Scoping study for Dangerous Substances Directive List II chemicals

by
Water Framework Directive - United Kingdom Technical Advisory Group (WFD-UKTAG)

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Executive summary

Under the Water Framework Directive (WFD), environmental quality standards (EQSs) for substances that are specific to Member States are required as a means of assuring that all surface waters reach good ecological status by 2015. Such substances are covered under Annex VIII of the WFD and are known as specific pollutants.

In 2005, the Environment Agency performed an exercise on behalf of the UK Technical Advisory Group (UKTAG) to prioritise the Dangerous Substances Directive (DSD) 76/464/EEC List II substances that had not at that time been considered as specific pollutants under the WFD. Substances already identified as WFD Annex X priority substances/priority hazardous substances, those that were no longer authorised for use and chemicals unsuitable for going through the prioritisation process were also removed from the list of chemicals to consider. The prioritisation of the remaining substances covered under the existing DSD Regulations took into account relevant monitoring data for five years (up to and including 2003), usage data and hazard information. As a result of this exercise, a number of substances were identified as candidates for WFD standards derivation and have subsequently undergone review. However, 12 List II substances under the DSD were not scheduled as specific pollutants and UKTAG considered that existing measures and policies for these substances would deliver progressive reductions without the need for further action at this time. These 12 substances are:

- bentazone
- biphenyl
- 4-chloro-3-methylphenol
- chloronitrotoluenes
- 2-chlorophenol
- dichlorvos
- fenitrothion
- malathion
- 1,1,1-trichloroethane
- 1,1,2-trichloroethane
- triphenyltin
- xylene.

However, the DSD will be repealed in 2013 and consequently the current EQS values for these 12 substances will no longer stand. UKTAG also concluded that the situation with respect to these substances would need to be reviewed before the repeal of the DSD to identify if any of them are still being discharged in significant quantities. If this is found to be the case, the UKTAG will bring forward proposals for the derivation of EQSs.

This scoping study reviews the situation for these 12 substances, as proposed by UKTAG, to determine if the EQSs for all or some of these chemicals can be repealed or whether additional work on the development of EQSs needs to be carried out before 2013.

Environment Agency monitoring data for England and Wales were collated covering a period from January 2004 to September 2008. A statistical examination of the data revealed that for river water, groundwater and estuarine water, the majority of the

reported samples (typically >90 per cent) are less than the analytical limit of detections. The monitoring data were compared with the corresponding annual average and maximum acceptable concentration EQSs as set under the DSD. Levels of the substances of interest were shown to be generally compliant for all examined waters with the exception of where the limit of detection is greater than the EQS (dichlorvos) or where samples were taken after a pollution incident (some xylene data).

Examination of readily available marketing and use data indicated that extensive marketing and use controls exist for most of these substances and that future trends in concentrations in water are likely to be downwards, below the already very low levels. Of the substances used in any quantity, only bentazone levels in the aquatic environment are likely to exhibit a relatively stable concentration, rather than a decreasing trend, owing to the current lack of source control. However, bentazone is a candidate priority substance under the WFD so could be subject to EQS derivation by the European Commission in the future.

It was concluded that owing to their low (EQS compliant) concentrations in the environment, combined with extensive marketing and use restrictions or bans, these substances are no longer of high concern in England and Wales and, therefore, do not require being treated as specific pollutants under the WFD.

While the content of this document is predominantly concerned with England and Wales, the situation for Scotland and Northern Ireland has also been reviewed herein.

Scottish Environment Protection Agency (SEPA) surface and groundwater monitoring data were collated covering a period from January 2008 to December 2010 for the majority of the 12 substances listed above. Overall, 91.5 per cent of samples were less than the analytical limits of detection and no EQS breaches were observed. None of the substances is monitored in Scotland's marine waters as they are not perceived to be a threat to Scotland's marine environment. As concluded by the Environment Agency assessment, SEPA conclude that these substances are no longer of great concern, so do not require to be treated as specific pollutants under the WFD.

Northern Ireland Environment Agency 2007–2008 OSPAR and surveillance monitoring data were assessed for many of the substances listed. There were very few detections (aside from xylene), and no breaches of EQS were observed.

Contents

1 Introduction

Under the Water Framework Directive (WFD) 2000/60/EC[1], environmental quality standards (EQSs) that are specific to Member States are required as a means of assuring that all surface waters reach good ecological status by 2015. Such substances are covered under Annex VIII of the WFD. A methodology has been developed with which to identify and prioritise Annex VIII chemicals (also known as specific pollutants) and this method is outlined in the publication on prioritisation (Environment Agency, 2007).

In 2005, an exercise was performed to prioritise the Dangerous Substances Directive (DSD) 76/464/EEC List II substances covered under the existing DSD Regulations[2] that had not at that time been identified as specific pollutants or priority substances/priority hazardous substances. Chemicals no longer used in the UK or unsuitable for going through the process were removed from the list as part of the prioritisation exercise (their status is reviewed in Appendix A)[3]. The study took into account monitoring data for five years (up to and including 2003), usage data and hazard information. As a result of this exercise, a number of substances were identified as candidates for WFD standards derivation and have subsequently undergone review.

However, 12 List II substances under the DSD Regulations were not scheduled as specific pollutants under the WFD. These substances are reported in Table 1, Part C, of the UK Technical Advisory Group (UKTAG) final report on proposals for specific pollutants (UKTAG, 2008). Following an assessment, the UKTAG advised that the existing EQSs and controls for these 12 substances need not be reviewed and should continue to be used, and that the substances should not be treated as specific pollutants under the WFD. Specifically this advice covers the following substances:

bentazone	biphenyl	4-chloro-3-methylphenol
chloronitrotoluenes	2-chlorophenol	dichlorvos
fenitrothion	malathion	1,1,1-trichloroethane
1,1,2-trichloroethane	triphenyltin	xylene (m, p and o)

The UKTAG suggested that existing measures and policies for these substances would deliver progressive reductions without the need for further action at this time. However, the UKTAG also concluded that this situation needed to be reviewed before the repeal of the DSD in 2013 to identify any of these substances that are still being discharged in significant quantities. If this was found to be the case, the UKTAG would bring forward proposals for the derivation of EQSs.

The following sections present the objectives of the study and the findings relating to the environmental monitoring data for these substances in relation to their EQSs. The report predominantly considers the situation in England and Wales. However, Sections 7 and 8 take account of the situation in Scotland and Northern Ireland, respectively.

[1] Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy.

[2] In England and Wales, Regulations 1997/2560 and 1998/389 (DoE, 1997a, 1998). In Scotland, Regulations 1998/250 and 1998/1344 (Scottish Office, 1998a, 1998b). In Northern Ireland, the Surface Waters (Dangerous Substances) (Classification) Regulations (Northern Ireland) 1998.

[3] Substances covered in Circulars 7/89 and 16/89 [Circular 7/89 (Department of the Environment), Circular 16/89 (Welsh Office); Water and the Environment. The implementation of European Community directives on pollution caused by certain dangerous substances discharged into the aquatic environment; 30 March] that have not been identified as specific pollutants or priority substances/priority hazardous substances are also reviewed in Appendix A. List II substances under Circular 34/1985 Implementation of EC Directive 76/464/EEC issued by the Scottish Development Department all have requirements as specific pollutants or priority substances.

2 Objectives

The purpose of this investigation is to undertake the review proposed by UKTAG in the specific pollutants report. Specifically, this report aims to determine:

- Whether concentrations of the identified chemicals are being detected in surface waters in quantities that may be close to or exceed the current DSD EQS;
- Whether current or future trends in marketing and use may cause this to be the case in years to come.

This was achieved by considering monitoring and use/marketing data available since 2004.

The outcomes of the project will inform policy as to whether the selected substances are, or may be of future, national concern in surface waters and so should be treated as specific pollutants under the WFD.

3 Methodology

3.1 Datasets

The Environment Agency supplied all available environmental surface water monitoring data for England and Wales for all of the identified substances from 2004 until present. This section and Sections 4–6 relate to those data. Sections 7 and 8 consider data from Scotland and Northern Ireland, respectively.

3.2 Data manipulation

3.2.1 Sample selection

The data was supplied in a Microsoft Access format containing separate tables for each of the Environment Agency's regions (Thames, North East, North West, Southern, South West, Wales, Anglian and Midlands).

Data was exported into Microsoft Excel to facilitate sorting and statistical manipulation. Care was taken to ensure data sets were not greater than 65,000 lines long (the export limit for Excel).

The key objective was to assess the compliance of English and Welsh surface waters for these DSD List II substances based on general surface water monitoring data. Consequently, the database held a significant amount of superfluous data for materials such as leachates, canal water, borehole water, crude sewage and sewage effluent, storm sewer overflows, surface drainage, etc. Within each material description, a number of sampling purposes are also listed, including National Agency policy monitoring, planned investigations, compliance auditing, statutory environmental monitoring, pollution incidents, statutory failure monitoring and unplanned reactive monitoring. To ensure consistency and to prevent bias, the following codes (and hence sample types) were selected in order to carry out the data analysis (Table 3.1).

Table 3.1 Summary of sample types used in the data analysis

Sample Code	Sample description/type	Purpose	Material description
F1	Freshwater – RQO RE1[1]	Environmental monitoring statutory (EU directives)	River/running surface water
F2	Freshwater – RQO RE2[1]	Environmental monitoring statutory (EU directives)	River/running surface water
F3	Freshwater – RQO RE3[1]	Environmental monitoring statutory (EU directives)	River/running surface water
F4	Freshwater – RQO RE4[1]	Environmental monitoring statutory (EU directives)	River/running surface water
F5	Freshwater – RQO RE5[1]	Environmental monitoring statutory (EU directives)	River/running surface water
F6	Freshwater – non-classified river points	Environmental monitoring statutory (EU directives)	River/running surface water
F6	Freshwater – non-classified river points	Planned investigation (operational monitoring)	Estuarine water

Sample Code	Sample description/type	Purpose	Material description
FZ[2]	Freshwater – unspecified	Environmental monitoring statutory (EU directives)	River/running surface water
FZ[2]	Freshwater – unspecified	Monitoring (UK govt policy – not GQA or RE[1])	River/running surface water
FZ[2]	Freshwater – unspecified	Planned investigation (operational monitoring)	River/running surface water
FZ[2]	Freshwater – unspecified	Environmental monitoring statutory (EU directives)	Estuarine water
CE	Saline water – estuarine sites – nonbathing/shellfish	Environmental monitoring statutory (EU directives)	Estuarine water
CE	Saline water – estuarine sites – nonbathing/shellfish	Monitoring (national agency policy)	Estuarine water

[1] Seven measures (dissolved oxygen, biological oxygen demand, total and un-ionised ammonia, zinc, copper and pH) are used as indicators of the health of rivers and have been grouped into the River Ecosystem (RE) Classification. These RE classes are used to set quality targets [river quality objectives (RQOs)]. If the target is not met, the Environment Agency aims to find the cause and set out the action needed to improve the quality of the rivers. RE1 is set for highest quality rivers and RE5 for the poorest quality.
[2] All Welsh freshwaters are categorised as FZ.

3.2.2 Data analysis

A large proportion of the available data are reported as less than the limit of detection (LOD)[4]. This leads to a number of issues regarding data manipulation and analysis. To ignore all data reported as less than the LOD results in a very limited dataset and an overestimate of the true situation, biased towards higher measured values. To take less than LOD values at face value will also lead to an overestimate of true concentrations as in many cases actual concentrations will be significantly less than the LOD.

A compromise is to set all less than values to half the LOD (e.g. a value of 0.05 µg/l substituted for a <0.1 µg/l reported value). This is an accepted method of data manipulation and leads to less overall bias in the calculated averages. Indeed, this is also the method currently used to assess monitoring data for compliance with the DSD.

3.3 Environmental quality standards

All of the identified substances have EQSs derived by the UK regulators under the Dangerous Substances Directive [European Union (EU), 1976] (Table 3.2). In most cases, EQSs are derived as annual averages, with which to assess long-term trends and to protect aquatic life from chronic pollution, and maximum acceptable concentrations (MACs), which are generally higher values, but which should not be exceeded for more than a 24-hour period. The MAC is designed to ensure the avoidance of short-term adverse impacts on aquatic biota resulting from episodic discharges, such as from storm sewer overflows, highway runoff and accidental agricultural or industrial discharges. For biphenyl and dichlorvos, however, only annual average EQSs are available, and for triphenyltin only a MAC has been derived [Department of the Environment (DoE), 1994, 1991a, 1988, respectively).

For statutory compliance assessment (DoE, 1997a, 1998), it is only the annual averages that apply, with the exception of the MAC for triphenyltin. For this project, the monitoring data were compared against the annual average EQSs, reflecting the main statutory

[4] While commonly referred to as values less than the LOD, these values are in fact derived from a comparison against a minimum reporting value (MRV), i.e. they are less than the MRV data. Such MRVs are derived from the analytical LOD and are usually equal to them or greater in value.

requirements. In addition, for completeness, reported maximum concentrations for each substance were also compared against the MAC to determine if sporadic elevated concentrations observed in water resulted in exceedances, indicating that the substances may be of concern with respect to their short-term acute toxicity.

Table 3.2 Summary of Dangerous Substances Directive environmental quality standards

Substance	Freshwater (µg/l)		Saline water (µg/l)	
	Annual average[1]	Maximum acceptable concentration	Annual average[1]	Maximum acceptable concentration
1,1,1-Trichloroethane	100	1,000[2]	100	1,000[2]
1,1,2-Trichloroethane	400	4,000	300	3,000
2-Chlorophenol	50[3]	250[3]	50	250[4]
4-Chloro-3-methylphenol	40	200	40	200[5]
Bentazone	500	5,000[6]	500	5,000[6]
Biphenyl	25[7]	–	25	–
Chloronitrotoluenes total	10	100	10	100[8]
Dichlorvos	0.001	–	0.04	0.6[9]
Fenitrothion	0.01	0.25[8]	0.01	0.25[10]
Malathion	0.01	0.5[9]	0.02	0.5[11]
Triphenyltin	–	0.02[1]	–	0.008[1]
Xylene	30[12]	300	30	300

[1] Statutory standards under Regulations 1997/2560 and 1998/389 (DoE, 1997a, 1998).
[2] Interim guideline value given in the DoE report (DoE, 1992a).
[3] Proposed annual average EQS (Environment Agency, 1997).
[4] Value given in the Environment Agency report (1997) for the total concentration for monochlorophenols in a mixture or as the individual congener. The report also states that where the prevention of fish tainting is a priority, values lower than the proposed EQSs may be adopted. The saltwater value is a tentative value.
[5] Tentative value given in the DoE report (1997b).
[6] Tentative value for freshwater and interim guideline value for saltwater in the DoE report (1996).
[7] Biphenyl EQS statutory EQS for annual average only (DoE, 1994).
[8] Interim guideline value given in the DoE report (1992b).
[9] After 24 hours (DoE, 1991a).
[10] Provisional value given in the DoE report (1991b).
[11] Tentative provisional value given in the DoE report (1991c).
[12] As total xylenes (DoE, 1997c).

4 England and Wales freshwater river data

4.1 Sample numbers

For English and Welsh freshwater river sampling sites [F1 to F6 and FZ (see Table 3.1)], a total of 85,412 samples were available from January 2004 to September 2008.

The number of samples taken shows a reasonable cross-section across the English regions and Wales, generally reflecting the size of the region (Table 4.2). For some substances a variety of isomers have been reported as well as a total concentration (e.g. chloronitrotoluenes, xylenes) for which the EQS has been derived.

The data presented in the tables demonstrate the large volume of samples taken to assess water quality for these DSD List II substances across the regions.

Table 4.1 Summary of sample numbers taken for freshwater rivers across the Environment Agency regions

Substance	Number of samples by Environment Agency region[1]								Total number of samples
	AN	MID	NE	NW	SO	SW	TH	WA	
1,1,1-Trichloroethane	1,116	1,683	1,738	705	349	986	724	1,021	8,322
1,1,2-Trichloroethane	263	1,014	810	606	232	167	578	250	3,920
1,2-Dimethylbenzene (*o*-xylene)	85	1,298	705	898	167	37	508	389	4,087
Dimethylbenzenes (xylene *m*/*p*- +*o*-isomers)	392	915	405	391	399	140	270	89	3,001
Xylene (*m* & *p*) (1,3+1,4-dimethylbenzene)	88	1,407	703	739	167	37	300	389	3,830
2-Chloro-4-nitrotoluene	234	238	575	381	241	90	481	325	2,565
2-Chloro-5-nitrotoluene	78	239	471	355	92	90	201	325	1,851
2-Chloro-6-nitrotoluene	234	239	574	347	234	90	484	325	2,527
4-Chloro-3-nitrotoluene	234	239	471	348	249	90	485	325	2,441
2-Nitro-4-chlorotoluene	234	239	464	360	249	90	486	325	2,447
Chloronitrotoluenes total	25	4	201	0	61	0	16	20	327
2-Chlorophenol	548	1,199	1,556	761	804	170	561	324	5,923
4-Chloro-3-methylphenol	227	1,167	381	700	236	130	475	253	3,569
Bentazone	550	92	304	578	228	128	633	1,103	3,616
Biphenyl	379	254	335	280	237	130	529	245	2,389
Dichlorvos	803	3,224	1,828	500	701	669	828	1,275	9,828
Fenitrothion	800	3,098	1,687	376	700	666	603	1,257	9,187
Malathion	780	3,111	1,843	363	690	864	582	1,260	9,493
Triphenyltin	1,056	891	1,105	810	506	239	993	489	6,089
Total	**8,126**	**20,551**	**16,156**	**9,498**	**6,542**	**4,813**	**9,737**	**9,989**	**85,412**

[1] AN = Anglian; MID = Midlands; NE = North East; NW = North West; SO = Southern; SW = South West; TH = Thames; WA = Wales.

Table 4.2 Summary of the percentage of samples taken for freshwater river monitoring across the Environment Agency regions

Substance	Percentage of samples (%) by Environment Agency region[1]							
	AN	MID	NE	NW	SO	SW	TH	WA
1,1,1-Trichloroethane	13	20	21	8	4	12	9	12
1,1,2-Trichloroethane	7	26	21	15	6	4	15	6
1,2-Dimethylbenzene (*o*-xylene)	2	32	17	22	4	1	12	10
Dimethylbenzenes (xylene *m*/*p*- +*o*-isomers)	13	30	13	13	13	5	9	3
Xylene (*m* & *p*) (1,3+1,4-dimethylbenzene)	2	37	18	19	4	1	8	10
2-Chloro-4-nitrotoluene	9	9	22	15	9	4	19	13
2-Chloro-5-nitrotoluene	4	13	25	19	5	5	11	18
2-Chloro-6-nitrotoluene	9	9	23	14	9	4	19	13
2-Nitro-4-chlorotoluene	10	10	19	15	10	4	20	13
4-Chloro-3-nitrotoluene	10	10	19	14	10	4	20	13
Chloronitrotoluenes total	8	1	61	0	19	0	5	6
2-Chlorophenol	9	20	26	13	14	3	9	5
4-Chloro-3-methylphenol	6	33	11	20	7	4	13	7
Bentazone	15	3	8	16	6	4	18	31
Biphenyl	16	11	14	12	10	5	22	10
Dichlorvos	8	33	19	5	7	7	8	13
Fenitrothion	9	34	18	4	8	7	7	14
Malathion	8	33	19	4	7	9	6	13
Triphenyltin	17	15	18	13	8	4	16	8
Total	**10**	**24**	**19**	**11**	**8**	**6**	**11**	**12**

[1] AN = Anglian; MID = Midlands; NE = North East; NW = North West; SO = Southern; SW = South West; TH = Thames; WA = Wales.

4.2 Limits of detection

Taking account of all classes of river quality (as classified using the RQO nomenclature) ranging from those considered of high quality (RE1) to those classified as bad (RE5) (38,500 samples), over 80 per cent of the data are less than the LOD for all substances, with the percentage in most cases greater than 90 per cent (Table 4.3). This indicates that these List II substances are rarely detected in English and Welsh surface waters. A similar situation occurs for estuarine and groundwaters (data not shown).

It should be noted that the percentages have been rounded to the nearest integer in Table 4.3; therefore, in some cases, there will be limited instances where data are reported above the LOD, but the information in the table will list them as 100 per cent less than the LOD.

Table 4.3 Summary of the percentage of samples less than the limit of detection by freshwater river quality objective class

Substance	Percentage of samples less than the LOD (%)[1]						
	FRESHWATER – RQO class						
	RE1	RE2	RE3	RE4	RE5	Non-classified	Un-specified
1,1,1-Trichloroethane	100	98	97	98	100	86	82
1,1,2-Trichloroethane	100	100	100	100	100	99	99
1,2-Dimethylbenzene (*o*-xylene)	90	92	95	91	91	92	97

Substance	Percentage of samples less than the LOD (%)[1]						
	FRESHWATER – RQO class						
	RE1	RE2	RE3	RE4	RE5	Non-classified	Un-specified
Dimethylbenzenes (*m*/*p*/*o*-xylene isomers)	93	93	96	84	82	93	48
Xylene (*m* & *p*) (1,3+1,4-dimethylbenzene)	88	90	94	87	85	90	96
2-Chloro-4-nitrotoluene	n/a	100	n/a	n/a	n/a	n/a	100
2-Chloro-5-nitrotoluene	n/a	100	n/a	n/a	n/a	n/a	100
2-Chloro-6-nitrotoluene	n/a	100	n/a	n/a	n/a	n/a	100
2-Nitro-4-chlorotoluene	n/a	100	n/a	n/a	n/a	n/a	100
4-Chloro-3-nitrotoluene	n/a	98	n/a	n/a	n/a	n/a	100
Chloronitrotoluenes total	n/a	100	n/a	n/a	n/a	n/a	100
2-Chlorophenol	98	98	98	94	99	98	100
4-Chloro-3-methylphenol	99	99	98	97	95	97	100
Bentazone	98	90	85	82	97	98	100
Biphenyl	n/a	99	n/a	n/a	n/a	n/a	100
Dichlorvos	100	100	100	100	99	100	100
Fenitrothion	100	100	100	99	98	100	100
Malathion	99	100	99	99	99	100	100
Triphenyltin	98	98	99	98	96	97	98

[1] These data are rounded to the nearest percentage point. Therefore given the number of data reported, it is possible that in some cases isolated data above the LOD are reported.

For some substances, the average analytical LOD is close to or greater than the EQS (as is the case for dichlorvos) (Table 4.4). Under these situations an analysis of EQS compliance is likely to have a larger degree of uncertainty, or if the average LOD is greater than the EQS, will not be possible. The data in Table 4.4 show that for dichlorvos the reported analytical LOD is on average greater than the EQS (reflecting the very low EQS for dichlorvos of 1 ng/l). As a consequence, any judgement of compliance will be unreliable, even when less than values are divided by two, given that on average the LOD is over four times the EQS.

Reported xylene average LODs for some combinations of isomers are also close to, or higher than the EQS. Chloronitrotoluene and malathion average LODs are also approximately one third to a half of the EQS. To make definitive statements regarding compliance, the LOD should ideally be roughly one third of the EQS (Gardner, 1989).

It may, therefore, be concluded that compliance with the EQS cannot be assessed for dichlorvos and that conclusions drawn regarding compliance of river water monitoring data for xylenes, chloronitrotoluenes and possibly malathion will have greater uncertainty than for substances where the LOD is less than one third of the EQS.

However, these data are compared with the annual average EQSs. Short-term EQSs expressed as a MAC are significantly higher than the annual average value and so the percentage of the average LOD to the annual average EQS will be commensurately higher. For substances where MAC concentrations are available (all except biphenyl and dichlorvos), the percentages of the LOD of the MAC EQS are less than or equal to 5 per cent with the exception of total xylene concentrations for two RE classes (RE1 = 11 per cent and RE3 = 5.2 per cent; data not shown). Any conclusions drawn regarding comparisons of observed concentrations against a MAC can therefore be made with a high degree of confidence. It must be noted however, that in all cases the spread of reported LOD for each substance is significant and can cover several orders of magnitude, and so there will be cases where even though the average LOD is less than the EQS, at the upper range the LOD may be greater than the EQS.

Table 4.4 Summary of the percentage of the average limit of detection to the environmental quality standard (annual average) for the DSD List II substances by freshwater river quality objective class

Substance	Percentage of the LOD to EQS (%)[1]						
	FRESHWATER – RQO class						
	RE1	RE2	RE3	RE4	RE5	Non-classified	Un-specified
1,1,1-Trichloroethane	0.1	0.1	0.1	0.2	0.1	0.6	0.1
1,1,2-Trichloroethane	0.04	0.04	0.03	0.04	0.05	0.2	1.9
1,2-Dimethylbenzene (*o*-xylene)	49	10	22	22	0.3	12	14
Dimethylbenzenes (*m*/*p*/*o*-xylene isomers)	1.5	1.5	42	44	1.1	26	1.0
Xylene (*m* & *p*) (1,3+1,4-dimethylbenzene)	110	26	52	48	0.7	18	15
2-Chloro-4-nitrotoluene	5.9	4.1	3.8	6.1	4.9	10	10
2-Chloro-5-nitrotoluene	9.2	9.5	10	8.8	10	10	10
2-Chloro-6-nitrotoluene	5.9	4.0	3.7	6.2	4.9	10	10
2-Nitro-4-chlorotoluene	5.9	3.9	3.6	6.1	4.9	10	10
4-Chloro-3-nitrotoluene	6.4	4.4	3.8	6.8	5.0	10	10
Chloronitrotoluenes total	46	43	39	43	50	50	50
2-Chlorophenol	0.1	0.1	0.1	0.2	0.1	0.2	0.1
4-Chloro-3-methylphenol	0.1	0.1	0.1	0.2	0.1	0.3	0.1
Bentazone	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Biphenyl	22	22	29	14	16	10	18
Dichlorvos	435	446	458	486	459	233	220
Fenitrothion	19	19	19	28	20	11	11
Malathion	29	31	34	40	33	17	42
Triphenyltin[2]	9	10	20	9	10	8	10

[1] Cells in green represent a LOD less than one third of the EQS, cells in amber represent LODs that are between 30 and 100 per cent and cells in red represent LOD which are greater than the EQS.
[2] No annual average available; therefore, LOD compared with MAC.

4.3 Compliance assessment considering all data

Considering all data for all regions, it can be seen that average concentrations from January 2004 to September 2008 are less than the EQS (Table 4.5), with the exception of dichlorvos where, as already explained, the average LOD is greater than the EQS.

Table 4.5 Average concentrations of DSD List II substances by freshwater river quality objective class

Substance	Average concentration (µg/l)[1]						
	FRESHWATER – RQO class						
	RE1	RE2	RE3	RE4	RE5	Non-classified	Un-specified
1,1,1-Trichloroethane	0.06	0.06	0.07	0.08	0.05	9.130	0.68
1,1,2-Trichloroethane	0.08	0.08	0.06	0.08	0.10	0.356	4.99
1,2-Dimethylbenzene (*o*-xylene)	6.66	1.45	3.16	3.00	0.15	1.711	3.74
Dimethylbenzenes (*m*/*p*/*o*-xylene isomers)	0.32	0.31	6.14	5.75	2.31	3.841	0.79
Xylene (*m* & *p*) (1,3+1,4-dimethylbenzene)	14.59	3.55	7.37	6.28	1.41	2.708	12.26
2-Chloro-4-nitrotoluene	0.29	0.20	0.19	0.31	0.25	0.492	0.50
2-Chloro-5-nitrotoluene	0.46	0.47	0.50	0.44	0.50	0.499	0.50
2-Chloro-6-nitrotoluene	0.30	0.20	0.18	0.30	0.25	0.492	0.50

Substance	Average concentration (µg/l)[1]						
	FRESHWATER – RQO class						
	RE1	RE2	RE3	RE4	RE5	Non-classified	Un-specified
2-Nitro-4-chlorotoluene	0.29	0.20	0.18	0.30	0.24	0.492	0.50
4-Chloro-3-nitrotoluene	0.32	0.22	0.19	0.34	0.24	0.492	0.50
Chloronitrotoluenes total	2.31	2.15	1.85	2.12	2.50	2.500	2.50
2-Chlorophenol	0.03	0.02	0.03	0.06	0.01	0.061	0.02
4-Chloro-3-methylphenol	0.03	0.02	0.03	0.04	0.01	0.069	1.74
Bentazone	0.02	0.03	0.05	0.06	0.02	0.026	0.04
Biphenyl	2.77	2.97	3.94	2.40	2.03	1.300	2.27
Dichlorvos	0.002	0.002	0.002	0.002	0.002	0.001	0.001
Fenitrothion	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Malathion	0.002	0.002	0.002	0.002	0.002	0.001	0.002
Triphenyltin[2]	0.0010	0.0011	0.0022	0.0010	0.0011	0.0010	0.0012

[1] Cells in green represent an average concentration less than the EQS and cells in red represent an average concentration greater than the EQS.
[2] Average data compared against MAC in absence of an annual average EQS.

Even when considering the maximum concentration reported for each substance across the January 2004 to September 2008 dataset, there are few exceedances against the EQS expressed as a MAC (Table 4.6). Where maximum concentrations are greater than the EQS (expressed as a MAC) in most cases it is as a result of the reported LOD being significantly greater than the EQS (even when expressed as a MAC), meaning that even when it is divided by two as part of the statistical manipulation, the resultant concentration is still greater than the MAC EQS. A marginal exceedance for 1,1,1-trichloroethane is identified for nonclassified waters, but is traceable to a waste monitoring operation. For 1,2-dimethybenzene (*o*-xylene) and 4-chloro-3-methylphenol, single exceedances of the MAC are reported, and for xylene (*meta*- and *para*-isomers 1,3- and 1,4-dimethylbenzene) the MAC was exceeded only on two occasions for unspecified waters. Triphenyltin is only expressed as a MAC, but examining the individual data points within the database it is apparent that in many cases the exceedance of the EQS is a result of LODs being reported as greater than the EQS, such that when they are divided by two (using the accepted methodology for dealing with reported less than values) the resultant concentration is still greater than the EQS. This is the case even though the data in Table 4.4 suggest that the average LOD is a maximum of 20 per cent of the EQS. However, the range of reported LOD is wide and so in some cases at the upper end of the range the LOD will exceed the EQS by some margin. Instances of MAC exceedances for triphenyltin are limited to sporadic cases mostly in unspecified or nonclassified waters.

Table 4.6 Maximum concentrations of DSD List II substances by freshwater river quality objective class

Substance	Maximum concentration (µg/l)[1]						
	FRESHWATER – RQO class						
	RE1	RE2	RE3	RE4	RE5	Non-classified	Un-specified
1,1,1-Trichloroethane	0.25	0.5	0.916	2.5	0.05	1530[2]	80
1,1,2-Trichloroethane	0.25	0.25	0.25	0.25	0.25	100	179
1,2-Dimethylbenzene (*o*-xylene)	50	50	50	50	6.4	100	377
Dimethylbenzenes (*m*/*p*/*o*-xylene isomers)	3.63	6.51	150	150	23.4	150	5.38
Xylene (*m* & *p*) (1,3+1,4-dimethylbenzene)	100	100	100	100	17	200	2750
2-Chloro-4-nitrotoluene	1	1	2.5	2.5	0.5	0.5	1

Substance	Maximum concentration (µg/l)[1]						
	FRESHWATER – RQO class						
	RE1	RE2	RE3	RE4	RE5	Non-classified	Un-specified
2-Chloro-5-nitrotoluene	1	1	2.5	0.5	0.5	0.5	1
2-Chloro-6-nitrotoluene	0.5	0.5	2.5	2.5	0.5	0.5	1
4-Chloro-3-nitrotoluene	0.5	0.5	2.5	0.5	0.5	0.5	1
2-Nitro-4-chlorotoluene	0.5	0.5	2.5	0.5	0.5	0.5	1
Chloronitrotoluenes total	2.5	2.5	2.5	2.65	2.5	2.5	2.5
2-Chlorophenol	0.375	1.89	1.1	13.6	0.06	5	0.1
4-Chloro-3-methylphenol	0.125	0.449	3.24	0.77	0.05	5	433
Bentazone	0.24	1.108	3.69	1.13	0.13	0.2	0.1
Biphenyl	NO MAC AVAILABLE						
Dichlorvos	NO MAC AVAILABLE						
Fenitrothion	0.015	0.03	0.005	0.039	0.005	0.14	0.01
Malathion	0.025	0.03	0.04	0.109	0.01	0.016	0.088
Triphenyltin	0.006	0.106	1.0	0.03	0.0032	0.1	0.074

[1] Cells in green represent a maximum concentration less than the EQS (MAC), cells in amber represent maximum concentrations greater than the EQS (MAC), but are based on less than LOD data, and cells in red represent a measured concentration greater than the LOD and greater than the EQS (MAC).
[2] Waste monitoring investigation.

If the measured average concentrations are calculated as percentages of the LOD (Table 4.7), then the bias that the less than values have on the average concentration is obvious. Any average at or near 50 per cent of the LOD reflects the number of data where the result has been translated from a less than to one half of the LOD. This is the case for all of the substances with the exception of bentazone, and some of the poorer water classes for xylenes and 2-chlorophenol and for two instances where single very high values bias the average concentration (for 1,1,1-trichloroethane and 4-chloro-3-methylphenol).

Table 4.7 Average concentration as a percentage of the limit of detection by freshwater river quality objective class

Substance	Average concentration as a percentage of LOD (%)						
	FRESHWATER – RQO class						
	RE1	RE2	RE3	RE4	RE5	Non-classified	Un-specified
1,1,1-Trichloroethane	50	52	57	53	50	1,616[1]	828
1,1,2-Trichloroethane	50	50	50	50	50	50	64
1,2-Dimethylbenzene (*o*-xylene)	45	47	48	46	151	49	86
Dimethylbenzenes (*m*/*p*/*o*-xylene isomers)	68	68	49	43	715	48	271
Xylene (*m* & *p*) (1,3+1,4-dimethylbenzene)	44	46	47	44	707	49	277
2-Chloro-4-nitrotoluene	50	50	50	50	50	50	50
2-Chloro-5-nitrotoluene	50	50	50	50	50	50	50
2-Chloro-6-nitrotoluene	50	50	50	49	50	50	50
2-Nitro-4-chlorotoluene	50	50	50	50	50	50	50
4-Chloro-3-nitrotoluene	49	49	49	50	49	50	50
Chloronitrotoluenes total	50	50	47	50	50	50	50
2-Chlorophenol	53	68	61	76	52	52	50
4-Chloro-3-methylphenol	51	52	69	56	52	53	3,626[2]
Bentazone	54	83	110	131	55	52	50
Biphenyl	50	54	55	66	50	50	50
Dichlorvos	50	50	51	51	51	50	50

Fenitrothion	50	50	50	53	53	56	50
Malathion	53	51	52	56	53	51	52
Triphenyltin	54	55	54	57	53	62	57

[1] Reported data from a waste monitoring programme.
[2] Dominated by a single very high value.

The high proportion of less than LOD values makes any form of trend analysis very unreliable. Examining the data for classified rivers (RE1 to RE5) shows no particular trend if considering average concentrations (Table 4.8).

Table 4.8 Annual average concentrations for each substance

Substance	Annual average concentration (µg/l)				
	2004	2005	2006	2007	2008
1,1,1-Trichloroethane	0.07	0.08	0.07	0.06	0.05
1,1,2-Trichloroethane	0.05	0.05	0.05	0.12	0.25
1,2-Dimethylbenzene (*o*-xylene)	0.05	10.0	4.56	0.15	0.16
Dimethylbenzenes (*m*/*p*/*o*-xylene isomers)	0.24	10.22	9.43	0.48	0.61
Xylene (*m* & *p*) (1,3+1,4-dimethylbenzene)	0.07	26.1	11.1	0.31	0.43
2-Chloro-4-nitrotoluene	0.08	0.12	0.29	0.51	0.51
2-Chloro-5-nitrotoluene	0.40	0.43	0.46	0.50	0.51
2-Chloro-6-nitrotoluene	0.08	0.09	0.29	0.51	0.51
2-Nitro-4-chlorotoluene	0.07	0.07	0.29	0.50	0.51
4-Chloro-3-nitrotoluene	0.11	0.09	0.29	0.50	0.51
Chloronitrotoluenes total	1.55	1.15	1.82	2.50	2.50
2-Chlorophenol	0.04	0.03	0.03	0.03	0.13
4-Chloro-3-methylphenol	0.03	0.03	0.04	0.02	0.01
Bentazone	0.03	0.03	0.06	0.07	0.04
Biphenyl	4.75	1.10	0.64	1.25	1.32
Dichlorvos	0.002	0.003	0.002	0.002	0.002
Fenitrothion	0.001	0.001	0.001	0.001	0.001
Malathion	0.002	0.003	0.002	0.001	0.001
Triphenyltin	0.0008	0.0017	0.0011	0.0010	0.0018

5 England and Wales groundwater data

Under the WFD, groundwater must not contribute to a deterioration of surface water quality. For chalk streams in particular, groundwater can be a significant contributor to flow. Consequently, it is relevant to compare environmental monitoring data for groundwater with the surface water EQS to determine if the presence of elevated concentrations (above the EQS) could lead to negative impacts on surface water quality in the future.

A brief assessment of groundwater data from England and Wales shows the same pattern as for surface waters. Out of around 80,000 results, the majority of data were reported as less than the LOD across all regions (at least 97.5 per cent of the reported data between January 2004 and September 2008). For the substances where there are a small proportion of samples reported above the LOD, the pattern across all regions is relatively similar, with xylene, trichloroethane, 2-chlorophenol, 4-chloro-3-methylphenol and bentazone being occasionally detected at measurable levels (Table 5.1). There is widespread compliance with the EQS, with only exceedance of the dichlorvos, malathion and triphenyltin EQS owing to the LOD reported being higher than the EQS, with some high LODs being reported for some Anglian Region groundwater samples from landfill leachates biasing the mean concentration (Table 5.2). One very high mean xylene concentration was recorded for Thames Region as a result of a pollution investigation following the Buncefield oil fire.

Table 5.1 Summary of the percentage of groundwater samples greater than the limit of detection across the Environment Agency regions

Substance	Percentage of samples greater than the LOD (%) for different Environment Agency regions[1,2]							
	AN	MI	NE	NW	SO	SW	TH	WA
1,1,1-Trichloroethane	9	9	2	4	4	n/a	18	5
1,1,2-Trichloroethane	n/a	n/a	n/a	2	n/a	n/a	n/a	2
1,2-Dimethylbenzene (*o*-xylene)	8	12	12	16	14	11	9	9
1,3-Dimethylbenzene (*m*-xylene)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
1,4-Dimethylbenzene (*p*-xylene)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Dimethylbenzenes (*m*/*p*/*o*-xylene isomers)	9	n/a	1	n/a	5	n/a	7	10
Xylene (*m* & *p*) (1,3+1,4-dimethylbenzene)	9	16	14	18	22	11	11	9
2-Chloro-4-nitrotoluene	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
2-Chloro-5-nitrotoluene	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
2-Chloro-6-nitrotoluene	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
2-Nitro-4-chlorotoluene	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
4-Chloro-3-nitrotoluene	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
2-Chlorophenol	7	1	2	1	1	n/a	1	1
4-Chloro-3-methylphenol	n/a	3	n/a	1	1	n/a	1	1
Bentazone	11	2	3	n/a	12	n/a	7	2
Biphenyl	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Dichlorvos	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Fenitrothion	n/a	n/a	n/a	1	n/a	n/a	n/a	n/a
Malathion	n/a	n/a	n/a	n/a	n/a	n/a	n/a	1
Triphenyltin	n/a	n/a	n/a	n/a	3	n/a	n/a	n/a

[1] AN = Anglian; MID = Midlands; NE = North East; NW = North West; SO = Southern; SW = South West; TH = Thames; WA = Wales.
[2] Grey cells denote either no data or no occurrence of reported data greater than the LOD.

Table 5.2 Average concentrations of DSD List II substances in groundwater by Environment Agency region

Substance	Average concentration (µg/l) by Environment Agency region[1,2]							
	AN	MI	NE	NW	SO	SW	TH	WA
1,1,1-Trichloroethane	0.09	0.26	0.07	0.08	0.41	18.3	1.15	0.12
1,1,2-Trichloroethane	0.12	0.11	0.10	0.14	0.43	0.09	0.68	0.11
1,2-Dimethylbenzene (*o*-xylene)	2.05	0.59	3.34	0.16	0.59	0.10	0.83	0.71
1,3-Dimethylbenzene (*m*-xylene)	n/a	0.04	n/a	n/a	1.00	n/a	n/a	n/a
1,4-Dimethylbenzene (*p*-xylene)	n/a	0.06	n/a	n/a	n/a	n/a	n/a	n/a
Dimethylbenzenes (*m*/*p*/*o*-xylene isomers)	0.34	0.55	42	n/a	1.52	0.25	23,838[3]	0.25
Xylene (*m* & *p*) (1,3+1,4-dimethylbenzene}	2.11	1.30	6.65	0.30	0.79	0.22	3.20	0.81
2-Chloro-4-nitrotoluene	n/a	0.50	n/a	n/a	n/a	0.01	n/a	0.50
2-Chloro-5-nitrotoluene	n/a	0.50	n/a	n/a	n/a	n/a	n/a	0.50
2-Chloro-6-nitrotoluene	n/a	0.50	n/a	n/a	n/a	0.01	n/a	0.50
2-Nitro-4-chlorotoluene	n/a	0.50	n/a	n/a	n/a	0.01	n/a	0.50
4-Chloro-3-nitrotoluene	n/a	0.50	n/a	n/a	n/a	0.01	n/a	0.50
2-Chlorophenol	0.03	0.03	0.03	0.02	0.02	0.01	0.02	0.02
4-Chloro-3-methylphenol	0.01	0.03	0.02	0.03	0.01	0.01	0.02	0.02
Bentazone	0.03	0.02	0.04	0.02	0.36	0.02	0.01	0.02
Biphenyl	n/a	1.25	n/a	n/a	n/a	n/a	n/a	1.25
Dichlorvos	0.020	0.002	0.002	0.002	0.002	0.002	0.002	0.002
Fenitrothion	0.013	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Malathion	0.014	0.001	0.002	0.001	0.003	0.001	0.002	0.001
Triphenyltin[4]	0.025	0.0005	n/a	0.0008	0.0024	0.001	n/a	0.0010
Total number of samples	**2,969**	**19,361**	**9,975**	**13,608**	**8,459**	**2,088**	**22,142**	**5,295**

[1] AN = Anglian; MI = Midlands; NE = North East; NW = North West; SO = Southern; SW = South West; TH = Thames; WA = Wales.
[2] Green cells represent compliance with the surface water EQS (as an annual average), orange cells denote LODs greater than the EQS, red cells an exceedance and grey cells no data.
[3] Buncefield borehole, pollution incident (fire).
[4] EQS expressed as a MAC only.

6 England and Wales estuarine data

A brief assessment of the available estuarine data from England and Wales shows the same pattern as for surface waters. Out of around 20,000 results the majority of data were reported as less than the LOD across all regions (at least 92 per cent of the reported data between 2004 and 2008). There is widespread compliance with the EQS, reflecting the dilution of (generally more contaminated) river waters with sea water, as well as the slightly higher EQS for some of the organophosphorus pesticides. Average triphenyltin data are compared against the MAC EQS as there is no annual average. On examining the raw data, 18 results lie above the MAC (0.008 µg/l) out of a total of 2,012 reported data. Of those 18 results, 12 are reported as less than the LOD (<0.01 µg/l) leaving 6 data points reported as greater than the MAC. The reported concentrations above the MAC range from 0.012 to 0.039 µg/l and are isolated samples taken across the time period examined including samples from the Humber, Mersey and Thames.

Table 6.1 Average concentrations of DSD List II substances in estuarine water by Environment Agency region

Substance	Average concentration (µg/l) by Environment Agency region[1,2]						
	AN	MI	NE	NW	SO	SW	TH
1,1,1-Trichloroethane	0.05	0.05	0.07	0.05	0.05	0.0481	0.05
1,1,2-Trichloroethane	0.09	0.06	0.10	0.11	1.85	0.05	0.19
1,2-Dimethylbenzene (*o*-xylene)	0.10	n/a	10.9	0.61	0.20	0.05	0.08
Dimethylbenzenes (*m*/*p*/*o*-xylene isomers)	0.27	1.5	14.2	1.20	0.48	n/a	0.32
Xylene (*m* & *p*) (1,3+1,4-dimethylbenzene)	0.21	n/a	22.2	1.08	0.32	0.1	0.2
2-Chloro-4-nitrotoluene	0.23	0.5	0.36	n/a	0.24	n/a	0.16
2-Chloro-5-nitrotoluene	0.53	0.5	0.39	n/a	0.49	n/a	0.51
2-Chloro-6-nitrotoluene	0.23	0.5	0.35	n/a	0.24	n/a	0.16
2-Nitro-4-chlorotoluene	0.23	0.5	0.35	n/a	0.24	n/a	0.16
4-Chloro-3-nitrotoluene	0.23	0.5	0.39	n/a	0.30	n/a	0.17
Chloronitrotoluenes total	2.10	n/a	2.14	n/a	2.50	n/a	1.69
2-Chlorophenol	0.02	0.23	0.07	0.15	0.02	0.02	0.02
4-Chloro-3-methylphenol	0.01	0.24	0.07	0.15	0.02	0.02	0.01
Bentazone	0.02	n/a	0.03	n/a	0.03	0.0228	0.02
Biphenyl	2.91	n/a	0.80	1.25	3.24	n/a	2.32
Dichlorvos	0.003	0.001	0.002	0.001	0.002	0.002	0.002
Fenitrothion	0.001	0.0005	0.002	0.001	0.001	0.0005	0.001
Malathion	0.003	0.0008	0.002	0.001	0.001	0.001	0.001
Triphenyltin[3]	0.001	0.001	0.0009	0.0008	0.001	0.001	n/a
Total number of samples	**4,402**	**411**	**5,589**	**837**	**2,451**	**341**	**6,381**

[1] AN = Anglian; MI = Midlands; NE = North East; NW = North West; SO = Southern; SW = South West; TH = Thames; WA = Wales.
[2] Green cells represent compliance with the EQS (annual average) and grey cells no data.
[3] Average concentrations compared against MAC as there is no annual average EQS.

7 Scottish data summary

7.1 Dataset selection and manipulation

Sufficient data were available for most of the relevant substances in rivers and groundwater. Data collected between January 2008 and December 2010 were assessed. Those substances not monitored during that time are not considered to be of concern. None of the substances is currently monitored by SEPA in the marine environment.

Compliance was assessed in accordance with the Environment Agency assessments, against the standards set out in Table 3.2. Limits of detection were treated as outlined above (see Sections 3.2.2 and 4.2), i.e. a value equal to half the LOD was assigned where levels were below detection limits.

7.2 Freshwater river compliance assessment

A total of 4679 samples for the substances listed in Table 7.1 were taken across 72 locations for Scottish freshwater river sampling sites from January 2008 to December 2010. For some substances (e.g. xylenes), a variety of isomers have been reported as well as a total concentration for which the EQS has been derived.

Table 7.1 Summary of sample numbers and number of detections for Scottish freshwater rivers

Substance	Number of locations sampled	Total sample number	LOD (µg/l)	Number of detections	Mean value (µg/l)	Number of EQS failures
1,1,1-Trichloroethane	22	390	1.0	0	0.560	0
4-Chloro-2-nitrotoluene	20	150	0.007	0	0.0035	0
Bentazone	26	844	0.006	473	0.0148	0
Dichlorvos	69	689	0.007	0	0.0037	0[1]
Fenitrothion	69	775	0.005	1	0.0028	0
Malathion	69	759	0.009	0	0.0044	0
o-Xylene	22	358	0.0001	2	0.514	0
p- & *m*-Xylene	22	358	2.0	2	1.006	0
Xylene	22	356	3.0	7	1.579	0

[1] Limit of detection is greater than the EQS, therefore reliable compliance assessment is not possible.

The same analytical issues for dichlorvos mentioned in the Environment Agency assessment (Section 4.2) were observed in the data for Scotland. The reported analytical LOD for dichlorvos is greater than the EQS (reflecting the very low EQS for dichlorvos of 1 ng/l). Therefore, robust EQS compliance assessment is not possible, particularly because there were no analytical detections of dichlorvos at any location.

Overall, 90 per cent of samples were below the LODs. With the exception of bentazone, there were very few (or no) detections of any of the substances monitored. Levels of all the substances – with the exception of dichlorvos, which could not be assessed – were considerably below the EQSs at all locations.

7.3 Groundwater compliance assessment

A total of 1788 groundwater samples for the substances listed in Table 7.2 were taken across 77 locations from January 2008 to December 2010. For some substances (e.g. xylenes), a variety of isomers have been reported as well as a total concentration for which the EQS has been derived.

Table 7.2 Summary of sample numbers and number of detections for Scottish groundwaters

Substance	Number of locations sampled	Total sample number	LOD (µg/l)	Number of detections	Mean value (µg/l)	Number of EQS failures
1,1,1-Trichloroethane	20	109	1.0	2	0.895	0
Bentazone	64	648	0.006	58	0.018	0
Dichlorvos	52	270	0.007	0	0.004	0[1]
Fenitrothion	52	280	0.005	0	0.004	0
Malathion	50	189	0.0075	0	0.004	0
o-Xylene	20	94	1.0	0	0.546	0
p- & *m*-Xylene	20	91	2.0	0	1.000	0
Triphenyltin	5	17	0.0005	0	0.000	0
Xylene	20	90	3.0	7	1.652	0

[1] Limit of detection is greater than the EQS, therefore reliable compliance assessment is not possible.

Ninety-six per cent of samples were below the LODs, and levels of all substances – with the exception of dichlorvos, which could not be assessed – were considerably below the EQSs at all locations.

Bentazone was again the most widely detected substance, with levels many orders of magnitude below the EQS.

7.4 Estuarine data

None of the applicable substances is monitored by SEPA in the marine environment because it is not expected any of these substances pose a threat to marine environmental quality.

8 Northern Ireland data summary

The following substances were assessed using 2007–2008 OSPAR and surveillance monitoring data: bentazone, biphenyl, 4-chloro-3-methylphenol, chloronitrotoluenes, 2-chlorophenol, dichlorvos, fenitrothion, malathion, 1,1,1-trichloroethane, 1,1,2-trichloroethane, triphenyltin and xylene.

There were 62 positive detections of xylene, with levels ranging from 0.3–2.5 µg/l. There were five detections of 1,1,1-trichloroethane and one detection of fenitrothion. No breaches of EQSs were observed, and none of the substances appears to pose a major environmental threat in Northern Ireland.

9 Trends in marketing and use data

One of the objectives of the project was to establish the likely trends in environmental concentrations in these DSD List II substances. For substances identified as heavily controlled through marketing and use restrictions or bans, it is expected that environmental concentrations will decrease with time.

Data was obtained from the following:

- The Central Science Laboratory database[5]
- The European Chemical Substances Information System database[6]

The data obtained are summarised in Table 9.1.

The pesticides on the list (malathion, dichlorvos and fenitrothion), with the exception of bentazone, are no longer authorised for use and so environmental levels are expected to decline with time. Pesticide usage data supports this assumption (Figure 9.1).

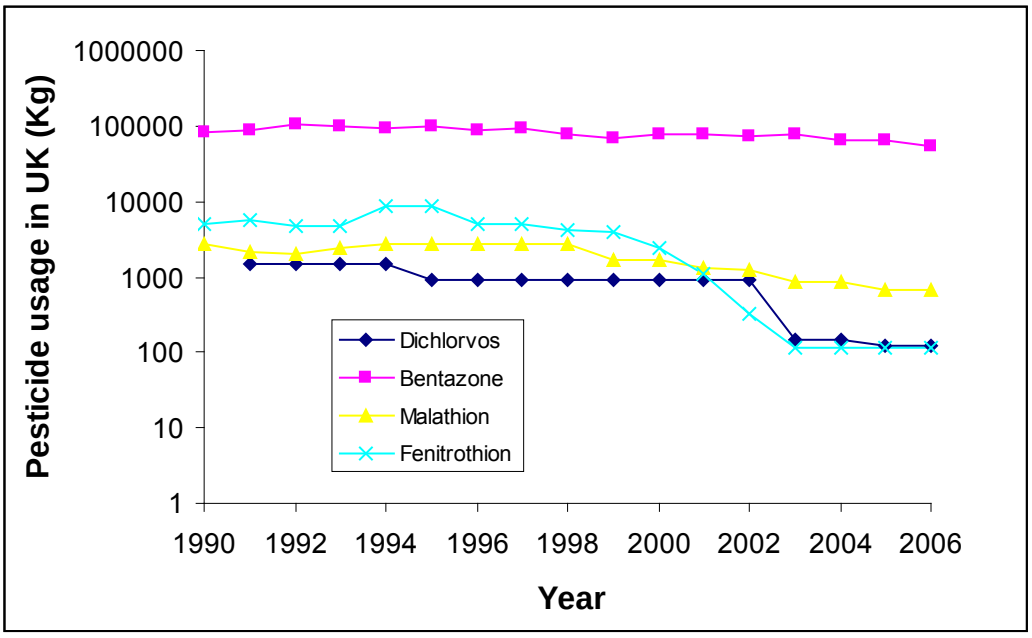

Figure 9.1 Summary of annual pesticide usage in the UK

Most of the other substances are also now controlled via numerous codes and statutory agreements to control emissions to air and water. For some substances, such as 4-chloro-3-methylphenol and chloronitrotoluenes, information on production and use is very limited.

[5] Pesticide usage statistics taken from the Central Science Laboratory (part of the Food and Environment Food Agency as of April 2009) database at http://pusstats.csl.gov.uk/myindex.cfm.
[6] Data taken from the European Chemical Substances Information System (ESIS) available from the European Commission Joint Research Centre, Institute for Health and Consumer Protection website at http://ecb.jrc.ec.europa.eu/esis/.

Table 9.1 Summary of usage and trend data

Substance	Number of manufacturers in UK	Total usage (kg) in UK (2006)	Use	Trend	Controls	Likely concentration trends in water
Triphenyltin	0	Unknown	Was used as an antifouling agent in boat/ship paints, quays, buoys, crab pots and fish nets, and as a fungicide in wood preservatives and on some agricultural crops. Triphenyltin hydroxide is also used as a stabiliser in plastics, such as PVC.	Mostly banned	Banned in pesticides. Banned in antifoulants. Controlled under Surface Waters (Dangerous Substances) (Classification) Regulations 1997 and Pollution Prevention and Control (PPC) Regulations 2000. It is a UK 'Red list' pollutant, the presence of which in the environment is of particular concern. Triphenyltin compounds are also listed as substances for priority action on their control under the OSPAR and Helsinki Conventions.	Decreasing
1,1,1-Trichloroethane	2	Unknown	1,1,1-Trichloroethane was used industrially and domestically as a degreaser, dry cleaning agent, and solvent in paints, glues and aerosol products, and was the main ingredient in correction fluid – now heavily controlled.	Decreasing	Restricted to <0.1% by weight in substances and preparations placed on the market for sale to the general public and/or in diffusive applications such as in surface cleaning and cleaning of fabrics.	Decreasing fast
1,1,2-Trichloroethane	0	Unknown	It is used as a solvent and as an intermediate in the production of 1,1-dichloroethane. May be present as an impurity in other chemicals.	Decreasing slowly	Prohibited to supply for use at work in diffusive applications such as in surface cleaning and the cleaning of fabrics except for the purposes of research and development or for the purpose of analysis (Office of Public Sector Information, 1998).	Decreasing slowly

Substance	Number of manufacturers in UK	Total usage (kg) in UK (2006)	Use	Trend	Controls	Likely concentration trends in water
2-Chlorophenol	1	Unknown	Disinfectant, intermediate in dye production.	Decreasing slowly	On various international regulatory priority lists for emissions reductions (Euro Chlor, 2008). Controlled under the Surface Water (Dangerous Substances) (Classification) Regulations 1998 and the PPC Regulations. Not listed under the Pesticide Safety Directorate as being authorised for use in the UK. Under European law it is controlled under EC Directive 76/464 'Pollution of the aquatic environment by dangerous substances'. Internationally, chlorophenol is regulated as a VOC (volatile organic compound) under the UN/ECE Convention on Long-Range Transboundary Air Pollution and Basel Conventions. It is also listed as a candidate substance for selection, assessment and prioritisation under the OSPAR and Helsinki Conventions.	Decreasing slowly
4-Chloro-3-methylphenol	1	Unknown	Plasticiser, fungicide.	Unknown	Controlled under the Surface Water (Dangerous Substances) (Classification) Regulations 1998 and the PPC Regulations.	Unknown; probably stable/slow decrease
Bentazone	No	52,786	Contact herbicide absorbed by the leaves and is used to control broad leafed weeds in winter and spring cereals.	Relatively stable	None beyond Biocidal Products Directive.	Stable
Biphenyl	2	EC production was reported as >10,000 tonnes/year in 1985 (SRI, 1985).	From industries producing, using, or handling biphenyl, or where it is used as a heat transfer agent in transformers. It occurs naturally in trace amounts in oil. Also used as a mould retardant in citrus fruit wrappers, creosote, in formation of plastics, optical brighteners, hydraulic fluids, dye carrier (typically 50% of use). May be found in landfill leachate.	Decreasing	Surface Waters (Dangerous Substances) (Classification) Regulations 1998. Reductions through VOC emission controls under UK Air Quality Strategy. The European legislation relevant to its release is EC Directive 76/464: Pollution of the aquatic environment by dangerous substances (plus daughter directives). Internationally it is also listed as a substance for priority action on its control under the OSPAR and Helsinki Conventions. As a VOC the main international legislation are the UN/ECE Convention on Long-Range Transboundary Air Pollution and Basel Conventions.	Decreasing

Substance	Number of manufacturers in UK	Total usage (kg) in UK (2006)	Use	Trend	Controls	Likely concentration trends in water
Chloronitrotoluenes	1	Unknown	Intermediate in chemical production.	Decreasing slowly	Controlled under the Surface Waters (Dangerous Substances) (Classification) Regulations 1998 and PPC Regulations. Chloronitrotoluenes are also listed as candidate substances for selection, assessment and prioritisation under the OSPAR and Helsinki Conventions.	Decreasing slowly
Dichlorvos	No	121	Pesticide	Significant drop in 2003, stable since then	Not authorised after 6 December 2007.	Decreasing to zero.
Fenitrothion	No	114	Pesticide	Significant drop in 2001, stable since then	Not authorised after 25 November 2007.	Decreasing to zero
Malathion	No	665	Pesticide	Decreasing slowly	Not authorised after 6 December 2007.	Decreasing to zero
Xylenes	8	Unknown	Xylene is used as a solvent, to manufacture petrol (90% of usage). Xylene based solvents are widely used in the paint and printing ink industries, for polyester fibre, film and fabricated items and perfumes, pesticide formulations, pharms and adhesives. It is also used for household products such as aerosol paints, lacquers, cleaning agents, and as a thinner for paints and varnishes. Individual isomers of xylene are used in the manufacture of certain plastics. Occurs naturally in coal and tar.	Declining	For air releases, categorised as a VOC. For water releases, included in European Pollutant Emission Register (EPER) reporting requirements. Releases to surface water controlled by Surface Water (Dangerous Substances) (Classification) Regulations 1998 and the PPC Regulations. The UK is also committed to reduce VOC emissions under its Air Quality Strategy. Xylene is also regulated under (EC) Regulation 793/93 – evaluation and control of risks of existing substances (second list of priority substances) and by the Solvents Directive. Internationally, xylene is covered under the OSPAR and Helsinki Conventions as a candidate substance for evaluation. As a VOC the main international legislation are the UN/ECE Convention on Long-Range Transboundary Air Pollution and Basel Conventions. Directive 99/13/EC on solvents (VOC emissions) will also apply.	Slowly decreasing

The Environment Agency Pollution Inventory[7] provides an emission database for chemicals discharged to the environment (see Appendix B). Discharges to controlled waters are summarised for a number of the chemicals of interest. In many cases discharges are recorded as zero, but for some substances year-on-year trends are provided. For high volume use chemicals, such as xylenes, a general decline in use in the two main industrial sectors (fuel and power and chemicals) has been observed over the nine years up to and including 2006 (Figure 9.2). The ubiquitous nature of xylene usage means that detectable levels are expected in discharges from wastewater treatment works. Biphenyl has also shown an overall decline in loads discharged from the chemical industry, and to a lesser extent from fuel and power (Appendix B).

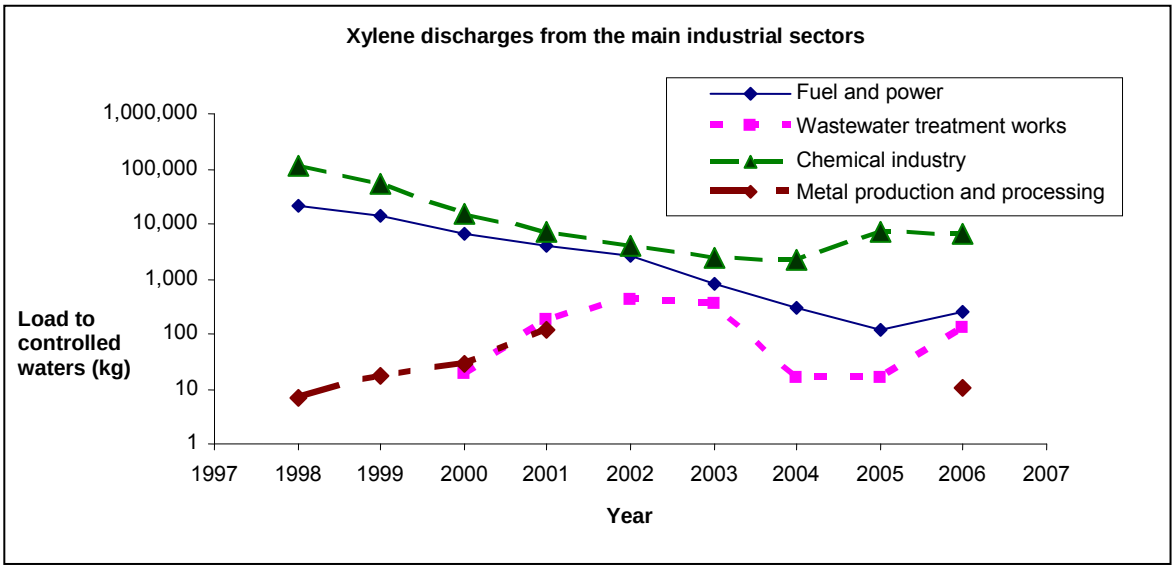

Figure 9.2 Annual discharge of xylenes to controlled waters taken from Environment Agency Pollution Inventory data

Wastewater treatment works receive wastewater from a variety of sources including industry, town centres, domestic waste and runoff. The chemicals of interest, therefore, tend to be detectable in effluents discharged to surface waters. However, marketing and use controls suggest that the quantities of chemicals discharged are either declining or are very minor (less than a total of one kilogramme per year). It must also be noted that no 2008 data are available at the time of writing to reflect bans on the authorisation of malathion, dichlorvos and fenitrothion (Figure 9.3).

These data therefore support the environmental monitoring data, showing a general decline in concentrations over time and only limited usage of substances still on the market.

[7] Environment Agency Pollution Inventory data available up to 2006, shown here and in Appendix B, taken from http://www.environment-agency.gov.uk/research/library/data/34217.aspx.

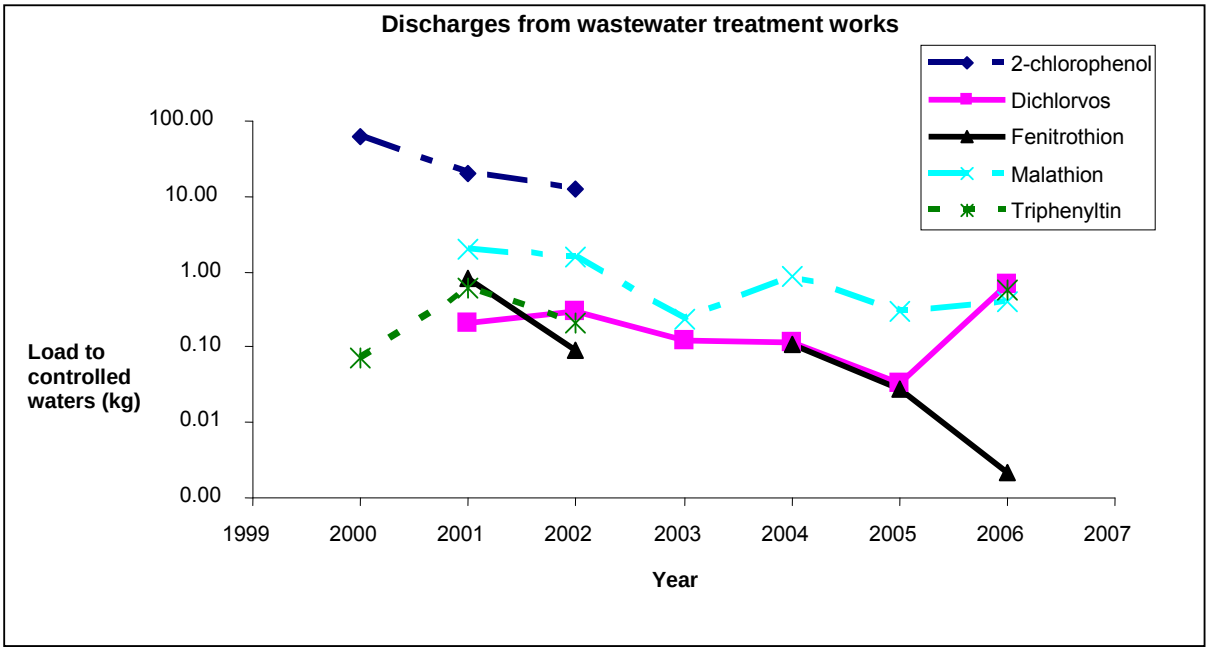

Figure 9.3 Annual discharge of chemicals from wastewater treatment works to controlled waters taken from Environment Agency Pollution Inventory data

10 Conclusions and recommendations

Based on the collation of available UK monitoring data and analysis of the controls of substances discharged to the aquatic environment, the following conclusions may be drawn for the substances reviewed (bentazone, biphenyl, 4-chloro-3-methylphenol, chloronitrotoluenes, 2-chlorophenol, dichlorvos, fenitrothion, malathion, 1,1,1-trichloroethane, 1,1,2-trichloroethane, triphenyltin and xylene):

- The Environment Agency has an extensive dataset of environmental monitoring data collected between January 2004 and September 2008 with which to assess compliance with the EQS for the indentified substances under the DSD.
- Around 90 per cent of all river, groundwater and estuarine water samples for England and Wales are reported as less than the LOD.
- In most cases (with the exception of dichlorvos), the analytical LOD is less than the corresponding EQS. Furthermore, the majority of the LODs are less than one third of the corresponding EQS and, thereby, are considered to provide sufficient analytical performance to allow a high degree of confidence in the conclusions regarding compliance.
- No compliance assessment could be carried out for dichlorvos owing to the analytical LOD being greater than the EQS in most cases. Based on the other pesticide data, however, compliance with the EQS would be expected in most cases.
- A high degree of confidence may be placed on the compliance of English and Welsh surface waters with the existing EQS (based on annual average values) set under the Dangerous Substances Directive, whether considering an annual average or maximum acceptable concentration (MAC).
- All Environment Agency regions show a similar trend, with no observed ‘hot spots’ where routine monitoring has highlighted a compliance issue.
- Marketing and use data suggest that in most cases the most persistent, bioaccumulating and toxic substances are the subject of wide ranging bans, meaning that environmental concentrations should fall in the future below current (already compliant) levels.
- Emission data taken from the Pollution Inventory supports these conclusions and confirms a general decreasing trend in discharges to English and Welsh controlled waters.
- Overall, it may be recommended that owing to their low (EQS compliant) concentrations in the environment, combined with extensive marketing and use restrictions or bans, that these substances are no longer a high concern to the Environment Agency and therefore do not require identification as specific pollutants under the WFD.
- Scottish and Northern Irish assessments are consistent with the above conclusions, i.e. none of these substances appears to pose an environmental threat.

The outcomes from this review are summarised in Table 10.1.

Table 10.1 Summary of the review of usage, trend and monitoring data

Substance	Source control/trend	Compliance with EQS[1]		
		Freshwaters	Ground water	Estuarine water
1,1,1-Trichloroethane	Extensive/decreasing	Compliant, very occasional exceedance of MAC in unclassified waters.	Compliant with AA EQS and MAC.	Compliant with AA EQS.
1,1,2-Trichloroethane	Limited/decreasing	Compliant with AA EQS and MAC.	Compliant with AA EQS and MAC.	Compliant with AA EQS.
Xylenes	Significant for atmospheric release/decreasing slowly	Compliant, very occasional exceedance of MAC in unclassified waters.	Generally compliant with AA EQS and MAC.	Compliant with AA EQS.
Chloronitrotoluenes total	Limited/decreasing slowly	Compliant with AA EQS and MAC.	Compliant with AA EQS and MAC.	Compliant with AA EQS.
2-Chlorophenol	Limited/decreasing slowly	Compliant with AA EQS and MAC.	Compliant with AA EQS and MAC.	Compliant with AA EQS.
4-Chloro-3-methylphenol	Limited/stable or slowly decreasing	Compliant with AA EQS, very occasional exceedance of MAC in unclassified waters.	Compliant with AA EQS and MAC.	Compliant with AA EQS.
Bentazone	None/stable	Compliant with AA EQS and MAC.	Compliant with AA EQS and MAC.	Compliant with AA EQS.
Biphenyl	Significant/decreasing	Compliant with AA EQS (no MAC available).	Few data, but compliant with AA EQS and MAC.	Compliant with AA EQS.
Dichlorvos	Banned/decreasing	Unknown owing to LOD > EQS (no MAC available).	Unknown owing to LOD > EQS.	Compliant with AA EQS.
Fenitrothion	Banned/decreasing	Compliant with AA EQS and MAC.	Compliant with AA EQS and MAC.	Compliant with AA EQS.
Malathion	Banned/decreasing	Compliant with AA EQS and MAC.	Compliant with AA EQS, where average concentrations > EQS is a result of LOD > EQS.	Compliant with AA EQS.
Triphenyltin	Mostly banned/decreasing	EQS expressed as MAC only. Limited and sporadic exceedance of MAC (based on reported data >LOD) in all classes of river.	Where average concentrations > EQS is a result of LOD > EQS and is based on comparison against MAC EQS.	Averages concentrations compliant with MAC EQS. Very limited and sporadic MAC exceedance (based on reported data > LOD).

[1] EQS = environmental quality standard; LOD = limit of detection; AA = annual average; MAC = maximum acceptable concentration.

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List of abbreviations

AA	Annual average
AN	Anglian Region (Environment Agency region)
DSD	Dangerous Substances Directive
EQS	Environmental quality standard
LOD	Limit of detection
MAC	Maximum acceptable concentration
MID	Midlands Region (Environment Agency region)
MRV	Minimum reporting value
NE	North East Region (Environment Agency region)
NW	North West Region (Environment Agency region)
PPC	Pollution Prevention and Control
RE	River ecosystem classification (RE1 to RE5)
RQO	River quality objectives, based on meeting RE classes
SO	Southern Region (Environment Agency region)
SW	South West Region (Environment Agency region)
TH	Thames Region (Environment Agency region)
VOC	Volatile organic compound
WA	Welsh Region (Environment Agency region)
WFD	Water Framework Directive

Appendix A: Review of remaining List II chemicals

A.1 List of remaining List II substances not selected as proposed specific pollutants

The following table shows those List II substances that are covered under the Dangerous Substances Directive with statutory or quasi-statutory EQSs, either specified in the corresponding 1997 and 1998 Regulations or in Circular 7/89[8] (Table A.1). Mevinphos is also mentioned in the 1998 Regulations, but is not listed as a dangerous substance.

Table A.1 Summary of remaining List II substances and their status

Substance	Legislative document	Additional information
Azinphos-methyl	1997 Regulations (England and Wales), 1998 Regulations (Scotland and Northern Ireland)	Not prioritised as no approval located and/or banned. Not currently approved as an agricultural pesticide in the UK or under Annex 1 of 91/414/EEC.
Demeton	1998 Regulations	Not prioritised as no approval located and/or banned. Not currently approved as an agricultural pesticide in the UK or under Annex 1 of 91/414/EEC.
Omethoate	1998 Regulations	Not prioritised as no approval located and/or banned. Not currently approved as an agricultural pesticide in the UK or under Annex 1 of 91/414/EEC.
Triazophos	1998 Regulations	Not prioritised as no approval located and/or banned. Not currently approved as an agricultural pesticide in the UK or under Annex 1 of 91/414/EEC.
Boron	Circular 1989 (England and Wales)	Not prioritised as prioritisation system only suitable for organics, but monitoring data were reviewed for the first specific pollutants report (UKTAG, 2008).
Vanadium	Circular 1989 (England and Wales)	Not prioritised as prioritisation system only suitable for organics, but monitoring data were reviewed for the first specific pollutants report (UKTAG, 2008).
PCSDs	Circular 1989 (England and Wales)	Not prioritised as no approval located and/or banned. No reference to use found under pesticide or biocide directives.
Cyfluthrin	Circular 1989 (England and Wales)	Prioritised list II (ranking 3–5); not added to the list of remaining 12 substances in the specific pollutants report following review of monitoring data (UKTAG, 2008). Under Annex 1 of 91/414/EEC, but not currently approved as an agricultural pesticide in the UK. To be considered under the Biocides Directive as an insecticide.
Sulcofuron	Circular 1989 (England and Wales)	Not prioritised as no approval located and/or banned. No reference to use found under pesticide or biocide directives.
Flucofuron	Circular 1989 (England and Wales)	Not prioritised as no approval located and/or banned. No reference to use found under pesticide or biocide directives.

[8] England and Wales: Statutory Instrument 1997 No. 2560; Water Resources, England and Wales. The Surface Waters (Dangerous Substances) (Classification) Regulations 1997; DOE 1146; Statutory Instrument 1998 No. 389; Water Resources, England and Wales. The Surface Waters (Dangerous Substances) (Classification) Regulations 1998; DOE 1247; and Circular 7/89 (Department of the Environment), Circular 16/89 (Welsh Office); Water and the Environment. The implementation of European Community directives on pollution caused by certain dangerous substances discharged into the aquatic environment; 30 March 1989. Scotland: The Surface Waters (Dangerous Substances) (Classification) (Scotland) Regulations 1998 (SI 1998/250) and the Surface Waters (Dangerous Substances) (Classification) (Scotland) (No.2) Regulations 1998 (SI 1998/1344. Northern Ireland: The Surface Waters (Dangerous Substances) (Classification) Regulations (Northern Ireland) 1998.

A.2 Assessment of monitoring data

All England and Wales freshwater and saline water monitoring data from the beginning of January 2004 until end of January 2009[9] were reviewed following the removal of superfluous information (based on the sampling point description, material description and/or purpose code), such as unspecified sampling point data, sewage effluent data and unplanned reactive monitoring data from pollution incidents, etc. The final main dataset was based on routine statutory monitoring. The results are given in Table A.2, along with the corresponding EQSs for the substances of interest, and are summarised for England and Wales. Planned investigative monitoring data were also reviewed for any anomalies and the results are included in the comments section of the table. Similarly, groundwater data were also considered and any positive detections have been noted in the table[10].

The review is based on direct sample comparison against the available EQSs for that substance rather than a statistical approach; therefore, the results are likely to represent a conservative view. For example, while 8 samples out of 7788 were reported as above the EQS for azinphos-methyl in England, these related to data for four regions. Midlands had four samples with concentrations greater than the EQS which did all relate to the same site; however, when these were considered with other data taken over the same year as a mean value, the freshwater annual average EQS was not exceeded when setting the 'less than' concentrations to half their value and was marginally exceeded in 2004 using less than values at face value. All monitored concentrations of azinphos-methyl at the Midlands site were reported as less than values from April 2006 onwards.

For some data, the samples were recorded as less than values greater than the EQS (see comments in Table A.2). Most samples were reported as less than values that were below the EQS, although some cases typically had less than values reported at the EQS or above, e.g. omethoate and cyfluthrin, making it difficult to reach conclusions regarding compliance. While commonly referred to as values less than the LOD, these less than values are in fact based on a comparison against a minimum reporting value (MRV). Such MRVs are derived from the analytical LOD and are usually equal to them or greater in value. The LODs and MRVs in freshwater for all the substances reviewed are shown in Table A.3. The table shows that for omethoate, triazophos and cyfluthrin, the LODs and MRVs relating to the period of the monitoring data used in this review are close (up to half) or equal to the corresponding EQS values. Currently, we are unable to achieve the right level of MRV to assess concentrations against the EQS for cyfluthrin. However, the information given in Table A.1 suggests that discharges of omethoate, triazophos and cyfluthrin are unlikely to be of concern.

The majority of exceedences of the threshold value of mevinphos were in the Midlands (12 samples); however, no exceedences were reported in this region after May 2006.

Based on the number of available samples for a substance in a particular medium, EQS exceedance was limited and in the range 0–1.12% (the upper limit in this case from a direct comparison of one sample exceeding a 95%ile EQS). Positive detections of substances found through planned investigations do not appear to indicate any issues when compared with results from the statutory monitoring data.

Boron and vanadium are naturally occurring so tend to have a larger percentage of positive detections, although face-value comparison of all the data against the corresponding EQSs shows few exceedances (<1%).

The data do not highlight any issues with any of the substances considered for England and Wales.

[9] In the case of boron, vanadium and cyfluthrin, data up to February 2011 were considered.
[10] Because boron and vanadium are naturally occurring substances, comparisons against their EQSs were also noted when reviewing the groundwater data.

Monitoring data are limited for these substances in Scotland, with only azinphos-methyl and vanadium analysed in surface waters during the last three years. There was only one positive detection for azinphos-methyl out of 658 samples. There were only four detections of total vanadium from 6715 samples, and no threat to the EQS. The data do not highlight any issues with any of the substances considered for Scotland.

Table A.2 Assessment of the available monitoring data for England and Wales for the remaining List II substances[1]

Substance	Dangerous Substances Directive EQS	Data for England			Data for Wales			Other comments
		No. of samples	No. of positive detections[2]	No. of samples >EQS	No. of samples	No. of positive detections[2]	No. of samples >EQS	
Azinphos-methyl	FW: 0.01 µg/l AA SW: 0.01 µg/l AA GW: n/a	7788 1328 8887	14 (0.18%) 2 (0.15%) 17 (0.19%)	8 (0.10%) 1 (0.07%)	247 0 688	1 (0.40%) 0 3 (0.44%)	1 (0.40%) 0	43 FW and 13 SW samples for England had reported less than values that were at or above the EQS; 36 GW samples had reported less than values that were at or above the FW EQS, one of these was in Wales. Planned investigations (Midlands) showed 3 positive detections in FW in the range 0.002–0.00574 µg/l (<EQS).
Demeton	FW: 0.5 µg/l AA SW: 0.5 µg/l AA GW: n/a	4226 1122 6	4 (0.09%) 2 (0.18%) 0	1 (0.02%) 0	70 0 0	0 0	0 0	All available data on demeton derivatives considered; the sum of three of the positive FW detections taken at the same time and site were still below the EQS. Only 1 sample (Midlands) had a reported less than value that was above the EQS. The only planned investigation (Anglian) with a positive result, 0.019 µg/l (<EQS), was in FW for demeton-S-methyl sulphone.
Omethoate	FW: 0.01 µg/l AA GW: n/a	1444 0	0 0	0	242 0	1 (0.41%) 0	0	Apart from 1 sample, the FW samples for England and Wales had reported less than values that were at or above the EQS.
Triazophos	FW: 0.005 µg/l AA SW: 0.005 µg/l AA GW: n/a	4517 1139 8888	14 (0.31%) 0 7 (0.08%)	8 (0.18%) 0	249 0 700	0 0 0	0 0	723 FW and 289 SW samples had reported less than values that were at or above the EQS; 1066 GW samples had reported less than values that were at or above the FW EQS. The only planned investigation (Midlands) with a positive result, 0.012 µg/l (>EQS), was in FW.

Substance	Dangerous Substances Directive EQS	Data for England			Data for Wales			Other comments
		No. of samples	No. of positive detections[2]	No. of samples >EQS	No. of samples	No. of positive detections[2]	No. of samples >EQS	
Boron[3]	FW: 2 mg/l total AA SW: 7 mg/l total AA GW: n/a	18580 2959 34186	4825 (25.97%) 2488 (84.08%) 6131 (17.93%)	35 (0.19%) 3 (0.10%) 234 (0.68%)	3933 19 3147	696 (17.70%) 4 (21.05%) 568 (18.05%)	4 (0.10%) 0 1 (0.03%)	2 GW samples had reported less than values that were at or above the FW EQS. Planned investigations in FW showed 1357 positive detections in the range 10–5410 µg/l (33 samples > EQS) in England and 286 positive detections in the range 73–5090 µg/l (6 samples > EQS) in Wales. Planned investigations in SW showed 470 positive detections in the range 10–5410 µg/l (<EQS) in England and 44 positive detections in the range 534–2340 µg/l (<EQS) in Wales. Planned investigations in GW showed 700 positive detections in the range 10–34000 µg/l (6 samples > FW EQS) in England and 120 positive detections in the range 9.63–438 µg/l (<EQS) in Wales.
Vanadium[4]	FW hardness banded: 0-200 mg/l $CaCO_3$: 20 µg/l total AA +200 mg/l $CaCO_3$: 60 µg/l total AA SW: 100 µg/l total AA GW: n/a	16779 3482 34017	2487 (14.82%) 442 (12.69%) 1630 (4.79%)	3 (0.02%) 4 (0.11%) 40 (0.12%)	3741 51 3119	92 (2.46%) 0 415 (13.31%)	0 0 12 (0.38%)	25 FW samples from 4 sites could not be assessed owing to a lack of hardness data. 4 GW samples had reported less than values that were above the FW EQS. Planned investigations in FW showed 126 positive detections in the range 1.01–48.4 µg/l (< the relevant EQSs; 1 sample could not be assessed owing to lack of hardness data) in England and 56 positive detections in the range 2.05–56.2 µg/l (1 sample > the relevant EQS) in Wales. Planned investigations (Anglian and North East) in SW showed 45 positive detections in the range 1.14–70.4 µg/l (<EQS). Planned investigations in GW showed 264 positive detections in the range 1.01–96.2 µg/l (6 samples > the relevant FW EQSs; the reported LOD of 1 sample was > the FW EQS) in England and 52 positive detections in the range 2.02–7400 µg/l (3 samples > the relevant FW EQSs) in Wales.

Substance	Dangerous Substances Directive EQS	Data for England			Data for Wales			Other comments
		No. of samples	No. of positive detections[2]	No. of samples >EQS	No. of samples	No. of positive detections[2]	No. of samples >EQS	
PCSDs	FW: 0.05 µg/l total 95%ile SW: 0.05 µg/l total 95%ile GW: n/a	2623 460 0	22 (0.84%) 15 (3.26%) 0	5 (0.19%) 0	50 0 0	1 (2.00%) 0 0	0 0	11 FW samples for England had reported less than values that were above the EQS. Planned investigations (Midlands, North East and Thames) showed 4 positive detections in FW in the range 0.006–0.1 µg/l (1 sample > the EQS in Thames).
Cyfluthrin	FW: 0.001 µg/l total 95%ile SW: 0.001 µg/l total 95%ile GW: n/a	4075 716 683	18 (0.44%) 3 (0.42%) 0	17 (0.42%) 3 (0.42%)	89 2 18	1 (1.12%) 0 0	1 (1.12%) 0	Generally, the reported less than values were at or above the EQS. The only planned investigation (North East) with a positive result, 0.00335 µg/l (>EQS), was in SW.
Sulcofuron	FW: 25 µg/l total 95%ile SW: 25 µg/l total 95%ile GW: n/a	1930 495 0	7 (0.36%) 0 0	0 0	49 0 0	0 0 0	0 0	Planned investigations (Midlands) showed 2 positive detections in FW in the range 0.32–0.35 µg/l (<EQS).
Flucofuron	FW: 1.0 µg/l total 95%ile SW: 1.0 µg/l total 95%ile GW: n/a	1811 515 0	8 (0.44%) 1 0	0 0	49 0 0	1 (2.04%) 0 0	0 0	2 FW and 4 SW samples for England had reported less than values that were above the EQS.
Mevinphos[5]	FW: 0.02 µg/l GW: n/a	4947 9022	26 (0.53%) 18 (0.20%)	14 (0.28%)	247 702	0 0	0 0	245 FW samples for England had reported less than values that were at or above the threshold value, one FW sample was reported as a greater than value; 160 GW samples had reported less than values that were at or above the FW threshold value, one of these was in Wales. Planned investigations showed 11 positive detections in FW in the range 0.009–0.472 µg/l (7 samples > the threshold value).

[1] EQS = environmental quality standard; LOD = limit of detection; FW = freshwater; SW = saltwater; AA = annual average; GW = groundwater. Values in brackets denote percentage of results relative to number of samples.
[2] Above the limit of detection.
[3] Results for total boron. Dissolved boron data from routine statutory monitoring and planned investigations were also reviewed and showed no samples with concentrations greater than the corresponding total boron EQSs in either FW or SW in England and only one sample with a greater concentration in FW in Wales. Dissolved concentrations higher than the FW total boron EQS were observed in GW, but cases were limited with the greatest number of occurrences reported for Anglian Region (ca. 2% of samples).
[4] Results for total vanadium. Dissolved vanadium data from routine statutory monitoring and planned investigations were also reviewed and showed no samples with concentrations greater than the corresponding total vanadium EQSs in either FW or SW in England and only one sample with a greater concentration in FW in Wales. No dissolved concentrations higher than the FW total vanadium EQS were observed in GW, although one sample was not possible to assess owing to lack of accompanying hardness data.
[5] Mevinphos is not classed as a dangerous substance under the DSD Regulations, but a threshold value for freshwater samples is given in Regulation 98/389 and this is the value that has been used here.

Table A.3 Limits of detection and minimum reporting values in freshwater for the reviewed List II substances

Compound	Theoretical LOD (µg/l)	Achieved LOD (µg/l)	Current MRV in freshwater (µg/l)
Azinphos-methyl	<0.00066	<0.001	<0.003
demeton-o	<0.003	<0.010	<0.010
demeton-s-methyl	<0.002	<0.005	<0.010
demeton-s-methyl sulphone	<0.0009	<0.005	<0.010
Omethoate	<0.00090	<0.005	<0.010
Triazophos	<0.00158	<0.005	<0.004
Boron	<24.9000	<25.00	<100.0
Vanadium	<0.10000	<0.100	<2.000
PCSD	<0.002	<0.002	<0.002
Cyfluthrin	<0.00036	<0.001	<0.003
Sulcofuron	<0.063	<0.2	<0.012
Flucofuron	<0.043	<0.2	<0.093
Mevinphos	<0.00202	<0.005	<0.008

A.3 Summary

The above review of those substances that did not undergo the prioritisation process suggests that these chemicals are unlikely to be discharged in significant quantities and/or have not been found in quantities that suggest they are of concern in water.

All of the DSD List II substances considered, with the exception of boron and vanadium, are currently not authorised for use in the UK.

A basic review of the monitoring data for England and Wales shows that the substances are not found at widespread levels of concern: comparison against the EQSs shows exceedances are limited and there are few positive detections in water for the organic compounds considered. Boron and vanadium are naturally occurring so tend to have a larger percentage of positive detections, although face value comparison of all the data against the corresponding EQSs shows few exceedances (<1%).

For omethoate, triazophos and cyfluthrin, the LODs and MRVs relating to the period of the monitoring data used in this review are close or equal to the corresponding EQS values. Omethoate and cyfluthrin, in particular, have large quantities of data reported as less than values which makes it difficult to reach conclusions for these substances regarding compliance. However, available information on authorisation suggests that discharges of omethoate and cyfluthrin are unlikely to be of concern.

Mevinphos is not classed as a dangerous substance under the DSD Regulations, but does have an associated threshold value; exceedance of this value is also limited.

Overall, the data do not highlight any issues with any of the substances considered.

Limited data for azinphos-methyl and vanadium analysed in surface waters in Scotland do not highlight any issues with these substances.

Appendix B: Environment Agency Pollution Inventory data

	Load discharged (Kg) by industrial sector									
Data extracted July 2007	**ANIMAL, VEGETABLE AND FOOD**									
Controlled waters	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**Total**
1,1,2-Trichloroethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.00**
2-Chlorophenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.00**
4-Chloro-3-methylphenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.00**
Biphenyl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.00**
Chloronitrotoluenes	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Dichlorvos	0.00	0.00	0.00	0.00	0	0.0519	0.06	0.07	0	**0.18**
Fenitrothion	0.00	0.00	0.00	0.00	0	0.0519	0.06	0.07	0	**0.18**
Malathion	0.00	0.00	0.00	0.00	0	0.0159	0.06	0.07	38.1	**38.25**
Triclosan	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Triphenyltin	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Xylene - all isomers	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
	FUEL AND POWER PRODUCTION AND ASSOCIATED PROCESSES									
	1998	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**Total**
1,1,2-Trichloroethane	**0.00**	**0.00**	**0.38**	**0.34**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.72**
2-Chlorophenol	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
4-Chloro-3-methylphenol	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Biphenyl	**2.40**	**1.45**	**16.30**	**10.30**	**1.38**	**0.00**	**0.00**	**0.00**	**0.00**	**31.83**
Chloronitrotoluenes	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Dichlorvos	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Fenitrothion	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Malathion	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Triclosan	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Triphenyltin	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Xylene - all isomers	**20878**	**14162**	**6666**	**3825**	**2519**	**789**	**298**	**118**	**248**	**49,503.78**
	METAL PRODUCTION AND PROCESSING									
	1998	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**Total**
1,1,2-Trichloroethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.00**
2-Chlorophenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.00**
4-Chloro-3-methylphenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.00**
Biphenyl	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Chloronitrotoluenes	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Dichlorvos	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Fenitrothion	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Malathion	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	53.90	**53.90**
Triclosan	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Triphenyltin	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Xylene - all isomers	7	17	27	120	0	0	0	0	10.8	**181.65**

	PAPER, PULP AND BOARD									
	1998	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**Total**
1,1,2-Trichloroethane		0.00	0.00	0.00	0.00	0.00	0.00	0	0	**0.00**
2-Chlorophenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.00**
4-Chloro-3-methylphenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.00**
Biphenyl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.00**
Chloronitrotoluenes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.00**
Dichlorvos	4.9	0	0.59	0	0.095	0.0083	0.026	**0.00**	**0.00**	**5.66**
Fenitrothion	4.7	0	0	0.05	0.095	0.0083	0.026	0.002	0	**4.94**
Malathion	2.8	0	0	0.05	0.095	0.0083	0.026	0.002	0	**2.98**
Triclosan	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Triphenyltin	18.9	0	0	0.02	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**18.92**
Xylene - all isomers	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.00**
	WASTEWATER TREATMENT WORKS									
	2000	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**Total**		
1,1,2-Trichloroethane	0	0	16.1	0	0	0	0	16.10		
2-Chlorophenol	61.7	20.4	12.6	0	0	0	0	95		
4-Chloro-3-methylphenol	0	232.7	0	0	0	0	0	232		
Biphenyl	0	0	0	0.00	0.00	0.00	0.00	0.00		
Chloronitrotoluenes	0	0	75.3	0	0	0	0	75.33		
Dichlorvos	0	0.214	0.29	0.125	0.118	0.033	0.672	1.45		
Fenitrothion	0	0.8	0.09	0	0.11	0.028	0.002	1.03		
Malathion	0	2.0177	1.6	0.23	0.86	0.29	0.39	5.38		
Triphenyltin	0.073	0.59	0.21	0.00	0.00	0.00	0.57	1.44		
Xylene - all isomers	19	185	414	337	16	16	132	1119		
	THE CHEMICAL INDUSTRY									
	1998	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**Total**
1,1,2-Trichloroethane	0	38.6	55.92	27.9	0	0	0	0	0	122.42
2-Chlorophenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4-Chloro-3-methylphenol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Biphenyl	5000	172	229	189	319	176	445	253	0	6783.00
Chloronitrotoluenes	45	1.3	14.9	5.7	0	0	0	0	0	66.90
Dichlorvos	0	0	0	0	0	0	0	0	0	0.00
Fenitrothion	0	0	0	0	0	0	0	0	0	0.00
Malathion	0	0	0	0	0	0	0	0	0	0.00
Triclosan	0	0	0	0	0	0	0	0	5.9	5.90
Triphenyltin	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Xylene - all isomers	112335	53292	15070	7033	4026	2487	2181	7344	6540	210310