chlorine species and chloramines (Krasner and Barrett 1985)

Chemical	Odour threshold mg l^{-1}	Flavour (or taste) threshold mg l^{-1}
Hypochlorous acid	0.28	0.24
Hypochlorite ion	0.36	0.30
Monochloramine	0.65	0.48
Dichloramine	0.15	0.13
Trichloramine	0.02	Not determined

Whilst chlorine, chlorine dioxide, ozone and potassium permanganate can all be used to oxidise odorous residues, and also have the advantage that they also act as disinfectants they are not effective against all types of causative chemicals and oxidation is generally not effective for removing musty odours. Potassium permanganate has been widely used on the USA and it is applied before filtration as it is reduced to form manganese oxides which help to remove odours. The use of potassium permanganate for taste and odour control appears to be chemical specific and it will not oxidise tertiary alcohols such as geosmin and MIB (McGuire 1999); Suffet et al. 1995).

Laboratory tests on the removal of two well known chemicals which impart earthy/musty odours, namely geosmin and 2-methylisoborneol (MIB) using activated carbon have shown the method to be more effective than oxidation. (Evins et al. 1990; Gillogly et al. 1996). Unlike oxidation which transforms the odorous chemical adsorption removes the residue from the water. Activated carbon is most commonly used in powdered form (PAC) and is added as a slurry into the water stream either before sedimentation or before rapid filtration. Granular activated carbon (GAC) is usually applied after filtration in purpose built adsorbers and is a more expensive treatment process. The major advantage of PAC is that it can be applied only when a problem arises, it is cheaper per unit weight and extensive plant construction is not required. The use of GAC in beds generally provides a larger proportion of the adsorptive capacity than can be achieved using PAC dosed into sedimentation tanks. In addition GAC can be regenerated and reused whereas PAC has to be disposed of as part of the waterworks sludge.

6. POINT OF USE DEVICES

Point of use devices (POUs) are treatment systems installed at consumers taps and are intended to treat water for drinking and cooking. Point of entry devices are installed on the main water supply and treat all the water entering the premises.

In recent years POUs have become common household appliances which are regarded both as devices to protect the consumer from a perceived risk from harmful residues present in drinking water and to improve general aesthetic quality (i.e. appearance, taste and odour). Data from the Toronto Community Health surveys reported household usage of PoUs in Toronto increased from 4% in 1981 to 19% in 1988 (Auslander and Langlois 1993). The data from the Canadian 1988 consumer telephone survey is shown in Table 6.1.

Table 6.1 Point of use devices and domestic application in 200 Toronto domestic households (Auslander and Langlois 1993)

Characteristics of use	Regular users to whom this applies (n=20)	Percentage
Use of treated water		
• As drinking water	19	95%
• Making hot beverages	18	90%
• Making cold beverages	19	95%
• Preparing baby food	6	30%
• Other cooking purposes	19	95%
• Other uses (washing etc)	19	55%
Preference over tap water		
• Health reasons	18	90%
• Aesthetic reasons (e.g. taste and odour)	7	35%
• Other reasons (e.g. washing)	0	0%

Characteristics of use	Regular users to whom this applies (n=20)	Percentage
Process of PoU device		
• Activated carbon	12	60%
• Reverse osmosis	2	10%
• Distillation	2	10%
• Ceramic filter	1	5%

Various types of PoUs are used to improved the aesthetic qualities of drinking water and to remove chemical residues. The most common devices incorporate activated carbon filters, which are intended to remove organic chemicals and to improve the taste, smell and appearance of drinking water.

It is possible that the activated carbon filters used in PoUs could, without taking precautions, become a source of contamination in product water. If PoUs are used over extended periods the filter could become saturated with contaminants resulting in sudden breakthrough into the finished drinking water at levels higher than in the source water. The Quality Water Group of British Water have provided recommendations regarding the service life of point of use devices containing activated carbon. In practice such problems can be avoided by regular replacement of filter cartridges although specific data on GAC cartridge capacities for chemicals responsible for taste and odour, other than chlorine, is not available in the literature. Manufacturers generally express the performance of such products in terms of ‘rated in service life’ and ‘rated capacity’. Some manufacturers may claim different rated capacities for different chemicals (i.e. substance-specific capacities) whilst the rated life of the filter would be given as the smallest substance-specific capacity. Alternatively, the rated life could also mean the maximum usage period or maximum influent water volume between cartridge changes that might be recommended to prevent microbial growth, independent of chemical reduction capacity.

The growth of bacteria or attendant production of odorous chemicals in PoUs is unlikely to be significant provided devices are properly maintained and cartridges are changed regularly (Schubert et al. 2000 ; G. Stanfield personal comm. 2001).

A range of other techniques are used in PoUs primarily for removing chemical residues from drinking water. These include:

- Reverse osmosis
- Aluminium oxide
- Ion exchange
- Distillation

The most widely used point of entry devices are water softeners which are intended to prevent limescale formation in pipes, water heaters and kettles. However, the purpose of these devices is not related to any perceived health concerns.

Contacts at 8 PoU device manufacturers and 4 GAC filtration media producers were approached to request any information specifically relating to their performance of their products for taste and odour removal (Table 6.4). Manufacturers were asked to provide any information on the removal of specific chemicals known to cause taste and odour problems in drinking water.

The responses received from manufacturers have indicated that very little research results are available which specifically relate to the removal of odorous organic chemicals from drinking water.

Although many organic chemicals could be used to test the efficacy of GAC to remove odorous residues PoU manufacturers have simply concentrated on improving their products' abilities to reduce free chlorine levels from waters to indicate their effectiveness in reducing T&O complaints. Unfortunately procurement of other data directly related to the reduction of organic chemical residues by POU products was not successful. Apart from the practicality of using chlorine residual removal as a surrogate for ‘taste and odour’ residue removal in general, the analytical costs associated with testing GAC products for reduction of a diverse range of trace organic chemicals would be considerable.

Although it is generally assumed that PoUs based on activated carbon will remove many organic chemicals responsible for taste or odour problems from challenge waters no data was available from manufacturers to confirm this. The removal of some of the highly polar organic chemicals that may cause taste and odour problems by activated carbon may be less effective than for more hydrophobic chemicals. For example, chemicals such as 2-ethyl-5,5’-dimethyl-1,3-dioxane (EDD), 2-butoxyethanol and 2,2-dimethyl-1,3-propane-diol, which were responsible for the Wem incident have low log K_{ow} values and have very high solubilities (Table 6.2). Other structurally similar chemicals have been identified as causing taste and odour incidents in the U.S.A. (Ives et al. 1994). However, further experimental investigations would be required to determine the efficiency of activated carbon removal of taste and odour chemicals with a range of physicochemical properties. Removal tests would best be carried out by using ^{14}C-radiolabelled surrogate chemicals and scintillation counting for the higher solubility chemicals at low concentrations. However, solvent extraction or SPE and GCMS would be appropriate for the more hydrophobic chemicals.

Table 6.2 Hydrophobicities and solubilities of chemicals responsible for the Wem Incident 1994

Chemical	Log Kow	Solubility
2,ethyl-5,5'-dimethyl-1,3-dioxane (EDD)	2.63	455 mg l^{-1} (25°C)
2-butoxyethanol	0.57	60,000 mg l^{-1} (25°C)*
2,2-dimethyl-1,3-propane-diol	0.16	80,000 mg l^{-1} (25°C)*

* compounds effectively miscible with water

ANSI/NSF Standard 42 –2001 presents minimum requirements for materials, design, construction and performance of drinking water treatment units that are designed to reduce specific aesthetic-related contaminants in public or private water suppliers. The Standard includes guidance on specific physical testing, pressure testing and hydrostatic testing of pressure vessels. However, under ANSI/NSF Standard 42 qualification for taste and odour reduction claims are only allowed for activated carbon systems and for free chlorine reduction as classified in Table 6.3. Although there is a provision in ANSI/NSF Standard 42 for testing products for chloramine reduction claims, results from such tests are not allowed to be used to claim any associated taste and odour reduction.

Table 6.3 NSF/ANSI Standard 42 classification of activated carbon products in terms of chlorine reduction

Class	Percentage reduction in free available chlorine (FAC)
I	>=75%
II	50-74%
III	25-49%

The dechlorinating action of activated carbon can be represented by the following mechanism (Eurocarb Technical Information Report):

$$C^* + HOCl \rightarrow C^*O + H^+ + Cl^-$$

Where C* is a reactive site within the internal surface of the carbon particle and C*O is a surface oxide. The surface oxides formed during the dechlorination process are unstable and decompose to form carbon dioxide i.e.

$$2C^*O \rightarrow C + CO_2$$

The efficiency with which GACs remove chlorine residues will depend on other factors such as :

- The presence of dissolved organic compounds will reduce the carbon surfaces effectiveness because their adsorption will reduce the number of active sites available for dechlorination.
- Dechlorination efficiency decreases with increasing pH.
- Dechlorination efficiency increases with increasing temperature.

The efficiency with which a GAC can remove chlorine can be quantified using the dechlorination half-value test (DIN 19603). This method determines the bed depth of activated carbon required to halve the chlorination for a given flow rate.

$$D = \frac{h \times \sqrt{v}}{\log 2} \times \log \frac{Co}{C}$$

where D = bed depth (cms)

v = flow rate (cm sec^{-1})

h (dechlorination half value for v = 1 cm sec^{-1})

Co = original chlorine concentration

C = product water chlorine concentration

Table 6.4 Point of Use device and filter media (GAC) manufacturers approached for information on performance data

Company/Organisation
Amway Corporation
Brita Corporation and Brita GmbH
European Bottled Water Association
US Filter
Carbonit Filtertechnik
Sutcliffe Speakman carbons Ltd
Eurocarb Products Ltd
Kenwood
KX Industries L.P.

Six responses were received and a summary of the testing procedures used or recommended which specifically relate to taste and odour removal is given in Table 6.5.

Table 6.5 Summary of GAC testing procedures identified by manufacturers

ORGANISATION	TESTING
Carbonit	Simple in-house methylene blue and garlic removal tests
KX Industries	Chlorine removal tests
AMWAY	Chlorine removal (presumption of organic residue removal)
Regunathan and Associates	Free chlorine reduction tests (as surrogate for removal of all T & O residues)
European Bottled Water Association	Chlorine removal tests
Eurocarb	Residual free chlorine tests

7. CASE HISTORIES

Bruchet (1999) investigated 140 analytical reports relating to taste and odour incidents mainly at Lyonnaise des Eaux water treatment works between 1994 and 1997. The main purpose of the investigations was to identify the causative agents and to provide advice on treatment modifications. Of the 140 reports, only 72 were regarded as being sufficiently well documented. The taste and odour incidents included problems with raw ground and surface waters, treated drinking waters and some bottled waters and the incidents were classified according to the dominant descriptors reported by panellists and as a percentage of the total (Figure 7.1). Four main odour groups were identified on the flavour wheel, including medicinal-phenolic (32%), earthy-musty-mouldy (25%), chemical-hydrocarbon-miscellaneous (24%) and chlorinous-ozonous (10%). Although no data were given, the author noted that the relative contributions from each taste from the study of panellist data did not accurately match the relative proportions of tastes and odours as reported in customer complaints. This may have been due to different perceptions of taste and odours between consumers and trained panellists, or the reporting of consumer complaints using inappropriate descriptors. However, it is interesting to note that taste panellist reports of 'chlorinous' episodes only represented 10% of the total number of incidents. This low percentage could also be influenced by the fact that chlorinous episodes may be difficult to recognise after sample transportation. The identities of some of the chemicals reported as being responsible for the tastes and odours are shown in Table 7.1.

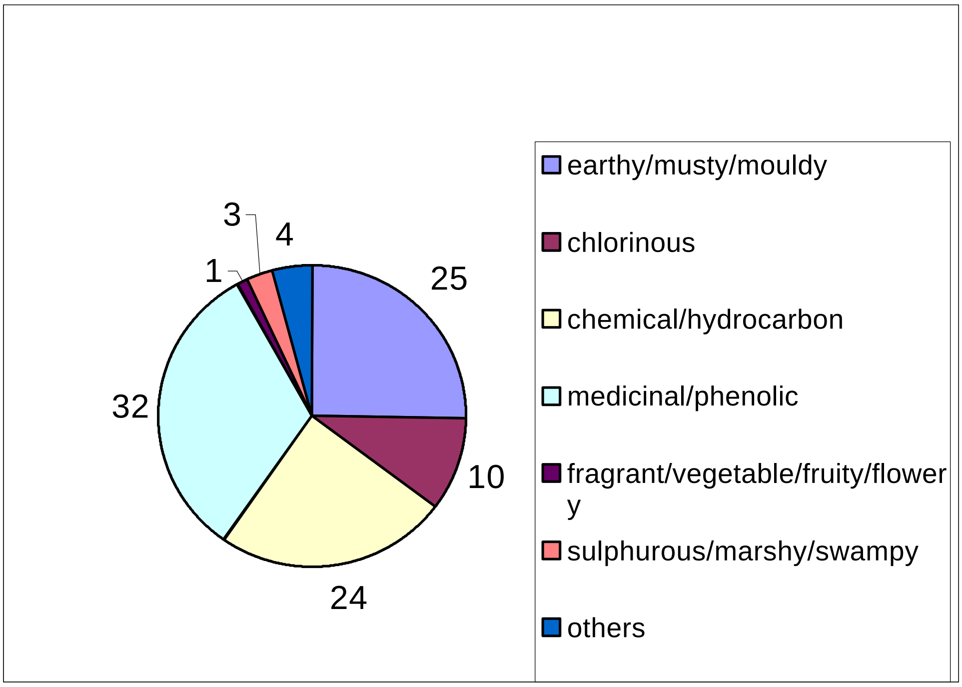

Figure 7.1 **Classification and percentage proportions of taste and odour episodes between 1994-97 using the flavour wheel (from Bruchet 1999)**

Table 7.1 Summary of recent survey of chemicals responsible for selected taste and odour episodes in France from 1994-1997 (Bruchet 1999)

Taste and odour descriptor	Total no. of episodes	Chemicals identified as responsible	No. episodes attributed to this chemical	Concentration detected	Taste and odour threshold
Earthy-musty-muddy	21	Geosmin or methylisoborneol	8	1-47 ng l^{-1}	1-10 ng l^{-1}
		2,3,6- and 2,4,6-trichloroanisole	5	1-80 ng l^{-1}	7 ng l^{-1}
		unknown	8	-	-
Chlorinous	7	Chlorine residual	1	0.25 ppm	0.15 ppm
		Unknown	6		

8. CONCLUSIONS

1. Tastes and odours are major factors influencing the consumers' perception of drinking water quality. Consumers generally believe that if their drinking water tastes or smells 'off ', then it is probably not safe to drink. Assessments of consumer survey data following taste and odour incidents indicate that the reporting of symptoms or health problems can in some cases be related to psychological factors or anxiety caused by an incident rather than to any actual toxic effects from the contamination. Higher rates of reported symptoms could be attributed to the consumers' ability to detect an unusual taste or smell, rather than to a toxic effect of the chemical contamination. These findings highlight the seriousness of effects of taste and odour incidents in undermining consumer confidence. Consumers often simply associate 'off-taste' in drinking water with potential for health effects.

2. Water companies are largely successful in meeting the requirements of the Regulator in terms of providing water free from harmful chemical contaminants as defined by the limits set in the Water Supply (Water Quality) Regulations. However, the consumers' yardstick for 'safe' is largely based on aesthetic qualities and it is on this basis that they tend to judge drinking water quality.

3. There does not appear to be any direct relationship between taste and odour and effects on health. Some chemicals are toxic at concentrations in water which do not produce characteristic taste or odour, whereas chemicals such as chlorophenols are typically detected by consumers at concentrations well below those likely to result in health effects.

4. Some chemicals responsible for taste and odour incidents can be detected by consumers at very low concentrations (ng to $\mu g\ l^{-1}$) which are below any level which could be of health concern. However, the absence of a detectable taste or odour in drinking water does not necessarily indicate that consumers are not exposed to undesirable contaminants in drinking water.

5. In many cases, the precise cause of taste and odour problems is not established. This is often because water samples contemporary with the incident are not available or because the event was ephemeral. More rapid sample screening and identification of the extent and causes of taste and odour problems would be achieved by the use of integrating sample preconcentration techniques such as solid phase extraction (SPE) and solid phase micro-extraction with mass spectrometry (SPME-GCMS). There is considerable scope for assessing the utility of different SPME microextraction fibres for target suites of taste and odour compounds from both natural and anthropogenic sources.

6. Significant discrepancies between the taste and odour descriptors used by consumers and those provided by trained taste and odour panellists can result in misleading data on which to base taste and odour investigations. Consumers' may recognise off-flavours, but are in many cases ill-equipped to provide accurate

descriptors. A combination of the use of trained panellists and rapid analytical screening methods would enable more effective taste and odour identification.

7. The number of customer complaints relating to taste and flavour of drinking water which can be directly attributed to problems with washing machine supply hoses is significant. These problems would be reduced by enforcing the use of non-metallic fittings tested to BS6920 and approved by WRAS or by a check valve immediately upstream of the hose.

   Some taste and odour problems are caused or exacerbated by cold water pipes being unduly warmed especially by undue proximity to hot water pipes. Standard (9 mm) insulation to a cold water pipe is sufficient to prevent undue heat again, providing any adjacent hot water pipe is as a minimum, similarly insulated. Dead ends can also lead to taste and odour problems and should be minimised.

8. Although many WRAS recommendations relate to good plumbing practice during pipe and appliance installation in domestic premises, these activities are effectively outside the direct control of water companies. The recent implementation of the Water Industry Approved Plumbers' Scheme (WIAPS) may improve plumbing practices in domestic premises and avoid some taste and odour problems which result within consumers' premises. However, it is likely that improvements will have most impact in new premises or installations.

9. Although it is generally assumed that PoUs based on activated carbon will remove many organic chemicals responsible for taste or odour problems from challenge waters no specific data was available from manufacturers to confirm this. Claims for taste and odour removal using PoUs are generally only supported by tests to establish 'free chlorine' reduction.

10. The removal of some of the highly polar organic chemicals that may cause taste and odour problems by activated carbon may be less effective than for more hydrophobic chemicals (e.g. ethers and diols responsible for the Wem incident which commonly have very high solubilities and are effectively miscible with water). Further investigations are required to determine the efficiency of activated carbon removal of taste and odour chemicals with a range of physicochemical properties. Removal tests would best be carried out by using ^{14}C-radiolabelled surrogate chemicals and scintillation counting for the higher solubility chemicals at low concentrations.

11. The development of strategies or 'tool-kits' for water companies to enable better prevention, identification and optimised treatment for specific taste and odour problems could result in swifter resolution of taste and odour incidents and maintain better public relations. 'Tool-kits' could include operational monitoring or screening methods for taste and odour chemicals, micro-organisms identification methods, optimisation of removal techniques, and intake protection methods. The use of 'surrogate' chemical indicators for identification of causative organisms may also be applicable. Although GAC has been widely used for contaminant removal from drinking water there is scope for better optimisation of this technique solely for taste and odour removal applications.

ANNEX A – TASTE & ODOUR THRESHOLD CONCENTRATIONS FOR SPECIFIC ORGANIC CHEMICALS (YOUNG ET AL. 1996)

Table 1 - Odour threshold concentrations for specific organic chemicals (Young et al. 1996)

N.B. although odour thresholds are reported this does not necessarily indicate that they have been identified as causing taste or odour problems in drinking water.

Chemical	Panel size	Geometric mean odour threshold concentration ($\mu g\ l^{-1}$)	Lowest concentration at which an odour was detected ($\mu g\ l^{-1}$)
Pesticides			
Atrazine	8	N.D.	9200 (3)
Bromoxynil	8	N.D.	>11000
Carbaryl	8	280 (5)	37 (1)
Chlorfenvinphos	8	340 (5)	240 (3)
Chlormequat dichloride	8	N.D.	>8700
Chlortoluron	8	N.D.	>9000
Diazinon	9	170 (7)	40 (1)
Dichlobenil	9	200 (3)	40 (1)
Dichlorprop	8	N.D.	>9100
Diquat dibromide	8	N.D.	>8900
Diuron	8	N.D.	>8000
Isoproturon	8	N.D.	>8000
Linuron	8	N.D.	>9700
Maleic hydrazide	8	N.D.	>9900
MCPA	8	-	460 (1)
MCPB	8	N.D.	>10000
Mecoprop	8	N.D.	>8100
Paraquat dichloride	8	N.D.	>8600
Pirimicarb	8	N.D.	>1100
Propyzamide	8	3000 (6)	700 (1)
Phenolic and anisole compounds			
4-chloroanisole	8	20 (8)	<2 (1)
4-chloro-2-methylphenol	7	200 (6)	62 (1)
4-chloro-3-methylphenol	9	5 (8)	2.5 (3)
2-chloro-4-methylphenol	9	0.3 (7)	0.15 (4)
2-chlorophenol	8	0.4 (6)	0.09 (2)
4-chlorophenol	9	20 (8)	10 (3)

Chemical	Panel size	Geometric mean odour threshold concentration ($\mu g\ l^{-1}$)	Lowest concentration at which an odour was detected ($\mu g\ l^{-1}$)
2,4-dichloroanisole	9	0.5 (9)	0.2 (3)
2,4-dichlorophenol	8	29 (4)	5 (1)
2,6-dichlorophenol	8	22 (8)	6 (3)
Pentachlorophenol	9	23 (3)	9 (1)
Phenol	9	31 (7)	10 (2)
2,4,6-trichloroanisole	6	0.0009 (6)	0.00008 (1)
2,4,5-trichlorophenol	10	350 (9)	63 (1)
2,4,6-trichlorophenol	8	-	380 (1)
Naturally occurring organic compounds			
Geosmin	10	0.0038 (10)	0.0013 (4)
2-isobutyl-3-methoxypyrazine	8	0.001 (8)	<0.00005 (1)
2-isopropyl-3-methoxypyrazine	6	0.0002 (6)	<0.00003 (2)
2-methyl-isoborneol	10	0.015 (10)	0.0063 (2)
Other organic compounds			
Benzene	10	-	190 (8)
Chlorobenzene	8	-	190 (6)
Chloroform	9	30000	7500 (1)
2-chlorotoluene	9	-	980 (2)
3-chlorotoluene	7	500	150 (1)
4-chlorotoluene	10	150	60 (3)
1,2-dichlorobenzene	9	-	200 (2)
1,3-dichlorobenzene	8	170 (7)	77 (1)
1,4-dichlorobenzene	9	18 (8)	4.5 (2)
Ethyl benzene	8	550 (8)	150 (1)
Isopropylbenzene	9	70 (7)	10 (1)
4-isopropyltoluene	9	400 (8)	25 (1)
Methyl-t-butyl ether	9	34 (7)	15 (3)
Naphthalene	9	6 (9)	2.5 (2)
Styrene	8	65 (5)	37 (2)
Toluene	8	-	960 (5)
1,1,1-trichloroethane	9	20000 (5)	3200 (1)

N.D. = not detected
Number of panellists detecting an odour in parentheses.

Table 2 - Taste threshold concentrations for specific organic chemicals (Young et al. 1996)

N.B. although taste thresholds are reported this does not necessarily indicate that they have been identified as causing taste or odour problems in drinking water.

Chemical	Panel size	Geometric mean taste threshold concentration (µg l^{-1})	Lowest concentration at which a taste was detected (µg l^{-1})
Pesticides			
Atrazine	8	N.D.	20 (1)
Carbaryl	8	140 (5)	44 (1)
Chlorfenvinphos	8	N.D.	3.6 (1)
Chlormequat dichloride	8	N.D.	>1400
Chlortoluron	8	N.D.	>740
Diazinon	9	N.D.	>55
Diquat dibromide	8	N.D.	>56
Isoproturon	8	N.D.	37 (2)
Maleic hydrazide	8	N.D.	9900 (1)
MCPA	8	N.D.	4.1 (1)
MCPB	8	N.D.	>950
Mecoprop	8	N.D.	>650
Paraquat dichloride	8	N.D.	>28
Pirimicarb	8	N.D.	>580
Phenolic and anisole compounds			
4-chloroanisole	8	10 (7)	6.2 (4)
4-chloro-2-methylphenol	7	10 (4)	2.5 (1)
4-chloro-3-methylphenol	9	9 (9)	2.5 (1)
2-chloro-4-methylphenol	9	0.3 (7)	<0.05 (1)
2-chlorophenol	8	0.97 (6)	0.14 (1)
4-chlorophenol	9	62 (2)	39 (1)
2,4-dichloroanisole	9	0.4 (8)	0.08 (1)
2,4-dichlorophenol	8	2.5 (4)	0.98 (2)
2,6-dichlorophenol	9	0.02 (7)	0.006 (2)
Pentachlorophenol	9	N.D.	8 (1)
Phenol	8	N.D.	<2 (1)
2,4,6-trichloroanisole	8	0.05 (8)	0.025 (4)
2,4,5-trichlorophenol	10	N.D.	100 (2)
2,4,6-trichlorophenol	8	N.D.	>12
Naturally occurring organic compounds			
Geosmin	10	0.016 (8)	0.0075 (2)
2-isobutyl-3-methoxypyrazine	8	0.003 (8)	0.0004 (1)

Chemical	Panel size	Geometric mean taste threshold concentration ($\mu g\ l^{-1}$)	Lowest concentration at which a taste was detected ($\mu g\ l^{-1}$)
2-isopropyl-3-methoxypyrazine	7	0.02 (7)	0.009 (4)
2-methyl-isoborneol	10	0.018 (8)	0.0025 (1)
Other organic compounds			
Chlorobenzene	8	N.D.	190 (2)
Chloroform	9	2000 (4)	1200 (1)
2-chlorotoluene	9	N.D.	980 (2)
3-chlorotoluene	7	770 (4)	390 (1)
4-chlorotoluene	10	44 (3)	24 (1)
1,2-dichlorobenzene	9	N.D.	200 (1)
1,3-dichlorobenzene	8	N.D.	190
1,4-dichlorobenzene	9	32 (9)	11 (2)
Ethyl benzene	8	780 (8)	390 (2)
Isopropylbenzene	9	N.D.	60 (1)
4-isopropyltoluene	9	N.D.	>1000
Methyl-t-butyl ether	9	48 (5)	40 (4)
Naphthalene	9	50 (9)	25 (3)
Styrene	8	N.D.	94 (2)
Toluene	8	N.D.	960 (2)
1,1,1-trichloroethane	9	N.D.	1500 (1)
Inorganic compounds			
Aluminium sulphate	9 (a)	7400 (3)	4000 (1)
	9(b)	N.D.	>10000
Copper sulphate	9 (a)	N.D.	>990
	9 (b)	N.D.	>930

a) tested in soft water
b) tested in hard water
Number of panellists in parentheses

9. REFERENCES

Anselme C. and Suffet I.H. and Mallevialle J. (1988). Effects of ozonation on tastes and odours. JAWWA, 45-51.

ANSI/NSF 42 – 2001. Drinking water treatment units – Aesthetic effects. American National Standard/NSF International Standard.

Auslander B.A. and Langlois P.H. (1993). Toronto Tap water : Perception of its quality and use of alternatives. Canadian J. of Public Health, 84, 2, 99-102.

Barcelo D. Environmental Protection Agency and other methods for the determination of priority pesticides and their transformation products in water. *J. of Chromatog*. 1993; 643: (1/2), 117-143.

Berglind L., Holtan H. and Skulberg O.M. (1983). Case studies on off-flavours in some Norwegian lakes. Wat. Sci. Tech. 15(6/7), 199-209.

Blevins W.T., Schrader K.K. and Saadoun I. (1995). Comparative physiology of geosmin production by *Streptomyces Halstedii* and *Anabena Sp*. Wat. Sci. Tech. 31, 11, 127-133.

Bruchet A. (1999). Solved and unsolved cases of taste and odour episodes in the files of inspector Cluzeau. Wat. Sci. Tech. Vol. 40, No.6, 15-21.

Canter L.W., Nelson D.I. and Everett J.W. (1992-93). Public perception of water quality risks – influencing factors and enhancement opportunities. J. Environmental Systems, Vol. 22(2), 163-187.

Cognet L., Jacq P. and Malleviale J. (1986). Surface water quality monitoring : the Mont Valerien alarm station. Eau Industries Nuisances, 105, 31-34.

Cognet L., Jacq P. and Mallevialle J. (1987). Automatic monitoring of surface water quality: The warning station of the Le Mont Valerien Water Treatment Plant. Aqua, 1, 2-27.

Colbourne J.S. (1985). Materials usage and their effects on the microbiological quality of water supplies. Journal of Applied Bacteriology Symposium Supplement 1985, 47S-59S.

Dottridge J., Hall M. and Firth S. (2000). A review of current MTBE usage and occurrence in ground water in England and Wales. Komex Europe Research report for the Environment Agency ISBN 1 85705 399 0.

Evins C., Liebeschuetz J. and Williams S.M. (1990). Aesthetic water quality problems in distribution systems. A source document for the water Mains Rehabilitation Manual. Foundation for Water Research. ISBN

Farrimond M.S., Carr R.J., Crymble S., Platt A. and Sidhu S. (1995). “It may meet the standards, but do customers like to drink the water ?” AWWA Annual Conference and Exposition, Anaheim, California, 18-22 June 1995.

Font G, Manes J, Molto, JC and Pico Y. Solid-phase extraction in multi-residue pesticide analysis. *J. of Chromatog*. 1993; 642: (1/2), 135-161.

Gardner M.J., James H.A. and Watts C.D. (1995). A strategy for the identification of organic chemicals present in source and drinking waters following pollution incidents. WRc plc.

Gardner M.J., Rogers H.R. and Comber S.D.W. (2000). Solid phase extraction techniques for drinking water abstraction monitoring and investigation of pollution. Journal of Water Supply : Research and Technology - AQUA, 49.2, 103-109.

Gerber N.N. and Lechevalier H.A. (1965). Geosmin, an earthy-smelling substance isolated from Actinomycetes. Applied Microbiol. 13, 935.

Harland B.J., Nicholson P.J.D. and Gillings E. (1987). Determination of volatile organic compounds in aqueous systems by membrane inlet mass spectrometry. Wat. Res. 21(1), 107-113.

Hayes K.P. and Burch M.D. (1989). Odorous compounds associated with algal blooms in South Australian waters. Wat.Res. 23, 115-121.

Ives K.J., Hammerton D. and Packham R.F. (1994). The River Severn Pollution Incident of April 1994 and its impact on Public Water Supplies. Report for Severn Trent Water Ltd, 11 August 1994.

Izaguirre G. and Taylor W.D. (1995). Geosmin and 2-methylisoborneol production in a major aqueduct system. Wat. Sci. Tech. Vol. 31, No. 11, pp. 41-48.

Jardine C.G. , Gibson N. and Hrudey S.E. (1999). Detection of odour and health risk perception of drinking water. Wat. Sci. Tech. Vo. 40, No.6, 91-98.

Johnson J.D. and Jensen J.N. (1986). THM and TOX formation : routes, rates and precursors. JAWWA, 78, 156-162.

LaPack M.A. and Tou J.C. (1991). Membrane extraction mass spectrometry for the on-line analysis of gas and liquid process streams. Anal. Chem. 63, 1631-1637.

Laine J.M., Baudin I. And Chevalier M.R. (1997). Performance of the Cristal Process for removal. 5th International Symposium on off-flavours in the aquatic environment. 13-16 October 1997, Paris, France. IAWQ.

Lundgren B.V., Grimvall A. and Savenhed R. (1988). Formation and removal of off-flavour compounds during ozonation and filtration through biologically active sand filters. Wat. Sci. tech. 20, 8/9, 245-253.

Mallevialle J. and Suffet I.H. (1987). Identification and treatment of taste and odours in drinking water. American Water Works Association Research Foundation, Lyonnaise des Eaux. ISBN 0-89867-392-5

McGuire M.J. (1995). Off-flavour as the consumer's measure of drinking water safety. Wat. Sci. Tech. 31, 11, 1-8.

McGuire M.J. (1999). Advances in treatment processes to solve off-flavour problems in drinking water. Wat. Sci. Tech. Vol. 40, No. 6, 153-163.

Nystrom A., Grimvall A., Krantz-Rulcker C., Savenhed R. and Akerstrand K. (1992). Drinking water off-flavour caused by 2,4,6-trichloroanisole. Wat. Sci. Tech. 25, 2, 241-249.

Preti G., Gittelman T.S., Staudte P.B. and Luitwieler P. (1993). Letting the nose lead the way: malodorous compounds in drinking water. Analyt. Chem. 65(15), 699-702.

Rennie P.J. (1987). Chromatography in the analysis of water: monitoring phenol in river water using automated HPLC. Analytical Proceedings, 24(10), 295-297.

Rigal S. and Danjou J. (1997). Taste and odour episodes in drinking water distribution systems in relationship with the use of synthetic materials. 5th International Symposium on off-flavours in the aquatic environment, Paris, 13-16 October 1997. IAWQ.

Rogers H.R. (1997). Influence of suspended solids and back diffusion on organic contaminant uptake by semi-permeable membranes (SPMDs). Chemosphere, 35, 8, 1651-1657.

Rogers H.R. and Comber S.D.W. (1998). Solid-phase micro-extraction (SPME) fibre performance in turbid aqueous samples. Chemosphere, 37, 8, 1413-1418.

Sablic A. (1984). On the prediction of soil sorption coefficients of organic pollutants from molecular structure: application of molecular topology model. Environ, Sci. Technol. 21, 358-366.

Safferman R.S. (1967). Earthy-smelling substances from a blue-green alga. Environ. Sci. Technol. 1, 429.

Schubert R.W., Fricker C. and Delattre J.M. (2000). 'Bacterial regrowth in post-treatment devices'.

Shirey RE. Fast analysis of environmental samples, using solid phase microextraction (SPME) and capillary GC. Recent developments in separation technologies. *Supelco reporter* 1994; 13:(5), 2-4.

Shirey R, Mani V and Butler M. Solid Phase Microextraction of alcohols and polar analytes for capillary GC. *Supelco reporter* 1995; 14: (5), 4-5.

Stocking A.J., Suffet I.H., McGuire M.J. and Kavanaugh M.C. (2001). Implications of an MTBE odour study for setting drinking water standards. JAWWA, March 2001, 95-105.

Suffet I.H., Khiari D. and Bruchet A. (1999). The drinking water taste and odour wheel for the millennium: beyond geosmin and 2-methylisoborneol. Wat. Sci. Tech. Vol. 40, No. 6, 1-13.

Suffet I.H., Mallevialle J. and Kawczynski E. (1995). Advances in Taste and odour treatment and control. American Water Works Association Research Foundation Lyonnaise des Eaux. ISBN 0-89867-744-0

Taylor P.B. (2000). Advisory report to the Drinking Water Inspectorate Secretary of State's Specifications for flexible hose supplies. Report No. DETR/DWI 11841-1, 21 December 2000.

Thorell B., Boren H., Grimvall A., Hystrom A. and Savenhed R. (1992). Characterization and identification of odorous compounds in ozonated waters. Wat. Sci. Tech. 25, 2, 139-146.

Ventura F., Matia L., Romero J., Boldez M., Marti I. and Martin J. (1998). Taste and odour events in Barcelona's water supply. Wat. Sci. Technol. 31(11), 63-68.

Walker CC, Lott HM and Barker SA. Matrix solid-phase dispersion extraction and the analysis of drugs and environmental pollutants in aquatic species. *J. of Chromatog*. 1993; 642: (1/2) 225-242.

Watson S.B., Brownlee B., Satchwill T. and McCauley E. (1999). The use of solid phase microextraction (SPME) to monitor for major organoleptic compounds produced by chrysophytes in surface waters. Wat. Sci. Tech. Vol. 40, No. 6, 251-256.

Warren I. (1989). In-situ epoxy resin lining – Operational Guidelines and Code of Practice. A source document for the Water Mains Rehabilitation Manual. Water Research Centre plc.

Whang C-W and Pawliszyn J. Solid phase microextraction coupled to capillary electrophoresis. *Anal. Commun*. 1998; 35: 353-356.

Wnorowski A.U. and Scott W.E. (1992). Incidence of off-flavours in South African surface waters. Wat. Sci. Tech. 25, (2), 225-232.

WRAS (2000). Water Regulations Guide, First Edition. Water Regulations Advisory Scheme.

Yagi M., Kajino M., Matsuo U., Ashitani K., Kita T. and Nakamura T. (1983). Odour problems in Lake Biwa. Water Sci. Tech. 15(6/7), 311-321.

Young W.F., Lacey R.F., Fawell J.K. and Coggon D. (1995). Assessing the value of epidemiological studies of acute chemical contamination incidents affecting drinking water. WRc report to DoE No. EPG 1/9/65

Young W.F., Horth H., Crane R., Ogden T. and Arnott M. (1996). Taste and odour threshold concentrations of potential potable water contaminants. Wat. Res. 30, No.2, 331-340.

Zhang Z and Pawliszyn J. Headspace solid-phase microextraction. *Anal. Chem*. 1993; 65: 1843-1852.