

EXPOSURE TO ENDOCRINE DISRUPTORS *VIA*
MATERIALS IN CONTACT WITH DRINKING WATER

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Exposure to Endocrine Disruptors *via* Materials in Contact with Drinking Water

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

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ENDOCRINE DISRUPTORS

EXECUTIVE SUMMARY

Recently there has been much media and public concern about the potential health effects of so-called endocrine disruptors. Many commonly used industrial chemicals are now considered to be endocrine disruptors and some are used in the manufacture of materials for use in contact with drinking water. Although, it is generally believed that drinking water is not a significant route of human exposure to endocrine disruptors, it is prudent to investigate the potential of materials in contact with drinking water to leach endocrine disruptors into drinking water.

In order to select endocrine disruptors for this study the following steps were taken:

1. A literature study was undertaken to find compounds reported to show endocrine disrupting properties, this list is given in Appendix A.
2. Chemicals were then rejected from this list if:
 - the evidence was considered clearly insufficient to show endocrine disruption;
 - they were not considered to be in common use in materials used in contact with drinking water.

The final list of chemicals is given in Table 2.1. Four groups of compounds were identified, namely: phthalates; bisphenols; alkyl phenols; alkyl phenol ethoxylates and polyethoxylates. Manufacturers were contacted to find out whether their products contained any of these chemicals.

It became apparent that a variety of materials used in contact with drinking water contain chemicals that are currently suspected to be endocrine disruptors. Most of these materials were site-applied products.

In all cases, when the materials were tested in the laboratory, any detected levels of endocrine disruptors were found to decrease over time. However, relating the laboratory leaching test results to worst case concentrations in actual drinking water was difficult. What constituted a worst case, in terms of the surface area in contact with water, the contact time and whether any high initial leaching would be flushed to waste was not always clear.

The indications were that after initially high short-term leaching, concentrations would be very low and probably negligible. However, at least one product requires further, more detailed, consideration.

Field testing of epoxy resins showed that long-term leaching, again sometimes after relatively high short-term leaching, was very low, usually not detectable. It would appear from these results that chronic exposure to suspected endocrine disruptors from materials in contact with drinking water is unlikely to be significant. However, initial exposure from newly installed products may require consideration of whether flushing procedures need to be modified.

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In addition, it may be appropriate to reconsider controls on the application of site-applied materials, such as the maximum area that may be treated, in a particular time frame, in relation to the volume of water in contact and residence times.

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1. INTRODUCTION

Recently there has been much media and public concern about the potential health effects of so-called endocrine disruptors. Many commonly used industrial chemicals are now considered to be endocrine disruptors and it is probable that some of these chemicals are used in the manufacture of materials for use in contact with drinking water. Although, it is generally believed that drinking water is not a significant route of human exposure to endocrine disruptors, it is prudent to investigate the potential of materials in contact with drinking water to leach endocrine disruptors into drinking water.

In order to assess any possible risk from endocrine disrupting chemicals in materials in contact with drinking water four factors must be considered:

- the toxicity of the chemicals;
- their use in materials in contact with drinking water;
- the prevalence of these materials;
- the rate at which the endocrine disruptor leaches from the material.

The possible endocrine disrupting chemicals are covered in the literature review in Section 2. Some of these are used in plastic materials in contact with drinking water.

The prevalence and use of these materials has been ascertained by writing to a number of manufacturers to ask for information on the use of the suspected endocrine disruptors in their materials and products. A summary of the results of this survey is given in Table 3.4.

It is possible that some of the endocrine disruptors in materials in contact with drinking water may cause contamination. Leaching tests in the laboratory and in the field have been carried out to find the leaching rate of the suspected endocrine disruptors into water.

2. ENDOCRINE DISRUPTORS

2.1 Endocrine disruption

The idea that substances which impact on the endocrine system could cause adverse effects at much lower doses than required for cytotoxic effects is not new (Fawell 1983). However, it was not until clear evidence emerged of adverse effects on reproductive development in wildlife exposed to chemicals in the environment, that the subject began to receive widespread attention. In man, there has been evidence presented of declining sperm quality and suggestions that male birth abnormalities such as cryptorchidism (undescended testes) and hypospadias (urethra opening on the underside of the penis), although there remains controversy over the extent of such changes. In addition, testicular and prostate cancer in men have been increasing in incidence for some time as has breast cancer in women (IEH 1995). Although there are many possible causes for these changes, including changes in lifestyle and diet, it has been suggested, by some scientists and pressure groups, that exposure to industrial chemicals which cause endocrine disruption is the major cause. There is no clear evidence to support this hypothesis at present but there is a considerable research effort being directed at the issue in many parts of the world and, in the meantime, there are increasing calls for a precautionary approach to be taken in regulating such chemicals.

Since a number of chemicals which are proposed as having endocrine disrupting properties are used in the manufacture of materials which come into contact with drinking water, it is appropriate to determine which substances are present in materials and to determine for which of these there is evidence that they possess endocrine disrupting properties.

2.2 Identification of chemicals with suspected endocrine disrupting properties

Endocrine disrupting properties can be identified in a number of ways. There are a number of *in vitro* assays which detect the ability of a substance to bind to a hormone receptor on a cell triggering a response indicated by a marker, or by blocking the binding of the natural hormone which would bind to that receptor. The assays available to date all relate to the reproductive hormones, oestrogens or androgens. Such tests are relatively simplistic and do not necessarily reflect the way that a substance behaves in the intact animal. However, they do identify potential activity.

There are also a number of *in vivo* assays and endpoints which can be examined in more traditional toxicity tests. These assays can reflect the impact of absorption, distribution and metabolism but there are often significant differences in metabolism between species, which require that great care is taken in extrapolating such data to man.

In order to prepare a priority list of chemicals from materials which would require closer attention, the following approach was used:

1. A literature study was undertaken to identify any substances which were reported to show endocrine disrupting activity. No attempt was made, at this stage, to weigh the balance of evidence where conflicting evidence existed. The search also represents a snapshot of the literature at a point in time since research is continuing and more data are emerging on a regular basis.
2. Chemicals were then rejected from the list if:
 - the published evidence was considered to be insufficient to determine whether endocrine disrupting properties had been shown.
 - they were not considered to be in common use in materials used in contact with drinking water.

The final list of substances is given in Table 2.1. It shows that four groups of compounds were identified, namely: phthalates; bisphenols; alkyl phenols; alkyl phenol ethoxylates and their polyethoxylates.

Table 2.1 Suspected endocrine disruptors of potential relevance to materials in contact with drinking water

Compound	Acronym
Alkyl phenols	
Butyl phenol	BP
Nonyl phenol	NP
Octyl phenol	OP
Pentyl phenol	PP
Butylated hydroxyanisole: 2,6-di-tert-butyl-4-methoxyphenol	BHA
Antioxidants based on alkyl phenols	AP
Alkyl phenols ethoxylates and polyethoxylates	
Nonyl phenol polyethoxylate	NPP
Nonyl phenol ethoxylate	NPE
Octyl phenol polyethoxylate	OPP
Octyl phenol ethoxylate	OPE
Bisphenols	
Bisphenol A: 2,2-Di-(4-hydroxyphenyl)propane	BisA
Bisphenol A diglycidyl ether:	BADGE
2,2-Di-(4-(2,3-epoxypropoxy)phenyl)propane	
Bisphenol F: Di-(4-hydroxyphenyl)methane	BisF
Bisphenol F diglycidyl ether:	BFDGE
Di-(4-(2,3-epoxypropoxy)phenyl)methane	

Compound	Acronym
Phthalates	
Bis(2-ethylhexyl) phthalate	DEHP
Butyl benzyl phthalate	BBP
Dibutyl phthalate	DBP
Diethyl phthalate	DEP
Di- <i>iso</i> -butyl phthalate	DIBP
Di- <i>iso</i> -decyl phthalate	DIDP
Di- <i>iso</i> -nonyl phthalate	DINP
Dimethyl phthalate	DMP
Ditridecyl phthalate	DTDP

2.3 Specific references to endocrine disrupting activity of the chemicals of potential relevance to materials in contact with drinking water

The following sections provide a number of published studies which report endocrine disrupting activity in either *in vitro* or *in vivo* assays. These are not critically reviewed but provide a basis for listing substances with suspected endocrine disrupting properties. Since research is continuing not all the more recent studies can be included. One difficulty of evaluating such data is the inability to replicate some studies such as the rat study by Sharpe *et al.* (1995) which included several different substances.

2.3.1 Alkyl phenols and their ethoxylates

Alkyl phenols and their derivatives are widely used as additives in a wide range of plastic materials and resins. The phenols and their ethoxylates have been identified in liquids in contact with plastics and have been tested for endocrine disrupting activity *in vitro* and *in vivo*. In particular alkyl phenols have been shown to contribute significantly to the induction of vitellogenin, an egg yolk protein under the control of oestrogen, in male rainbow trout. Care must be taken in interpreting the data from many of the assays in which alkyl phenols have been tested but the assays are listed in Table 2.2 and a comparison of oestrogenic potency from a study using a breast cancer cell line are given in Table 2.3. The comparison of potency using single doses is not advisable under normal circumstances since comparative potency can vary at different points of the dose response curve if these are not parallel, however these data give some indication of potency relative to 17 β -oestradiol. In general the parent alkyl phenols are the most potent oestrogens and the larger the derived molecule, the lower the activity.

Table 2.2 Endocrine disruption assays of alkyl phenols

Compound	Assay	Result	Reference
<i>p</i> -Nonyl phenol	<i>In vitro</i> binding to human sex hormone binding globulin	Positive	Arnold <i>et al</i> 1996 Danzo 1997
<i>p</i> -Nonyl phenol	<i>In vitro</i> inactivation of mouse HeLa uteri cells	Positive	Shelby <i>et al</i> 1996
<i>p</i> -Nonyl phenol	<i>In vivo</i> mouse uterine mass increase	Positive	Shelby <i>et al</i> 1996
<i>p</i> -Nonyl phenol	<i>In vivo</i> rat testes mass decrease	Positive	Sharpe <i>et al</i> 1995
<i>p</i> -Octyl phenol	<i>In vivo</i> rat testes mass decrease	Positive	Sharpe <i>et al</i> 1995
BHA: Butylated hydroxyanisole	<i>In vitro</i> proliferation of oestrogen sensitive cells	Positive	Soto <i>et al</i> 1995
BHT: Butylated hydroxytoluene	<i>In vitro</i> proliferation of oestrogen sensitive cells	Negative	Soto <i>et al</i> 1995

Table 2.3 Comparative oestrogenic activity of various alkyl phenols

Compound	Concentration (μM) ^a	Relative proliferative potency (%) ^b
17β-Oestradiol	0.00005	100
<i>m</i> -Octylphenol	0.1	0.03
<i>p</i> -Nonylphenol	1	0.003
<i>p-tert</i> -Pentylphenol	10	0.0003
Nonylphenol (technical grade)	10	0.0003
<i>p-iso</i> -Pentylphenol	10	0.0003
<i>p-sec</i> -Butylphenol	10	0.0003
<i>p-tert</i> -Butylphenol	10	0.0003
<i>p</i> -Propylphenol	10	-
<i>p</i> -Ethylphenol	10	-
Phenol	10	-

Note ^a Minimum concentration at which maximal cell yield is seen.

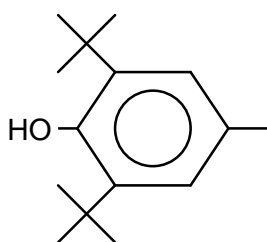
^b This value indicates the relative proliferative effect, compared to 17β-Oestradiol, taking concentration into account.
(Soto *et al.* 1995).

A large number of different antioxidants are used in polymeric material in contact with drinking water (such as plastic pipes). Many of these compounds contain alkylphenol

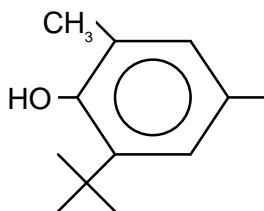
groups (Kiwa 1994, Munteanu *et al.* 1987). The structures of some of the more common alkylphenol antioxidants are shown in Table 2.4.

Table 2.4 Trade names and structures of some common alkyl phenol based antioxidants

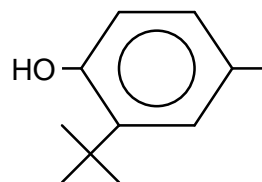
Trade name	Manufacturer	Structure
Ethanox TM 702	Ethyl Corp	RCH_2R
Irganox TM 1010	Ciba-Geigy	$C(CH_2COO(CH_2)_2R)_4$
Irganox TM 1024	Ciba-Geigy	$R(CH_2)_2CO(NH)_2CO(CH_2)_2R$
Irganox TM 1035	Ciba-Geigy	$S((CH_2)_2COO(CH_2)_2R)_2$
Irganox TM 1076	Ciba-Geigy	$R(CH_2)_2COOC_{18}H_{37}$
Irganox TM 245	Ciba-Geigy	$R^1(CH_2)_2COO((CH_2)_2O)_3CO(CH_2)_2R^1$
Topanol TM CA	I.C.I.	$R^2_2CHCH_2CHR^2CH_3$
Vulkanox TM BKF	Bayer A.G.	$R^3CH_2R^3$
TMB-6 TM	Societe Francaise d'Oran. Synthese	R^4SR^4
Irgafos TM 168	Ciba-Geigy	R^5_3P



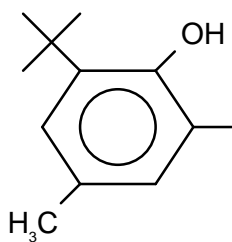
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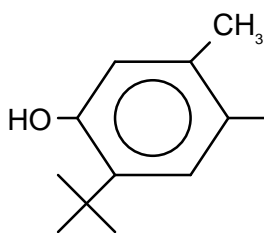
R¹



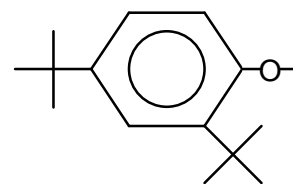
R²



R³



R⁴



R⁵

Note: (Munteanu *et al.* 1987)

Most modern antioxidants are of high molecular weight and low water solubility. In contact with food, plastics containing antioxidants, can exhibit low level leaching and chemical degradation during their working life (Schwope *et al.* 1987). Consequently, antioxidants and there degradation products, such as alkylphenol and dialkylphenol, may

leach into water in contact with materials containing them. The lack of data on the endocrine disruption properties of antioxidants and the nature of alkylphenol degradation products makes it difficult to identify compounds for study. Further testing of the endocrine disrupting character of antioxidants and their alkylphenol degradation products should be considered.

p-Alkylphenol ethoxylates and *p*-alkylphenol polyethoxylates (APE and APP) are industrial non-ionic surfactants used in paints and many other products (DEPA 1995). *p*-Alkylphenol hexaethoxylates are used as additives to concrete mixtures to act as air entrainers to prevent frost damage (Lawrence 1994).

2.3.2 Bisphenols

Three bisphenols are commonly used for the synthesis of polymers and epoxy resins; these are outlined in Table 2.5.

Table 2.5 Bisphenols used for the synthesis of polymers and epoxy resins

Bisphenol	Acronym	Chemical Name	Formula
Bisphenol A	BisA	2,2-Di-(4-hydroxyphenyl)-propane	$(\text{HOC}_6\text{H}_4)_2\text{C}(\text{CH}_3)_2$
Bisphenol F	BisF	Di-(4-hydroxyphenyl)-methane	$(\text{HOC}_6\text{H}_4)_2\text{CH}_2$
Bisphenol S	BisS	Di-(4-hydroxyphenyl)-sulphone	$(\text{HOC}_6\text{H}_4)_2\text{SO}_2$

Polycarbonate is formed by the reaction of BisA with phosgene (COCl_2) to produce a linear carbonic acid polyester. Polycarbonate is a clear, rigid and hard material with a high impact and tensile strength (Briston and Katan 1974).

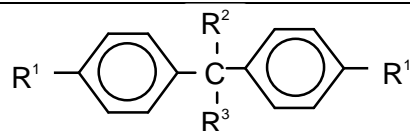
Polysulphone is formed by the condensation of BisA and BisS. It has similar properties to polycarbonate but can be used at temperatures in excess of 190 °C (Briston and Katan 1974).

Epoxy resins made from bisphenols are formed in two stages. Firstly BisA is reacted with epichlorohydrin ($\text{CH}_2\text{ClCH}(\text{O})\text{CH}_2$) to produce bisphenol A diglycidyl ether (BADGE, 2,2-di-(4-(2,3-epoxypropoxy)phenyl)propane). BADGE is then hardened by epoxy ring-opening condensation reactions. Epoxy resins are tough, chemically resistant, materials, which can be formed *in situ* as pipe and tank liners (Briston and Katan 1974). However BADGE and BisA can leach from the product into the water (Branton *et al.* 1995, Watts *et al.* 1983).

Various bisphenols have been compared with oestradiol by looking at their effect on the proliferation of cells sensitive to oestrogen. Data for a number of bisphenols and oestradiol are given in Table 2.6 (Perez *et al.* 1998).

Table 2.6 Data for the endocrine disruption of bisphenols

Compound	Acronym	R ^{1 a}	R ^{2 a}	R ^{3 a}	AP ^b
Oestradiol	E ₂	-	-	-	100
4,4-Bis(4-hydroxyphenyl)heptane	MM5	-OH	-C ₃ H ₇	-C ₃ H ₇	1
3,3-Bis(4-hydroxyphenyl)pentane	MM4	-OH	-C ₂ H ₅	-C ₂ H ₅	0.1
Bisphenol A	BisA	-OH	-CH ₃	-CH ₃	0.01
2,2-Bis(4-hydroxyphenyl)perfluoropropane	MM7	-OH	-CF ₃	-CF ₃	0.01
2,2-Bis(4-hydroxyphenyl)butane	MM3	-OH	-C ₂ H ₅	-CH ₃	0.01
1,1-Bis(4-hydroxyphenyl)propane	MM2	-OH	-C ₂ H ₅	-H	0.01
Bisphenol F	BisF	-OH	-H	-H	0.001
Bisphenol A dimethylacrylate	BisADMA	-OOC(CH ₃)=CH ₂	-CH ₃	-CH ₃	0.001
Bisphenol A bischloroformate	BisACF	-OOCCl	-CH ₃	-CH ₃	0.001
1,1-Bis(4-hydroxyphenyl)ethane	MM1	-OH	-CH ₃	-H	0.001
Bisphenol A ethoxylate diacrylate	BisAEDA	-O(CH ₂) ₂ COO(CH ₂) ₂	-CH ₃	-CH ₃	0.0001
Bisphenol A diglycidyl ether	BADGE	-OCH ₂ CH(O)CH ₂	-CH ₃	-CH ₃	0.0001
Bis(4-hydroxyphenyl)ketone	MM8	-OH	=O	-	0.0001
2,2-Bis(4-hydroxyphenyl)propanol	MM9	-OH	-CH ₂ OH	-CH ₃	0.0001
Bisphenol A propoxylate	PBisA	-OCH ₂ CHOHCH ₃	-CH ₃	-CH ₃	0
Bisphenol A ethoxylate	EBisA	-O(CH ₂) ₂ OH	-CH ₃	-CH ₃	0
Bisphenol A diglycidyl ether dimethylacrylate	BAGDEDMA	-OCH ₂ CHOHCH ₂ OOCC(CH ₃)CH ₂	-CH ₃	-CH ₃	0



Note: ^a Substituents are positioned

^b Approximate potency - Potency of 17 β -Oestradiol = 100. (Perez *et al.*1998).

Epoxy resins are of particular interest when looking at drinking water applications as they have been used in many drinking water pipe *in situ* lining programmes. Epoxy resins are also used in the lining of food cans to stop metal corrosion and contamination. The liquor around canned vegetables was found to be oestrogenic (using the E-screen test). This was alleged to be due to BisA in the resin lining of the can (which was detected by HPLC), not in the vegetables. Tinned vegetables are autoclaved after packing and so the tins are subjected to higher temperatures. They are then stored leading to much longer contact times than water distribution pipes and tanks (Brnton *et al.* 1995).

Polycarbonate flasks used for autoclaving culture medium were found to cause increased growth of breast cancer cells MCF-7 when compared with cells grown in medium autoclaved in glass bottles. BisA was found in the medium treated in polycarbonate bottles by HPLC and the increased growth was assumed to be due to this compound (Feldman and Krishnan 1995).

No data showing whether BisS was an endocrine disruptor could be found.

Bisphenol-based epoxy resins could be a source of low levels of endocrine disrupting chemicals in drinking water supplies. Polycarbonates and polysulphones are not commonly used in water distribution networks but are used to produce bottles used for the storage of mineral waters.

2.3.3 Phthalates

Phthalate esters, based on *o*-phthalic acid, are the largest single group of plasticizers and are used mostly in polyvinyl chloride and cellulose polymers where they impart flexibility, extendability and processability (Gächter and Müller 1983).

The results of tests carried out *in vitro* using cell cultures in which the rate of cell proliferation is controlled by oestrogen are shown Table 2.7.

Table 2.7 Oestrogenic effects of various phthalates

Phthalate ester	Acronym	European usage (tons pa)	Approximate potency ^a	Maximum response ^b (%)
17β-Estradiol	-	-	1	100
Ditridecyl phthalate	DTDP	6,500	1x10 ⁻⁷	95
Butyl benzyl phthalate	BBP	35,000	1x10 ⁻⁶	50
Dibutyl phthalate	DBP	30,000	1x10 ⁻⁷	35
Di- <i>iso</i> -butyl phthalate	DIBP	30,000	1x10 ⁻⁷	30
Diethyl phthalate	DEP	15,000 ^c	5x10 ⁻⁷	30
Butyl cyclohexyl phthalate	BCHP	Negligible	-	20
<i>iso</i> -Hexylbenzyl phthalate	IHBP	Negligible	-	20

Phthalate ester	Acronym	European usage (tons pa)	Approximate potency ^a	Maximum response ^b (%)
Di- <i>iso</i> -nonyl phthalate	DINP	150,000	-	15
Diphenyl phthalate	DPhP	Negligible	-	10
2-Ethylhexyl <i>isodecyl</i> phthalate	EHIDP	Negligible	na	na
Bis(2-ethylhexyl) hexahydrophthalate	DEHhP	Negligible	na	na
Bis(2-ethylhexyl) isophthalate	DEHIP	Negligible	na	na
Bis(2-ethylhexyl) phthalate	DEHP	450,000	na	na
Bis(2- <i>n</i> -butoxyethyl) phthalate	DBoEP	Negligible	na	na
Bis(ethoxyethyl) phthalate	DEoEP	Negligible	na	na
Bis(methoxyethyl) phthalate	BMoEP	Negligible	na	na
Bis[2-(2-ethoxyethoxy)ethyl] phthalate	DEoEoEP	Negligible	na	na
Butyl 2-ethylhexyl phthalate	BEHP	Negligible	na	na
Butyl decyl phthalate	BDcP	<1,000	na	na
Butyl <i>isodecyl</i> phthalate	BIDP	Negligible	na	na
Butyl octyl phthalate	BOP	<1,000	na	na
Diamyl phthalate	DPeP	Negligible	na	na
Dicyclohexyl phthalate	DCHP	<1,000	na	na
Diethyl phthalate	DHP	Not alone	na	na
Di- <i>iso</i> -decyl phthalate	DIDP	150,000	na	na
Di- <i>iso</i> -hexyl phthalate	DIHP	<2,000	na	na
Dimethyl <i>isophthalate</i>	DMIP	Negligible	na	na
Dimethyl phthalate	DMP	15,000 ^c	na	na
Di- <i>n</i> -octyl phthalate	DnOP	Not alone	na	na
Dioctyl <i>isophthalate</i>	DOIP	Negligible	na	na
Diundecyl phthalate	DUP	<2,000	na	na
Hexyl 2-ethylhexyl phthalate	HEHP	Negligible	na	na
Hexyl decyl phthalate	HDP	Negligible	na	na
<i>iso</i> -Decyl tridecyl phthalate	IDTDP	Negligible	na	na
Octyl- <i>iso</i> -decyl phthalate	OIDP	Negligible	na	na

Notes: ^a Potency of 17 β -Oestradiol = 1.
^b Response of 17 β -Oestradiol = 100 %.
^c DMP and DEP are produced together.
na Not active.
(Harris *et al.* 1997).

3. SURVEY OF MANUFACTURERS

The presence of the suspected endocrine disruptors in Table 2.1 in materials in contact with drinking water was assessed by writing to manufacturers of materials and components approved for use in contact with drinking water.

3.1 Selection of manufacturers

A letter was sent to selected manufacturers asking if they used endocrine disrupting chemicals in their products. Manufacturers that were contacted were selected from the categories of the Water Fittings and Materials Directory, Water Bylaws Scheme (WBS) (WBS 1997) shown in Table 3.1 (products listed in the Directory are approved by WBS after passing tests based on BS6920:1996) and from the categories of the DWI list of Regulation 25(1)(a) approved products (DWI 1997) shown in Table 3.2.

The categories from the WBS and DWI lists were selected based on those materials most likely to contain the suspected endocrine disruptors shown in Table 2.1.

Table 3.1 Categories of WBS approved products selected

WBS directory category ^a	Product type
5020	Acrylonitrile butadiene styrene copolymer (ABS)
5026-5036	Coatings, paints and linings (factory applied)
5038-5048	Coatings, paints and linings (site applied)
5050-5065	Concrete, cement and mortar
5120-5125	Glass reinforced plastics (GRP)
5170	Metal fillers
5200-5205	Polybutylene
5210	Polycarbonate
5215-5217	Polyester
5240-5245	Polyethylene
5260-5265	Polypropylene
5268-5270	Polystyrene
5280	Polysulphone
5295-5296	Polytetrafluoroethylene (PTFE) thermoplastic
5297	Polyurethane
5300-5305	Polyvinyl chloride (PVC, uPVC and CPVC)
5315-5420	Rubbers
5440-5505	Sealants for flat faced joints
5510-5550	Sealants for screwed joints

Note ^a (WBS 1997)

Table 3.2 Categories of Regulation 25(1)(a) products selected

DWI list of products category ^a	Product type
6	Pipes
7	Filters and membrane systems
8	Linings and coatings
9	Cementitious and associated products

Note ^a (DWI 1997)

DWI also expressed an interest in the possible human exposure to endocrine disruptors due to drinking water kept in water coolers. Water coolers are kept in offices and other public places and consist of a large water container (10 l or more) on a stand from which drinking water is dispensed. The water is delivered in the bottle, and so may have a long contact time if the bottle is stored or if usage is low. The material from which the bottles are made is regulated by the Food Safety Act 1990. Two manufactures of such bottles were contacted.

3.2 Information collected from manufacturers

The letter in Appendix B was sent to each of the selected manufacturers. Included with the letter was a questionnaire asking for concentration of additive in product (and any leaching information) and product type and name of any material which they manufactured containing any of the additives or compounds shown in Appendix C.

The replies to the letters and questionnaires are summarised in the following tables.

The numbers of replies are shown in Table 3.3. In some cases, manufacturers had been contacted regarding the presence of phthalates in their products earlier in the year (as part of a different exercise). In these cases, a letter was sent asking for information regarding the other chemicals in Annex C only.

Table 3.3 Level of response to letters sent regarding endocrine disruptors

Companies contacted regarding	Number	Replies	Percentage replying (%)
Phthalates	98	76	77.6
Endocrine disruptors	131	74	56.5

The exact number of products covered in the exercise has not been calculated (due to products being continually released, withdrawn and modified) but it is likely to be much higher than the number of manufacturers polled as many of them produce several products.

A summary of the occurrence of each chemical is given in Table 3.4 and the product types containing suspected endocrine disruptors are given in Table 3.5. The discrepancy in the totals on the two tables is due to some products containing more than one chemical of interest.

Table 3.4 Occurrences of suspected endocrine disruptors in materials in contact with drinking water

Chemical	Acronym	Occurrences
Butyl benzyl phthalate	BBP	1
Dibutyl phthalate ^a	DBP	2
Bis(2-ethylhexyl) phthalate	DEHP	2
Ethylhexyl benzyl phthalate	EHBP	1
Diethyl phthalate	DEP	-
Diisobutyl phthalate ^a	DIBP	-
Diisodecyl phthalate	DIDP	10
Diisononyl phthalate	DINP	-
Dimethyl phthalate	DMP	4
Ditridecyl phthalate	DTDP	-
Di- <i>iso</i> -undecyl phthalate	DIUDP	1
Dibutylethoxy phthalate	DBEP	1
Bisphenol A	BisA	8
Bisphenol A diglycidyl ether	BADGE	16
Bisphenol F	BisF	-
Bisphenol F diglycidyl ether	BFDGE	12
Butyl phenol	BP	1
Nonyl phenol	NP	4
Octyl phenol	OP	-
Pentyl phenol	PP	-
Other alkyl phenols including antioxidants	AP	15
Nonyl phenol polyethoxylate or nonyl phenol ethoxylate	NPP	1
Octyl phenol polyethoxylate or octyl phenol ethoxylate	OPP	-
Other alkyl phenol polyethoxylate or alkyl phenol ethoxylate	APP	2
Butylated hydroxyanisole	BHA	-
Total		80

Notes ^a May be the same compound labelled differently.

Table 3.5 Occurrences of suspected endocrine disruptors in various classes of materials in contact with drinking water

Code ^a	Material type	Occurrences
WBS(5015)	Acetyl material	1
WBS(5020)	ABS	1
WBS(5030)	Pipe and fitting factory applied coating	4
WBS(5034)	Tank factory applied coating	1
WBS(5036)	Factory applied coating	1
WBS(5038)	Concrete site applied coating	3
WBS(5040)	Metal site applied coating	2
WBS(5042)	Pipe and fitting site applied coating	2
WBS(5044)	Sheet site applied coating	1
WBS(5048)	Site applied coating	5
WBS(5063)	Concrete repair material	1
WBS(5070)	Epoxy resin	1
WBS(5120)	GRP components	1
WBS(5125)	GRP material	3
WBS(5140)	Hoses and tubing	1
WBS(5170)	Metal fillers	1
WBS(5180)	Nylon material	1
WBS(5245)	Polyethylene material	7
WBS(5253)	Polyphenylene material	1
WBS(5260)	Polypropylene components	1
WBS(5270)	Polystyrene material	1
WBS(5280)	Polysulphone material	1
WBS(5320)	Rubber material	1
WBS(5365)	EPDM rubber material	1
WBS(5390)	Nitrile rubber components	8
WBS(5440)	Flat faced joint sealants	1
WBS(5490)	Polyurethane flat faced joint sealants	2
WBS(5520)	Anaerobic screw joint sealants	1
Reg. 25(7)	Filters and membranes	2
Reg. 25(8)	Linings and coatings	7
	Test material under development	2
	Water cooler bottle	1
Total		67

Notes: ^a Reg25(x) and WBS(xxxx) show the category in which the material is listed in Table 3.1 and Table 3.2.

4. MATERIAL TESTING IN THE LABORATORY

A representative selection of samples, from the products identified in the survey of manufacturers, was then tested in the laboratory. These products are shown in Table 4.1.

Table 4.1 **Products tested in the laboratory**

Code	Material
A	Single component polyurethane sealant
B	Site-applied two-part epoxy coating
C	Single component polyurethane sealant
D	Nitrile rubber 'O' ring
E	Site-applied two component cement coating
F	Site-applied two component unsaturated ester copolymer coating
G	Factory applied fusion bonded epoxy powder coating
H	Site applied two component epoxy coating
I	11 l polycarbonate mineral water bottle
J	Polyester GRP tank

Where possible materials were tested as described in the "Procedure for determination of organic contaminants leaching from products used in contact with drinking water", Annex F of "Guidance Note on the Approval of Substances and Products Used in the Provision of Public Water Supplies" December 1995 revision, prepared by the CCM and issued by the DWI.

Materials A, B, C and D were sampled after 1, 25 and 73 hours because high concentrations of suspected endocrine disruptors were anticipated during the early stages of the leaching test.

Attempts were made to relate the laboratory findings to concentrations that could occur in drinking water in practice. Information on worst case situations was difficult to obtain. Such information would include:

- the highest surface-area-to-volume ratio (s/v);
- contact time and;
- whether the frequently observed high leaching rate in the first hour or so would be flushed to waste, intentionally or during disinfection procedures.

The estimates of worst case concentrations are provided for guidance and should not be treated as accurate simulations of actual practice.

4.1 Analytical methods

4.1.1 Determination of total organic carbon

The water samples for TOC analysis were collected in clean polyethylene bottles.

TOC was determined by a UV/persulphate oxidation technique with non-dispersive infra-red detection. The TOC instrument was calibrated externally with a standard solution of potassium hydrogen phthalate (10 mg l^{-1} as organic carbon). In addition, control standards were analysed with the samples using a solution of potassium hydrogen phthalate (5 mg l^{-1} as organic carbon). Data from the control standards are plotted on Shewart control charts and monitored for compliance. This method has been shown to have a relative standard deviation of 2.5% at 2 mg l^{-1} (i.e. standard deviation was $50 \text{ } \mu\text{g l}^{-1}$ at concentration of 2 mg l^{-1}), and a limit of detection of 0.3 mg l^{-1} . WRc has UKAS accreditation for low-level TOC determination. Control samples were analysed for TOC at intervals of every 10 samples.

The values for the control samples were found to be within the $\pm 2\sigma$ values of 5.50 and 4.92 mg l^{-1} which were specified as acceptance criteria on the control chart. This demonstrated that the performance of the method was acceptable during the period in which the samples were being analysed.

4.1.2 Determination of phthalates and nonyl phenol

NP, DMP, DEP, DBP, BBP, DBEP, BEHP, DPhP, DOP, DINP and DIDP were analysed for using GCMS.

Samples were collected in clean 1 l glass bottles with PTFE-lined lids and analysed as soon as possible after collection.

One litre of sample was spiked with $1 \text{ } \mu\text{g l}^{-1}$ of deuterated internal standards. The sample was then extracted with $2 \times 100 \text{ ml}$ of DCM and the combined extracts were frozen overnight. The extract was filtered to remove any ice crystals and the volume reduced to *ca.* 1 ml in a turbovap. Finally, the sample was concentrated to a known volume by nitrogen blowdown.

The GC was run at an initial temperature of 40°C for 3 minutes and then increased at 8°C per minute up to a final temperature of 300°C , which was maintained for 50 minutes.

Compounds under investigation were detected using a MS in SIM mode, set to collect data on the appropriate masses. Quantification was carried out by internal standard using the major ion fragment and confirmed using one or more of the other ions.

Validation data were collected to check the suitability of the method. This was carried out by analysing water samples spiked at an appropriate concentration with the compounds of interest. These samples showed the method to be satisfactory and were used to calculate the LOD for each compound, as shown in Table 4.2.

During analysis, AQC samples were made by spiking fresh test water with known quantities of the determinands and extracting and analysing them along with the leachates. AQC data collected during analysis showed the method to be working satisfactorily. Data collected from the AQC samples were used to calculate the recovery factors applied to the leachate samples, as shown in Table 4.2.

Table 4.2 Limits of detection and recoveries for NP and phthalates

Compound	LOD ($\mu\text{g l}^{-1}$)	Recovery (%)		
		Materials A-D	Materials E-I	Material J
NP	2.6	84	120	-
BBP	1.2	98	117	145
BEHP	1.6	-	145	106
DBEP	0.7	101	175	132
DBP	1.8	113	128	130
DEP	0.7	87	84	95
DIDP	1.3	127	107	113
DINP	1.3	75	101	113
DMP	1.7	-	-	107
DOP	0.6	-	113	127
DPhP	0.6	108	97	123

Phthalates are commonly used chemicals and are present in a wide range of products such as plastics, paints and cosmetics. Consequently, sporadic contamination of samples can occur from unknown sources during the experiment or analysis. Because of this, care must be taken in the interpretation of low concentrations of phthalates, particularly unusual “isolated” results occasionally found in samples and blanks.

4.1.3 Determination of bisphenol A, bisphenol F, bisphenol A diglycidyl ether and bisphenol F diglycidyl ether

BisA, BisF, BADGE and BFDGE were analysed using HPLC-UV.

Samples were collected in clean 1 l glass bottles with PTFE-lined lids and analysed as soon as possible after collection.

One litre of sample was spiked with $1 \mu\text{g l}^{-1}$ of deuterated internal standards and the pH adjusted to 2. The sample was then extracted with 2 x 100 ml of DCM and the combined extracts were frozen overnight. The extract was filtered to remove any ice crystals and the

volume reduced to *ca.* 1 ml in a turbovap then further reduced to 100 µl by nitrogen blowdown.

Sample was injected onto a HPLC fitted with a Spherisorb ODS 1 column with eluent of methanol and water flowing at 1 ml min⁻¹. The compounds of interest were monitored at 275 nm.

Validation data were collected to check the suitability of the method. This was carried out by analysing water samples spiked at an appropriate concentration with the compounds of interest. These samples showed the method to be satisfactory and were used to calculate the LOD for each compound, as shown in Table 4.3.

During analysis, AQC samples were made by spiking fresh test water with known quantities of the determinands and extracting and analysing them along with the leachates. AQC data collected during analysis showed the method to be working satisfactorily. Data collected from the AQC samples were used to calculate the recovery factors applied to the leachate samples, as shown in Table 4.3.

Table 4.3 Limits of detection and recoveries for BisA, BisF, BADGE, BFDGE

Compound	LOD (µg l ⁻¹)	Recovery (%)
BisA	2.2	58
BisF	3.9	100
BADGE	1.8	63
BFDGE	2.3	64

4.1.4 Determination of nonyl phenol(30)polyethoxylate

NP(30)P was analysed for using direct injection LCMS.

Samples were collected in clean 1 l glass bottles with PTFE-lined lids and analysed as soon as possible after collection.

One litre of sample was adjusted to pH 2 and extracted using a C18 solid phase cartridge. The cartridge was eluted with methanol and the extract was evaporated to dryness. The sample was reconstituted in 100 µl of mobile phase.

The sample was directly injected onto a LCMS system in plasmaspray mode using a mobile phase of 78% methanol, 22% water and 0.2% trifluoroacetic acid. The MS was set to acquire data in continuum mode over a mass range of 1200-1700 *m/z*. The compound was quantified using the TIC peak area.

Validation and AQC data collected showed the recovery of NP(30)P to be 45% and the LOD to be 3.0 $\mu\text{g l}^{-1}$.

4.2 Materials testing

4.2.1 Blanks

With each set of leaching tests a blank was included and analysed to detect any contamination. The blank was made by placing test water in a clean test vessel. The blank was then treated in the same manner as the samples. The blank data is presented in the following tables.

Table 4.4 Blank results, Materials A-D ($\mu\text{g l}^{-1}$)

Compound	Leaching Period / Elapsed time (h)		
	T1 / 1	T2 / 25	T3 / 73
DEP	<0.7	<0.7	<0.7
DBP	12.2	<1.8	<1.8
BBP	<1.2	<1.2	<1.2
DBEP	21.9	<0.7	<0.7
DPhP	<0.6	<0.6	<0.6
DINP	<1.3	<1.3	<1.3
DIDP	<1.3	<1.3	<1.3
NP	<2.6	<2.6	<2.6

Table 4.5 Blank results, Materials E-I ($\mu\text{g l}^{-1}$)

Compound	Leaching period / Elapsed time (h)		
	T1 / 24	T2 / 72	T3 / 144
NP	<2.6	<2.6	<2.6
BADGE	<1.8	<1.8	<1.8
BFDGE	<2.3	<2.3	<2.3
BisA	<2.2	<2.2	<2.2
BisF	<3.9	<3.9	<3.9
DEP	<0.7	<0.7	<0.7
DBP	<1.8	<1.8	<1.8
BBP	<1.2	<1.2	<1.2
DBEP	<0.7	<0.7	<0.7
BEHP	<1.6	<1.6	<1.6
DPhP	<0.6	<0.6	<0.6
DOP	<0.6	<0.6	<0.6
DINP	<1.3	<1.3	<1.3
DIDP	<1.3	<1.3	<1.3
NP(30)P	<3.0	<3.0	<3.0

Table 4.6 Blank results, Material J ($\mu\text{g l}^{-1}$)

Compound	Leaching period		
	T1 / 24	T2 / 72	T3 / 144
DMP	<1.7	<1.7	<1.7
DEP	<0.7	<0.7	<0.7
DBP	<1.8	<1.8	<1.8
BBP	<1.2	<1.2	<1.2
DBEP	<0.7	<0.7	<0.7
BEHP	<1.6	2.2	2.4
DPhP	<0.6	<0.6	<0.6
DOP	<0.6	<0.6	<0.6
DINP	<1.3	<1.3	<1.3
DIDP	<1.3	<1.3	<1.3

4.2.2 Leaching rates

Leaching rates given for the materials tested in the laboratory were calculated using the

formula: $R = \frac{cv}{at}$

where: R = the leaching rate ($\mu\text{g m}^{-2} \text{h}^{-1}$);

c = the blank and recovery corrected concentration found ($\mu\text{g l}^{-1}$);

v = the volume of water in which the test was carried out (l);

a = the area of the test sample (m^2) and;

t = the length of time the sample was leached (h).

4.2.3 Spiked procedural controls

The stability of the determinands was checked by using spiked procedural controls. During the leaching tests a spiked procedural control was produced by placing known amounts of the determinands in a test water in a test vessel. These controls were then treated in the same manner to the test samples. The purpose of these controls is to ensure that the substance being measured is reasonably stable under the conditions of the test. Results from these experiments are shown in Table 4.7.

Table 4.7 Spiked procedural control results ($\mu\text{g l}^{-1}$)

Compound	Leaching period / Elapsed time (h)		
	T1 / 24	T2 / 72	T3 / 144
Spiking level	9.6	9.6	9.6
DMP	10	14	19
DEP	9.3	11	12
DBP	8.2	7.4	8.2
BBP	6.1	7.6	6.5
DBEP	7.0	7.4	6.3
DPhP	4.9	3.3	3.7
DINP	8.4	8.4	8.0
DIDP	8.7	8.9	8.2
BADGE	7.0	7.4	6.3
BFDGE	4.9	3.3	3.7
BisA	8.4	8.4	8.0
NP(30)P	8.7	8.9	8.2

The results from these experiments show the stability of the compounds tested to be satisfactory. NP and BisF were not tested as data showing them to be stable during leaching tests had been produced previously.

4.2.4 Material A

Material A was a single component polyurethane sealant. It is approved under the Water Bylaws Scheme for use in low contact surface area to water volume situations.

The material was spread with a brush onto one side of each of four sand-blasted glass plates (240 x 260 mm) to a thickness of approximately 1 mm. These plates were fixed together using stainless steel nuts and bolts to give a sample with a total surface area of 0.25 m².

The sample was cured at the minimum cure conditions as stated in the manufacturers instructions for use.

The sample was placed in a glass tank and 2.9 l of test water was added. The tank was filled so that no headspace was left, covered and placed in an incubator at 25°C.

The tank was removed from the incubator after 1 h. A sample was taken for analysis (T1) and the tank was drained, refilled with test water and returned to the incubator.

After a subsequent 24 h the tank was removed from the incubator, a sample was taken for analysis (T2) and the tank was drained, refilled with test water and returned to the incubator.

A final sample (T3) was taken after another 48 h and the tank was drained.

Samples were analysed using the method given in Section 4.1.2. The results of the analysis are given in Table 4.8.

Table 4.8 Analytical results from Material A ($\mu\text{g l}^{-1}$)

Compound	Leaching Period / Elapsed time (h)		
	T1 / 1	T2 / 25	T3 / 73
DEP	<0.7	<0.7	<0.7
DBP	27	<1.8	2.0
BBP	<1.2	<1.2	<1.2
DBEP	100	19	<0.7
DPhP	<0.6	<0.6	<0.6
DINP	<1.3	13	<1.3
DIDP	<1.3	45	19
NP	<2.6	<2.6	<2.6

Note: Results blank and recovery corrected.

From the values obtained by analysis hourly leaching rates of the detected determinands can be calculated and are shown in Table 4.9.

Table 4.9 Hourly leaching rates from Material A ($\mu\text{g m}^{-2} \text{h}^{-1}$)

Compound	Leaching Period / Elapsed time (h)		
	T1 / 1	T2 / 25	T3 / 73
DBP	320	<1.5	0.49
DBEP	1200	16	<0.17
DINP	<15	11	<0.31
DIDP	<15	37	4.7

This material is approved for use in situations where the contact area is small compared with the water volume, i.e. joints between panels used to line tanks and reservoirs. If one assumes that this product is applied in the intended manner to a small tank (2m x 2m x 2m) and that it accounts for 0.2% of the surface area, then, in the first hour a concentration of about $0.01\mu\text{g l}^{-1}$ of phthalate would be achieved.

4.2.5 Material B

Material B was a two-part epoxy coating. It is approved under the Water Bylaws Scheme.

The material was mixed with a knife in accordance with the manufacturer's specifications then 30 g of the material was immediately spread with a brush onto one side of sand-blasted glass plates (240 x 260 mm). Four of these plates were fixed together using stainless steel nuts and bolts to give a sample with a total surface area of 0.25 m².

The sample was cured at the minimum cure conditions as stated in the manufacturer's instructions for use.

The sample was placed in a glass tank and 2.9 l of test water was added. The tank was filled so that no headspace was left, covered and placed in an incubator at 25°C.

The tank was removed from the incubator after 1 h, a sample taken for analysis (T1) and the tank was drained, refilled with test water and returned to the incubator.

After a subsequent 24 h the tank was removed from the incubator, a sample was taken for analysis (T2) and the tank was drained, refilled with test water and returned to the incubator.

A final sample (T3) was taken after another 48 h and the tank was drained.

Samples were analysed using the method given in Section 4.1.2. The results of the analysis are given in Table 4.10.

Table 4.10 Analytical results from Material B (µg l⁻¹)

Compound	Leaching Period / Elapsed time (h)		
	T1 / 1	T2 / 25	T3 / 73
DEP	<0.7	<0.7	<0.7
DBP	120	1900	2100
BBP	<1.2	3.1	<1.2
DBEP	35	13	3.7
DPhP	<0.6	<0.6	<0.6
DINP	<1.3	<1.3	<1.3
DIDP	<1.3	<1.3	<1.3
NP	14	500	560

Note: Results blank and recovery corrected.

From the values obtained by analysis hourly leaching rates of the detected determinands can be calculated and are shown in Table 4.11.

Table 4.11 Hourly leaching rates from Material B ($\mu\text{g m}^{-2} \text{h}^{-1}$)

Compound	Leaching Period / Elapsed time (h)		
	T1 / 1	T2 / 25	T3 / 73
DBP	1400	1600	510
BBP	<14	2.5	<0.29
DBEP	280	11	0.89
NP	160	410	130

The concentrations of all of the determinands measured in this leaching test decreased during the test period. The leaching rates of NP, DBP and DEBP are high. In the water supply network, the material may only be used in low contact surface area applications, under Regulation 25(1)(b). Such an application might include a coating for a valve, pump or ladder, therefore the final concentration of the leachates in the water would be low. However, if one assumes a coated 4m ladder (1.2 m^2) in a tank $10\text{m} \times 5\text{m} \times 5\text{m}$ then the concentration reached of all the compounds detected in the first few days would be about $0.7 \mu\text{g l}^{-1}$.

On consumer premises the material could be used as a lining for a cold water tank and, in principle, a pipe. Here the residence time could be long and the contact surface area relatively large, leading to higher concentrations of leachates in the water in the first few days after use.

4.2.6 Material C

Material C was a single component polyurethane sealant. It is approved under the Water Bylaws Scheme for use in low contact surface area to water volume situations.

The material was spread with a knife onto one side of each of four sand-blasted glass plates ($240 \times 260 \text{ mm}$) to a thickness of approximately 0.8 mm . These plates were fixed together using stainless steel nuts and bolts to give a sample with a total surface area of 0.25 m^2 .

The sample was cured at the minimum cure conditions as stated in the manufacturer's instructions for use.

The sample was placed in a glass tank and 3.0 l of test water was added. The tank was filled so that no headspace was left, covered and placed in an incubator at 25°C.

The tank was removed from the incubator after 1 h, a sample was taken for analysis (T1) and the tank was drained, refilled with test water and returned to the incubator.

After a subsequent 24 h the tank was removed from the incubator a sample was taken for analysis (T2) and the tank was drained, refilled with test water and returned to the incubator.

A final sample (T3) was taken after another 48 h and the tank was drained.

Samples were analysed using the method given in Section 4.1.2. The results of the analysis are given in Table 4.12.

Table 4.12 Analytical results from Material C ($\mu\text{g l}^{-1}$)

Compound	Leaching Period / Elapsed time (h)		
	T1 / 1	T2 / 25	T3 / 73
DEP	<0.7	<0.7	<0.7
DBP	<1.8	12	<1.8
BBP	10	12	32
DBEP	<0.7	17	21
DPhP	<0.6	<0.6	<0.6
DINP	<1.3	<1.3	<1.3
DIDP	<1.3	3.2	<1.3
NP	<2.6	<2.6	<2.6

Note: Results blank and recovery corrected.

From the values obtained by analysis hourly leaching rates of the detected determinands can be calculated and are shown in Table 4.13.

Table 4.13 Hourly leaching rates from Material C ($\mu\text{g m}^{-2} \text{h}^{-1}$)

Compound	Leaching Period / Elapsed time (h)		
	T1 / 1	T2 / 25	T3 / 73
DBP	<22	10	<0.45
BBP	120	11	8.0
DBEP	<8.4	14	5.2
DIDP	<16	2.7	<0.33

Leaching rates of phthalates from Material C fell over the period of the test. This material is approved for sealing flat-faced joints between panels used to line tanks and reservoirs, where the surface area will be small compared with the water volume. If one makes the assumptions made for material A then the compounds leached from this material would be highly diluted and therefore the final concentration in the water would be negligible.

4.2.7 Material D

Material D was a nitrile rubber 'O' ring. It is approved under the Water Bylaws Scheme.

The material was supplied as 'O' rings, a number of rings was used to give a total sample surface area of 0.25 m^2 .

The sample was placed in a glass tank and 2.85 l of test water was added. The tank was filled so that no headspace was left, covered and placed in an incubator at 25°C .

The tank was removed from the incubator after 1 h, a sample was taken for analysis (T1) and the tank was drained, refilled with test water and returned to the incubator.

After a subsequent 24 h the tank was removed from the incubator a sample was taken for analysis (T2) and the tank was drained, refilled with test water and returned to the incubator.

A final sample (T3) was taken after another 48 h and the tank drained.

Samples were analysed using the method given in Section 4.1.2. The results of the analysis are given in Table 4.14.

Table 4.14 Analytical results from Material D ($\mu\text{g l}^{-1}$)

Compound	Leaching Period / Elapsed time (h)		
	T1 / 1	T2 / 25	T3 / 73
DEP	19	69	210
DBP	25	150	190
BBP	17	12	<1.2
DBEP	15	<0.7	<0.7
DPhP	<0.6	<0.6	<0.6
DINP	17	<1.3	<1.3
DIDP	14	<1.3	<1.3
NP	<2.6	8.9	3.9

Note: Results blank and recovery corrected.

From the values obtained by analysis hourly leaching rates of the detected determinands can be calculated and are shown in Table 4.15.

Table 4.15 Hourly leaching rate for Material D ($\mu\text{g m}^{-2} \text{h}^{-1}$)

Compound	Leaching Period / Elapsed time (h)		
	T1 / 1	T2 / 25	T3 / 73
DEP	220	56	49
DBP	280	120	46
BBP	200	10.0	<0.29
DBEP	170	<0.57	<0.17
DINP	190	<1.1	<0.31
DIDP	160	<1.1	<0.31
NP	<30	7.3	0.93

A large number of different phthalates and NP were found in the leachates. Initial leaching rates of the phthalates and nonyl phenol were high. However, the results indicate that they drop during the period of the experiment. The exposed surface area of a 'O' ring used as

a seal would be extremely small. If one assumes 1 cm^2 to be in contact with 1 litre for the first three days (i.e. no flow) then a concentration of about $1\mu\text{g.l}^{-1}$ total compounds could be achieved. In practice concentrations would be negligible.

4.2.8 Material E

Material E was a two component cement coating. It is approved under the Water Bylaws Scheme.

The material was mixed in accordance with the manufacturer's instructions and 100 g was spread with a brush onto one side of each of five sand-blasted glass plates (240 x 260 mm). These plates were fixed together using stainless steel nuts and bolts to give a sample with a total surface area of 0.312 m^2 .

The sample was cured at the minimum cure conditions as stated in the manufacturer's instructions for use.

The sample was placed in a glass tank and 3.5 l of test water was added. The tank was covered so that no headspace was left and placed in an incubator at 25°C .

The tank was removed from the incubator after 24 h, a sample was taken for analysis (T1) and the tank was drained, refilled with test water and returned to the incubator.

After a subsequent 48 h the tank was removed from the incubator a sample was taken (T2) for analysis and the tank drained, refilled with test water and returned to the incubator.

A final sample (T3) was taken after another 72 h and the tank was drained.

Samples were analysed using the method given in Sections 4.1.1 and 4.1.4.. The results of the analysis are given in Table 4.12.

Table 4.16 Analytical results from Material E ($\mu\text{g l}^{-1}$)

Compound	Leaching period / Elapsed time (h)		
	T1 / 24	T2 / 72	T3 / 144
NP ^a	<2.6	<2.6	<2.6
BADGE ^a	<1.8	<1.8	<1.8
BFDGE ^a	<2.3	<2.3	<2.3
BisA ^a	<2.2	<2.2	<2.2
BisF ^a	<3.9	<3.9	<3.9
NP(30)P ^a	25000	3400	530
TOC ^b	145000	23700	8870

Note: ^a Results blank and recovery corrected.

^b Results blank corrected.

From the values obtained by analysis hourly leaching rates of the detected determinands can be calculated and are shown in Table 4.17.

Table 4.17 Hourly leaching rate from Material E ($\mu\text{g m}^{-2} \text{h}^{-1}$)

Compound	Leaching period / Elapsed time (h)		
	T1 / 24	T2 / 72	T3 / 144
NP(30)P	12000	780	82
TOC	68000	5500	1400

Cements are not normally tested under such extreme conditions when being considered for approval under Regulation 25, however, in order to maximise leaching this test was carried out as prescribed in Annex F of the CCM Guidance Note for non-cementitious materials.

Analysis was also carried out for NP, which was not found above the LOD. TOC indicates that leaching of other organic matter was also high, about 5-20% of the TOC appeared to be NP(30)P. It is possible that this material is used to coat large surface

areas, for example, of tanks. Thus over the first few days high levels of NP(30)P could be achieved. Even after three days the rate of leaching is high.

Further investigation of this material needs to be considered. However, DWI information letter 11/96 will prohibit the use of all surface coatings (except those which have a small surface area in contact with the water) from being used after April 2000. From that time onwards only materials approved under Regulation 25(1)(a) will be permitted. Therefore, this material can only be used as a repair material (with a small contact area) from April 2000.

4.2.9 Material F

Material F was a two component unsaturated ester copolymer coating. It is approved under the Water Bylaws Scheme.

The material was mixed in accordance with the manufacturer's instructions and spread with a brush to a thickness of about 1 mm onto one side of each of five sand-blasted glass plates (240 x 260 mm). These plates were fixed together using stainless steel nuts and bolts to give a sample with a total surface area of 0.312 m².

The sample was cured at the minimum cure conditions as stated in the manufacturer's instructions for use.

The sample was placed in a glass tank and 4.0 l of test water was added. The tank was filled so that no headspace was left, covered and placed in an incubator at 25°C.

The tank was removed from the incubator after 24 h, a sample was taken for analysis (T1) and the tank was drained, refilled with test water and returned to the incubator.

After a subsequent 48 h the tank was removed from the incubator a sample was taken for analysis (T2) and the tank was drained, refilled with test water and returned to the incubator.

A final sample (T3) was taken after another 72 h and the tank was drained.

Samples were analysed using the method given in Sections 4.1.1 and 4.1.2. The results of the analysis are given in Table 4.18.

Table 4.18 Analytical results from Material F ($\mu\text{g l}^{-1}$)

Compound	Leaching period / Elapsed time (h)		
	T1 / 24	T2 / 72	T3 / 144
DEP ^a	<0.7	<0.7	<0.7
DBP ^a	<1.8	<1.8	<1.8
BBP ^a	<1.2	<1.2	<1.2
DBEP ^a	<0.7	<0.7	<0.7
BEHP ^a	<1.6	<1.6	<1.6
DPhP ^a	<0.6	<0.6	<0.6
DOP ^a	<0.6	<0.6	<0.6
DINP ^a	<1.3	<1.3	<1.3
DIDP ^a	<1.3	<1.3	<1.3
TOC ^b	18000	3500	1300

Note: ^a Results blank and recovery corrected.

^b Results blank corrected.

From the values obtained by analysis hourly leaching rates of the detected determinands can be calculated and are shown in Table 4.19.

Table 4.19 Hourly leaching rates from Material F ($\mu\text{g m}^{-2} \text{h}^{-1}$)

Compound	Leaching period / Elapsed time (h)		
	T1 / 24	T2 / 72	T3 / 144
TOC	9600	940	230

Leaching from Material F was low. The TOC increase caused by the material was seen to drop during the leaching period..

4.2.10 Material G

Material G was a factory applied fusion-bonded epoxy powder coating. It is approved under the Water Bylaws Scheme.

The coating was factory applied by the manufacturer. The plates supplied were 1 mm aluminium completely coated with material to a depth of 300 µm. These were cut to give a sample with a surface area of 0.312 m².

The sample was placed in a glass tank and 4.0 l of test water was added. The tank was filled so that no headspace was left, covered and placed in an incubator at 25°C.

The tank was removed from the incubator after 24 h, a sample was taken for analysis (T1) and the tank was drained, refilled with test water and returned to the incubator.

After a subsequent 48 h the tank was removed from the incubator a sample was taken (T2) for analysis and the tank was drained, refilled with test water and returned to the incubator.

A final sample (T3) was taken after another 72 h and the tank was drained.

Samples were analysed using the method given in Sections 4.1.1 and 4.1.3.

None of the determinands analysed for were detected as shown in Table 4.20.

Table 4.20 Analytical results from Material G (µg l⁻¹)

Compound	Leaching period / Elapsed time (h)		
	T1 / 24	T2 / 72	T3 / 144
NP ^a	<2.6	<2.6	<2.6
BADGE ^a	<1.8	<1.8	<1.8
BFDGE ^a	<2.3	<2.3	<2.3
BisA ^a	<2.2	<2.2	<2.2
BisF ^a	<3.9	<3.9	<3.9
TOC ^b	<300	<300	<300

Note: ^a Results blank and recovery corrected.

^b Results blank corrected.

4.2.11 Material H

Material H was a two component epoxy coating. It is approved under the Water Bylaws Scheme.

The material was mixed in accordance with the manufacturer's instructions and spread with a paddle to a thickness of about 0.4 mm onto one side of each of five sand-blasted glass plates (240 x 260 mm). These plates were fixed together using stainless steel nuts and bolts to give a sample with a total surface area of 0.312 m².

The sample was cured at the minimum cure conditions as stated in the manufacturer's instructions for use.

The sample was placed in a glass tank and 3.9 l of test water was added. The tank was filled so that no headspace was left, covered and placed in an incubator at 25°C.

The tank was removed from the incubator after 24 h, a sample was taken for analysis (T1) and the tank was drained, refilled with test water and returned to the incubator.

After a subsequent 48 h the tank was removed from the incubator a sample was taken for analysis (T2) and the tank was drained, refilled with test water and returned to the incubator.

A final sample (T3) was taken after another 72 h and the tank was drained.

Samples were analysed using the method given in Sections 4.1.1 and 4.1.3. The results of the analysis are given in Table 4.21.

Table 4.21 Analytical results from Material H (µg l⁻¹)

Compound	Leaching period / Elapsed time (h)		
	T1 / 24	T2 / 72	T3 / 144
NP ^a	130	120	120
BADGE ^a	7.8	1.8	<1.8
BFDGE ^a	24	4.6	<2.3
BisA ^a	<2.2	<2.2	<2.2
BisF ^a	<3.9	<3.9	<3.9
TOC ^b	30000	5900	2000

Note: ^a Result blank and recovery corrected.

^b Result blank corrected.

From the values obtained by analysis hourly leaching rates of the determinands detected can be calculated and are shown in Table 4.22.

Table 4.22 Hourly leaching rates from Material H ($\mu\text{g m}^{-2} \text{h}^{-1}$)

Compound	Leaching period / Elapsed time (h)		
	T1 / 24	T2 / 72	T3 / 144
NP	68	31	21
BADGE	4.1	0.5	<0.31
BFDGE	13	1.2	<0.33
TOC	16000	2600	340

The leaching of all four determinands detected can be seen to be decreasing over the period of the test.

Material H was designed for use as a pump and valve coating. Under normal conditions, this application would only give rise to a small surface area in contact with the water and, except when flow rates are very low, the contact time would be short, producing very low concentrations of contaminants in the final water. Even with several days stagnation concentrations should be $<1\mu\text{g l}^{-1}$.

4.2.12 Material I

Material I was an eleven litre polycarbonate mineral water bottle. It is tested to “The Materials and Articles in Contact with Food Regulations 1987” (S.I. No. 1523) and “The Plastic Materials and Articles in Contact with Food Regulations 1992” (S.I. No. 3145) as amended. The product was made of 98% polycarbonate.

The bottle was rectangular cross section with a wide neck opening at the top and an integral handle. It had an approximate surface area of 0.33 m^2 .

The sample was filled with 11.8 l of test water. The bottle was filled so that no headspace was left, covered with a glass lid and placed in a incubator at 25°C .

After 24 h, a sample taken for analysis (T1) and the bottle was drained and refilled with test water.

After a subsequent 48 h a sample was taken for analysis (T2) and the bottle was drained and refilled with test water.

A final sample (T3) was taken after another 72 h and the bottle was drained.

Samples were analysed using the method given in Sections 4.1.1 and 4.1.3.

None of the determinands analysed were detected. The analytical results are shown in Table 4.23.

Table 4.23 Analytical results from Material I ($\mu\text{g l}^{-1}$)

Compound	Leaching period / Elapsed time (h)		
	T1 / 24	T2 / 72	T3 / 144
NP ^a	<2.6	<2.6	<2.6
BADGE ^a	<1.8	<1.8	<1.8
BFDGE ^a	<2.3	<2.3	<2.3
BisA ^a	<2.2	<2.2	<2.2
BisF ^a	<3.9	<3.9	<3.9
TOC ^b	<300	<300	<300

Note: ^a Result blank and recovery corrected.

^b Result blank corrected.

4.2.13 Material J

Material J was a polyester GRP tank. It is approved under the Water Bylaws Scheme.

The tank was an open topped cylinder, with a 5 mm wall thickness. The outside had been painted black. It had a surface area of 2.27 m² and a volume of 0.345 m³.

The sample was filled with 345 l of test water (borehole water). The tank was covered with a polypropylene lid so that no headspace was left and left at ambient temperature

After 24 h, a sample taken for analysis (T1) and the tank was drained and refilled with test water.

After a subsequent 48 h a sample taken for analysis (T2) and the tank was drained and refilled with test water.

A final sample (T3) was taken after another 72 h and the tank was drained.

Samples were analysed using the method given in Sections 4.1.1 and 4.1.2. The results of the analysis are given in Table 4.24.

Table 4.24 Analytical results from Material J ($\mu\text{g l}^{-1}$)

Compound	Leaching period / Elapsed time (h)		
	T1 / 24	T2 / 72	T3 / 144
DMP ^a	<1.7	6.3	<1.7
DEP ^a	<0.7	<0.7	<0.7
DBP ^a	<1.8	<1.8	<1.8
BBP ^a	<1.2	<1.2	<1.2
DBEP ^a	<0.7	<0.7	<0.7
BEHP ^a	10	<1.6	4.0
DPhP ^a	<0.6	<0.6	<0.6
DOP ^a	<0.6	<0.6	<0.6
DINP ^a	<1.3	<1.3	<1.3
DIDP ^a	<1.3	<1.3	<1.3
TOC ^b	<300	330	300

Note: ^a Result blank and recovery corrected.

^b Result blank corrected.

From the values obtained by analysis hourly leaching rates of the determinands can be calculated and are shown in Table 4.25.

Table 4.25 Hourly leaching rates from Material J ($\mu\text{g m}^{-2} \text{h}^{-1}$)

Compound	Leaching period / Elapsed time (h)		
	T1 / 24	T2 / 72	T3 / 144
DMP ^a	<11	33	<3.6
BEHP ^a	63	<2.2	8.4
TOC ^b	<1900	1800	630

Leaching from Material J varied over the period of the test. However, based on a 24 h residence time, the total phthalate found in water exiting the tank would not rise above $10 \mu\text{g l}^{-1}$ and would fall during service. The tank was prepared specifically for the test but under normal production conditions. The manufacturer says that such a small tank is unusual and normally tanks of ten times this volume are used. In this case the concentration found would be reduced by a factor of about two.

5. MATERIALS TESTING IN THE FIELD

5.1 Introduction

Two materials were tested in the field to examine the long term leaching of suspected endocrine disruptors. Both of the materials, selected from the survey of manufacturers, were *in situ* applied epoxy resins used for the renovation of water mains. These products have been shown to leach compounds such as bisphenol diglycidyl ethers and alkyl phenols (Watts *et al*, 1983).

The products tested were selected using the following criteria:

- the known composition of the products, some epoxy resins also contain alkyl phenols;
- the availability of satisfactory sites, a number of resin manufacturers were contacted to ascertain possible sites for testing;

Site visits were then arranged by WRc with the epoxy manufacturer, the water company and the relining contractor to take samples of water entering and leaving the relined pipe, approximately 3 days, 21 days and 90 days after relining.

5.2 Sampling protocol

Samples of water from the beginning and end of the pipe length under investigation were taken in the following way:

1. The tap or standpipe, from which the sample was being taken, was fully opened and the water was run to waste for one minute. This allowed any water, which had been standing in the service pipes or other connecting pipes, to be cleared.
2. Two clean 1 l glass bottles with PTFE-lined caps and one 100 ml polyethylene bottle were rinsed with water, which was discarded, and filled to the top, to leave no headspace.
3. 2 ml of 1 g l⁻¹ ascorbic acid solution was added to each of the glass bottles to dechlorinate the samples.
4. 20 µg l⁻¹ of BADGE, BFDGE and 4-TBP was added to one of the glass bottles to act as a field spiked control.
5. The samples were labelled and placed in a cardboard box, which excluded all light, for transit to the laboratory.

5.3 Analysis

5.3.1 Determination of total organic carbon

TOC was determined as described in Section 4.1.1. The water samples for TOC analysis were those collected in clean 100 ml polyethylene bottles.

The control samples were found to be acceptable during the period in which the samples were being analysed.

5.3.2 Determination of bisphenol A diglycidyl ether, bisphenol F diglycidyl ether and 4-tert-butyl phenol

Samples collected in glass bottles were analysed for BADGE, BFDGE and 4-TBP by either GCMS or HPLC-UV.

After the addition of deuterated internal standards, 1 l of sample was extracted with 2 x 100 ml of DCM. The extracts were combined, frozen overnight and filtered to remove any water. The extract was then evaporated to 1 ml in a turbovap and final volume reduced to 100 µl in a stream of nitrogen.

GCMS analysis was carried out using a DB5.625 column starting at 40°C for three minutes then being raised to 300°C at a rate of 8°C per minute. The detector was run in positive ion electron impact ionisation mode. Compounds of interest were quantified using the internal standards.

HPLC-UV analysis was carried out using a Spherisorb ODS1 column with a methanol/water mobile phase. The compounds of interest were monitored at 275 nm and quantified using a calibration of external standards.

Limits of detection for both methods used are shown in Table 5.1.

Table 5.1 Limits of detection for 4-TBP, BADGE and BFDGE

Compound	LOD (µg l ⁻¹)	
	GCMS	HPLC-UV
4-TBP	1.0	1.0
BADGE	1.0	2.0
BFDGE	1.0	2.0

5.4 Material testing

5.4.1 Leaching rates

Leaching rates given for the materials tested in the field were calculated as: $R = \frac{cv}{at}$

where: R = the leaching rate ($\mu\text{g m}^{-2} \text{h}^{-1}$);
 c = the outlet concentration corrected for the inlet concentration ($\mu\text{g l}^{-1}$);
 v = the volume of water in the pipe $v = 1000\pi r^2 l$ (l);
 a = the area of pipe in contact with the water $a = 2\pi r l$ (m^2);
 t = the residence time of the water in the pipe $t = \frac{\pi r^2 l}{f}$ (h);
 f = the flow rate through the pipe ($\text{m}^3 \text{h}^{-1}$)
 l = the length of pipe (m) and;
 r = the radius of the pipe (m).

This leads to the equation: $R = \frac{500cr}{t}$

5.4.2 Material K

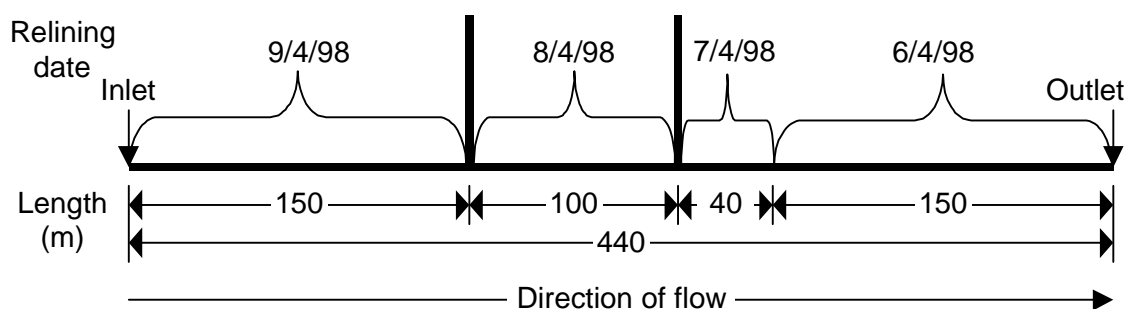
Material K was a two-part epoxy resin used for the relining and renovation of water mains, approved by the CCM under Regulation 25(1)(a).

Two sites were found where this product could be investigated.

5.4.2.1 Site 1

Site 1 was a 440 m stretch of 3" (76 mm) cast iron water main. Two branches (made of similar pipe) leave the main at 190 and 290 m. The water flowed into the pipe at the time of sampling at around $5 \text{ m}^3 \text{h}^{-1}$. Nominally, the water was resident in the pipe for 24 minutes (0.4 h), but the actual residence times will be higher due to water leaving the main along service pipes and branches. A diagram of the pipe under investigation is shown in Figure 5.1.

Figure 5.1 Diagram of site 1 used to test material L



The pipe was relined in four parts. The last relining, on the 9/4/98, was after the first samples had been taken. All of the relining was judged by the water company and relining contractors to be satisfactory.

Samples were taken from fire hydrant points using a standpipe in accordance with the protocol given in Section 5.2.

Results obtained from the analysis of the samples are shown in Table 5.2.

Table 5.2 Analytical results for Material K, Site 1

Date of sampling	TOC ¹ (mg l ⁻¹)	BADGE ¹ (µg l ⁻¹)	BFDGE ¹ (µg l ⁻¹)	4-TBP ¹ (µg l ⁻¹)
8/4/98 ³	0.40	<1	<1	3.9
29/4/98 ⁴	<0.30	<2	<2	<1
8/7/98 ⁴	²	<2	<2	<1

Note: ¹ Difference between inlet and outlet water.
² Sample not collected.
³ Results obtained by GCMS analysis.
⁴ Results obtained by HPLC-UV analysis.

The first batch of samples was taken during the relining process. 4-TBP and TOC were detected in the first sample, but not in subsequent samples. The leaching rate of 4-TBP was calculated to be 285 µg m⁻² h⁻¹ based on a residence time in the relined section of pipe (290 m) of 16 minutes (0.26 h). The limits of detection for BADGE and BFDGE were calculated as 73 µg m⁻² h⁻¹. Although these values relate to very newly lined pipe and should decrease quickly the short-term consumer exposure to 4-TBP from a low flow pipe, such as a “dead-end main” (a length of main feeding into a small number of consumers and hence a long residence time) could be relatively high.

5.4.2.2 Site 2

Site 2 consists of 225 m of 3" (76 mm) cast iron water main. The main runs parallel with a 5" (130 mm) cast iron main. The main is 4.25 km down a system of total length 6.5 km that has many branches and service pipes. The water flow entering the system was about $15 \text{ m}^3 \text{ h}^{-1}$. The main under examination is 65% of the way down the system and if the water loss is considered constant along the system, the water entering the section under examination would be $5.25 \text{ m}^3 \text{ h}^{-1}$. However, only 23% of the water flows down the 3" main (the rest being carried by the 5" main). Therefore, the actual flow in the main under examination is estimated to be $1.2 \text{ m}^3 \text{ h}^{-1}$. The water was calculated to be resident in the pipe for 51 minutes (0.85 h).

Relining of the whole system was started upstream on the 10/2/98 and had continued sequentially down the system from that time. The length of main under examination had been relined in three parts. The upstream 25 m of main was relined on the 31/3/98, the middle section (140 m) was relined on the 1/4/98 and the last 60 m was relined on the 2/4/98. All of the relinings were considered satisfactory by the water company and contractors.

Samples were taken from fire hydrant points using a standpipe in accordance with the protocol given in Section 5.2.

Results obtained from the analysis of the samples are shown in Table 5.3. TOC results are calculated as the difference between the inlet and outlet waters.

Table 5.3 Analytical results for Material K, Site 2

Date of sampling	TOC ¹ (mg l ⁻¹)	BADGE ¹ (µg l ⁻¹)	BFDGE ¹ (µg l ⁻¹)	4-TBP ¹ (µg l ⁻¹)
8/4/98 ³	<0.30	<1	<1	<1
29/4/98 ⁴	2.62	<2	<2	<1
8/7/98 ⁴	²	<2	<2	<1

Note: ¹ Difference between inlet and outlet water.

² Sample not collected.

³ Results obtained by GCMS analysis.

⁴ Results obtained by HPLC-UV analysis.

None of the determinands was detected above the LOD, which in the first samples was calculated to be $22.3 \text{ µg m}^{-2} \text{ h}^{-1}$. The high second TOC result may be due to contamination.

The samples taken from Site 1, which had been lined around the time of sampling, showed leaching of 4-TBP leaching, however the first samples taken from Site 2, which had been relined for a week, showed much lower levels of leaching. This would suggest that the

high level of 4-TBP leaching is not chronic, so long term exposure would be low. However, short term exposures for some customers at the end of long lengths of “dead end main” may be high.

5.4.3 Material L

Material L was a two-part epoxy resin used for *in situ* relining and renovation of water main.

One site was selected for the testing of material L. The site consists of 190 m of 4” (100 mm) iron water main. No flow data for the area were available because the flow was being disrupted due to sections of the system being shut down for relining. The main was relined during the week commencing 8/6/98.

All of the relining were found to be satisfactory by the water company and lining contractors.

Samples were taken from consumer taps in accordance with the protocol given in Section 5.2.

Table 5.4 Analytical results for Material L

Date of sampling	TOC ¹ (mg l ⁻¹)	BADGE ¹ (µg l ⁻¹)	BFDGE ¹ (µg l ⁻¹)	4-TBP ¹ (µg l ⁻¹)
9/6/98 ²	<0.30	<1	<1	<1
30/6/98 ³	<0.30	<2	<2	<1
11/9/98	<0.30	<2 ³	<2 ³	<1 ²

Note: ¹ Difference between inlet and outlet water.

² Results obtained by GCMS analysis.

³ Results obtained by HPLC-UV analysis.

Flow data were not available to enable an accurate calculation of leaching rates to be made. However, consumer exposure is below the LOD.

5.4.4 Material M

Material M was a two-part epoxy resin used for *in-situ* relining and renovation of water mains. Data regarding the leaching of BADGE and BFDGE was made available by the manufacturer. The data relates to six sites.

The sites were all dead end mains around 100 m long and 100 mm diameter. After relining a flow meter and recorder were fitted to the main. At regular intervals for the six months following relining samples of water were taken from a stand pipe at the end of the relined

main. The water samples were analysed for bisphenol diglycidyl ethers. The leaching rate data obtained from these studies are shown in Table 5.5.

The results show that the leaching rate takes about 1 week to drop below *ca* $4 \mu\text{g m}^{-2} \text{h}^{-1}$ from a maximum of around $1 \text{ mg m}^{-2} \text{h}^{-1}$. This rate of decrease in leaching rate suggests that the long-term exposure to bisphenol diglycidyl ethers from *in situ* epoxy lined pipes is very low. However, it is not clear what levels consumers at the end of long dead end mains (with high retention times) which are being sequentially lined with epoxy resin would be exposed to in the initial few months.

Table 5.5 Leaching of bisphenol diglycidyl ethers from Material M

Site 1		Site 2		Site 3		Site 4		Site 5		Site 6	
Sample time (h)	Leaching rate ($\mu\text{g m}^{-2} \text{h}^{-1}$)	Sample time (h)	Leaching rate ($\mu\text{g m}^{-2} \text{h}^{-1}$)	Sample time (h)	Leaching rate ($\mu\text{g m}^{-2} \text{h}^{-1}$)	Sample time (h)	Leaching rate ($\mu\text{g m}^{-2} \text{h}^{-1}$)	Sample time (h)	Leaching rate ($\mu\text{g m}^{-2} \text{h}^{-1}$)	Sample time (h)	Leaching rate ($\mu\text{g m}^{-2} \text{h}^{-1}$)
1	937.5	1	826.9	1	1969.4	1	812.5	1	483.7	1	1178.6
28	60.9	25.5	126.4	29	191.6	29	152.4	29	30.1	27	133.3
41	31.8	39.5	49.0	43	210.3	43	120.2	41	18.1	39	101.8
65	<5.8	63.5	39.6	67	119.2	67	47.0	113	4.7	111	28.8
1002	<5.8	833	<4.6	211	77.7	835	<3.2	857	<4.0	855	<4.1
1506	<5.8	1337	6.6	859	<3.3	1507	<3.2	1505	<4.0	1503	<4.1
2346	<5.8	2009	<4.6	1531	<3.3	2179	<3.2	2657	<4.0	2655	<4.1
3186	<5.8	3017	<4.6	2203	<3.3	3043	<3.2	3185	<4.0	3183	<4.1
3858	<5.8	3689	<4.6	3067	<3.3	3691	<3.2	3857	<4.0	3855	<4.1
4968	<5.8	4529	<4.6	3715	<3.3	4675	<3.2	4697	<4.0	4695	<4.1
				4699	<3.3						

6. CONCLUSIONS

There is considerable interest in chemicals which are suspected to possess the ability to cause disruption of endocrine systems, particularly those associated with reproductive organs and reproduction. Although there is no clear evidence yet that such substances are affecting man, there is evidence of effects on aquatic wildlife in particular circumstances.

A number of assays are currently being used to identify endocrine disrupting properties of a wide range of chemicals.

A list of suspected endocrine disruptors, for which there is published evidence of such activity in either *in vitro* or *in vivo* assays, and that could be used in the manufacture of materials used in contact with drinking water was compiled.

Manufacturers were contacted to find out whether any products contained any of these chemicals.

It was found that a variety of materials used in contact with drinking water contain chemicals that are currently suspected to be endocrine disruptors. Most of these materials were site-applied products.

Manufacturers stated that alkyl phenol based antioxidants were used in some materials. Most of these materials were factory made. Because of the lack of data on the endocrine disruption potential of antioxidants and the nature of the alkylphenol degradation products these materials were not investigated further.

In all cases when the materials were tested in the laboratory, any detected levels of endocrine disruptors leaching into water in contact with them were found to decrease over time. However, in many cases, when trying to relate the laboratory results to worst-case concentrations in actual drinking water, it was difficult to be certain what constituted a worst case, in terms of the area in contact with water, the contact time and whether any high initial leaching would be run to waste.

However, where calculations were made these indicated that concentrations in practice, sometimes after initially high short term leaching, would be very low and probably negligible. At least one product (Material E) requires further consideration.

Field testing of epoxy resins showed that long term leaching, sometimes after relatively high short term leaching, was very low, usually not detectable. It would appear from these results that chronic exposure to suspected endocrine disruptors from materials in contact with drinking water is unlikely to present a significant risk to consumers. However, acute exposure from newly installed products may need re-consideration, if only to decide on whether flushing procedures need to be made more rigorous.

In addition, it may be prudent to reconsider controls on application of site-applied materials, such as the maximum area that may be treated in relation to the volume of water in contact and residence times.

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APPENDIX A ENDOCRINE DISRUPTORS

Table 6.1 is a list of all the compounds with are alleged to have some form of endocrine disrupting character.

Table 6.1 Suspected endocrine disruptors found in the literature

Name	Reference
α -Hexachlorocyclohexane (α -HCH)	7
β -Hexachlorocyclohexane (β -HCH)	15 17
γ -Hexachlorocyclohexane (γ -HCH, Lindane)	5 6 7 15 17
1,1,1-Trichloro-2,2-bis(4-chlorophenyl)ethane (<i>p,p'</i> -DDT)	5 6 7 14 15 17
1,1-bis (4-hydroxyphenyl)ethane	13
1,1-bis (4-hydroxyphenyl)propane	13
1,2-Dibromo-3-chloropropane (DBCP)	5 15 17
1-Ethyl-2-(4'-hydroxyphenyl)-3-methyl-5-hydroxyindane (Indanestrol)	10
1-Ethyl-2-(4'-hydroxyphenyl)-3-methyl-5-hydroxyindene (Indenestrol A)	10
1-Methyl-1-(4-hydroxyphenyl)-2-(2,4-dihydroxyphenyl)-ethan-2-one (<i>O</i> -demethylangolensin)	1
1-Methyl-2-(4'-hydroxyphenyl)-3-ethyl-6-hydroxyindene (Indenestrol B)	10
2,2',3,3',6,6'-Hexachloro-4-biphenol	14
2,2',4,5-Tetrachloro-4-biphenol	14
2,2-bis (4-hydroxyphenyl)butane	13
2,2-bis (4-hydroxyphenyl)perfluoropropane	13
2,2-bis (4-hydroxyphenyl)propanol	13
2,2-Di-(4-hydroxyphenyl)-propane (Bisphenol A)	16 5 6 9 10 12 13 14 15 17
2,3,4,5-Tetrachloro-4-biphenol	14
2,3,4-Trichloro-4-biphenol	14
2,3,7,8-Tetrachlorodibenzodioxin (TCDD)	2 6 7 16
2,4,5-Trichlorophenol	6
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	5 15 17
2,4-Dichlorophenol	17
2,4-Dichlorophenoxyacetic acid (2,4-D)	15 17
2',3',4',5'-Tetrachloro-4-biphenol	4
2',4',6'-Trichloro-4-biphenol	4 14
2-Hydroxy-2',5'-dichlorobiphenol	14
3,3-bis (4-hydroxyphenyl)pentane	13
3,4-Di-(3',5'-difluoro-4'-hydroxyphenyl)-hex-3-ene (3,3'-5,5' tetrafluoro DES)	10
3,4-Di-(3'-hydroxyphenyl)-hex-3-ene (3,3' DES)	10
3,4-Di-(4'-hydroxyphenyl)-hex-3-ene (DES)	7 9 10

Name	Reference
3,4-Di-(4'-hydroxyphenyl)-hexa-2,4-diene (Dienestrol)	10
3,4-Di-(4'-hydroxyphenyl)-hexane (Hexestrol)	9 10
3-Hydroxy-2',3',4',5'-tetrachlorobiphenol	14
3-Hydroxy-2',5'-dichlorobiphenol	14
4,4'-Dihydroxy- α,β -diethylstilbene (diethylstilboestrol DES)	7
4,4'-Hydroxy-2'-chlorobiphenol	7
4,4-bis (4-hydroxyphenyl)heptane	13
4-Hydroxy-2,2',5-trichlorobiphenol	14
4-Hydroxy-2',3',4',5'-tetrachlorobiphenol	7 14
4-Hydroxy-2',4',6'-trichlorobiphenol	7 14
4-Hydroxy-2',5'-dichlorobiphenol	14
4-Hydroxy-biphenol	14
5,7-Dihydroxy-3-(4-hydroxyphenyl)-1,4-benzopyrone (Genistein)	1 7 10
7-Hydroxy-3-(4-hydroxyphenyl)-1,4-benzopyrone (Daidzein)	1 10
Adenosine 3'5'-cyclic monophosphate (cAMP)	8
Alachlor	5 15 17
Aldicarb	5 15 17
Aldrin	
Alkylphenol ethoxylates (APEs, APED)	5 6 7 15 16
Amitrole	5 15 17
Aniline dyes	
Aroclor	5 16
Aroclor (21-48% Cl)	7
Atrazine (chlorotriazine)	3 5 6 7 15 17
Benomyl	5 15 17
Benzidine based dyes	
Benzo[a]pyrene	7 17
Bis (4-hydroxyphenyl)ketone	13
Bisphenol A bischloroformate (BisACF)	13
Bisphenol A diglycidyl ether (BADGE)	13
Bisphenol A diglycidyl ether dimethylacrylate (BAGDEDMA)	13
Bisphenol A dimethylacrylate	12
Bisphenol A dimethylacrylate (BisADMA)	13
Bisphenol A ethoxylate (EBisA)	13
Bisphenol A ethoxylate diacrylate (BisAEDA)	13
Bisphenol A propoxylate (PBisA)	13
Bisphenol F (BisF)	13
Butyl benzyl phthalate (BBP)	5 6 16 14 17
Butylated hydroxyanisole (BHA)	6 14
Cadmium	17
Carbaryl	5 15 17
Carbendazim	5 15
Carbon disulphide	
Carbon tetrachloride	

Name	Reference
Chlordane	5 15 17
Chlordecone (Kepone)	6 7 8 9 14
Chloroform	
Chlorotriazine	7
Chlorpyrifos	
Clophen A (PCBs)	5
Coumestrol	7 9 10
Cypermethrin	17
DDD	5 15 17
Dicarboximides	15
Dichlorodiphenyldichloroethylene (DDE)	5 6 7 14 15
	17
Dicofol	5 15 17
Dicyclohexyl phthalate (DCHP)	17
Dieldrin	5 14 15 17
Diethyl phthalate (DEP)	17
Diethylhexyl adipate	17
Di-ethylhexyl phthalate (DEHP)	5 6 7 16 17
Di-hexyl phthalate (DHP)	17
Dimethyl phenol athracene	7
Dimethyl phthalate (DMP)	6
Di- <i>n</i> -butyl phthalate (DBP)	5 6 17
Di- <i>n</i> -pentyl phthalate (DPP)	17
Dioctyl phthalate (DOP)	6
Dioxins	17
Di-propyl phthalate (DprP)	17
Endosulfan (α and β)	6 9 14 17
Enterodiol	1 10
Enterolacetone	1 9 10
Equol	1 9 10
Esfenvalerate	17
Ethanol	
Ethoxylate	
Ethylenebisdithiocarbamates (EBDCs)	5 15
Ethylparathion	17
Fenvalerate	17
Furans	17
Heptachlor	5 15 17
Heptachlor-epoxide	5 15 17
Hexachlorobenzene (HCB)	5 15 17
Indol-3-carbinol	7
Iprodione	
Kanechlor (PCBs)	5
Ketoconazole class of fungicides	

Name	Reference
Lead	17
Linuron	
Malathion	5 15 17
Mancozeb	5 15 17
Maneb	5 15 17
Manganese	
Matairesinol	1
Mercury	17
Metam sodium	
Methanol	
Methomyl	5 17
Methoxychlor	5 6 7 11 14 15 17
Metiram	5 15 17
Metribuzin	5 15 17
Mirex	5 15 17
<i>m</i> -Octyl phenol	14
Monoethylhexyl phthalate (MEHP)	17
Nitrofen	17
Octachlorostyrene	17
<i>o-p'</i> -DDT	9 14 15 16
Oxychlorane	17
Parathion	17
Pentachlorophenol (PCP)	5 15 17
Pentaphenol ethoxylate	17
Permethrin	7 17
<i>p</i> -Ethyl phenol	14
<i>p</i> -Isopentyl phenol	14
<i>p</i> -Nonylphenol	11
<i>p</i> -Octylphenol	6 7 9 16
<i>p</i> -Octylphenol ethoxylate	6 7 9 16
Polychlorinated dibenzo- <i>p</i> -dioxins (PCDDs)	5 6 7 15
Polychlorinated dibenzofuranes (PCDFs)	2 5 6 7 15
Polycyclic aromatic hydrocarbons (PAH)	7
<i>p</i> -Propyl phenol	14
Procymidome	
<i>p-sec</i> -Butyl phenol	14
<i>p-tert</i> -Butyl phenol	14
<i>p-tert</i> -Pentyl phenol	14
Pyrethroids	17
Secoisolariciresinol	1
Simazine	7
Styrene dimer and trimer	17
Thiram	

Name	Reference
Toxaphene (camphechlor)	5 14 15 17
Transnonachlor	17
Tributyl tin (TBT)	5 15 17
Trifluralin	5 15 17
Tris-nonylphenol phosphite (TNPP)	6 16
Urethane	
Vinclozilin	6 7 15 17
Zearalenone	7 9 10
Zeranol	10
Zineb	5 15 17
Ziram	17

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APPENDIX B LETTER SENT TO MANUFACTURERS REGARDING POTENTIAL EXPOSURE TO ENDOCRINE DISRUPTORS VIA MATERIALS IN CONTACT WITH DRINKING WATER

Dear Sir,

POTENTIAL EXPOSURE TO ENDOCRINE DISRUPTORS VIA DRINKING WATER

The WRC have been appointed by the Department of the Environment, Transport and the Regions to carry out research into the possibility of exposure to endocrine disruptors from materials in contact with drinking water. As you may know endocrine disruptors are chemicals that possess the ability to interfere with endocrine systems, a number of unsubstantiated reports in the scientific literature suggests that drinking water might constitute a source of exposure to endocrine disruptors. Although, the current situation is that exposure from drinking water to such compounds does not appear to be significant, the situation needs to be assessed.

I am writing to ask for your assistance in identifying materials which are used in contact with drinking water and which might contain residues of chemicals possessing possible endocrine disrupting properties. It would be helpful if you could indicate on the enclosed questionnaire any products which contain possible endocrine disruptors and at what concentrations they are present. Any information you may have on the leaching characteristics of these substances would also be useful.

Please can I assure you that your response will be treated in confidence and none of the data will be used in a way that reveals product or manufacturer specific information.

If you have any problems or queries do not hesitate to contact Mike Fielding or myself.

Thank you for your cooperation.

Yours sincerely,

Guy Franklin
Drinking Water Chemistry

Enc.

APPENDIX C QUESTIONNAIRE SENT TO MANUFACTURERS

Additive / Compound	Product type and name	Concentration of additive in product (and any leaching information)
Bis(2-ethylhexyl) phthalate (DEHP)		
Butyl benzyl phthalate (BBP)		
Dibutyl phthalate (DBP)		
Diethyl phthalate (DEP)		
Diisobutyl phthalate (DIBP)		
Diisodecyl phthalate (DIDP)		
Diisononyl phthalate (DINP)		
Dimethyl phthalate (DMP)		
Ditridecyl phthalate (DTDP)		
Phthalate (unspecified)		
Bisphenol A(BisA) 2,2-Di-(4-hydroxyphenyl)propane		
Bisphenol A diglycidyl ether (BADGE) 2,2-Di-(4-(2,3-epoxypropoxy)phenyl)propane *		
Bisphenol F (BisF) Di-(4-hydroxyphenyl)methane *		
Bisphenol F diglycidyl ether (BisF) Di-(4-(2,3-epoxypropoxy)phenyl)methane *		
Butyl phenol 4-(1,1-dimethylpropyl)phenol		
Nonyl phenol		
Octyl phenol		
Pentyl phenol		
Alkyl phenols (unspecified) including antioxidants based on alky phenols *		
Nonyl phenol polyethoxylate (NPP) or nonyl phenol ethoxylate		
Octyl phenol polyethoxylate (OPP) or octyl phenol ethoxylate		
Alkyl phenol polyethoxylate or alkyl phenol ethoxylate (unspecified) *		
Butylated hydroxyanisole (BHA) 2,6-di-tert-butyl-4-methoxyphenol		
* These are not necessarily endocrine disrupting chemicals but are potentially related to, or associated with, endocrine disrupting chemicals.		

APPENDIX D GLOSSARY

4-TBP	4- <i>tert</i> -Butyl phenol
ABS	Acrylonitrile butadiene styrene copolymer
AP	Alkyl phenols
AQC	Analytical quality control
BADGE	Bisphenol A diglycidyl ether
BAGDEDMA	Bisphenol A diglycidyl ether dimethylacrylate
BBP	Butyl benzyl phthalate
BCHP	Butyl cyclohexyl phthalate
BDcP	Butyl decyl phthalate
BEHP	Butyl 2-ethylhexyl phthalate
BFDGE	Bisphenol F diglycidyl ether
BHA	Butylated hydroxyanisole (2,6-di- <i>tert</i> -butyl-4-methoxyphenol)
BHT	Butylated hydroxytoluene (2,6-dibutyl-4-methylphenol)
BIDP	Butyl <i>iso</i> -decyl phthalate
BisA	Bisphenol A
BisACF	Bisphenol A bischloroformate
BisADMA	Bisphenol A dimethylacrylate
BisAEDA	Bisphenol A ethoxylate diacrylate
BisF	Bisphenol F
BisS	Bisphenol S
BMoEP	Bis(methoxyethyl) phthalate
BOP	Butyl octyl phthalate
BP	Butyl phenol
CCM	Committee on chemicals and materials of construction for use in public water supply and swimming pools
DBEP	Di butylethoxy phthalate
DBoEP	Bis(2- <i>n</i> -butoxyethyl) phthalate
DBP	Dibutyl phthalate
DCHP	Dicyclohexyl phthalate
DCM	Dichloromethane
DEHhP	Bis(2-ethylhexyl) hexahydrophthalate
DEHIP	Bis(2-ethylhexyl) isophthalate
DEHP	Bis(2-ethylhexyl) phthalate
DEoEoEP	Bis[2-(2-ethoxyethoxy)ethyl] phthalate
DEoEP	Bis(ethoxyethyl) phthalate
DEP	Diethyl phthalate
DHP	Dihexyl phthalate
DIBP	Di- <i>iso</i> -butyl phthalate
DIDP	Di- <i>iso</i> -decyl phthalate
DIHP	Di- <i>iso</i> -hexyl phthalate
DINP	Di- <i>iso</i> -nonyl phthalate
DMIP	Dimethyl <i>iso</i> -phthalate
DMP	Dimethyl phthalate
DnOP	Di- <i>n</i> -octyl phthalate

DOIP	Dioctyl <i>iso</i> -phthalate
DOP	Dioctyl phthalate
DPeP	Diamyl phthalate
DPhP	Diphenyl phthalate
DTDP (DITP)	Ditridecyl phthalate
DUP	Diundecyl phthalate
DWI	Drinking Water Inspectorate
E ₂	Estradiol
EBisA	Bisphenol A ethoxylate
EHBP	Ethyl hexyl benzyl phthalate
EHIDP	2-Ethylhexyl- <i>iso</i> -decyl phthalate
GC	Gas chromatograph
GCMS	Gas chromatography mass spectrometry
GRP	Glass reinforced plastic
HDP	Hexyl decyl phthalate
HEHP	Hexyl 2-ethylhexyl phthalate
HPLC	High pressure liquid chromatography
IDTDP	<i>iso</i> -Decyl tridecyl phthalate
IHBP	<i>iso</i> -Hexylbenzyl phthalate
LCMS	Liquid chromatography mass spectrometry
LOD	Limit of detection
MM1	1,1-Bis(4-hydroxyphenyl)ethane
MM2	1,1-Bis(4-hydroxyphenyl)propane
MM3	2,2-Bis(4-hydroxyphenyl)butane
MM4	3,3-Bis(4-hydroxyphenyl)pentane
MM5	4,4-Bis(4-hydroxyphenyl)heptane
MM7	2,2-Bis(4-hydroxyphenyl)perfluoropropane
MM8	Bis(4-hydroxyphenyl)ketone
MM9	2,2-Bis(4-hydroxyphenyl)propanol
MS	Mass spectrometer
NP	Nonyl phenol
NPE	Nonyl phenol ethoxylate
NPP	Nonyl phenol polyethoxylate
OIDP	Octyl- <i>iso</i> -decyl phthalate
OP	Octyl phenol
OPE	Octyl phenol ethoxylate
OPP	Octyl phenol polyethoxylate
PBisA	Bisphenol A propoxylate
PP	Pentyl phenol
PTFE	Poly tetrafluoroethylene
PVC	Poly vinyl chloride
SIM	Single ion monitoring
TIC	Total ion chromatogram
TOC	Total organic carbon
UV	Ultra violet
WBS	Water Bylaws Scheme